Titanium Dioxide (TiO_2) Nanoporous Surface Layer Removal

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Introduction

- Nanostructured surfaces improve bone cell adhesion to orthopedic implants, thereby increasing their lifespan in the human body.
- TiO_2 nanotube surfaces highly encourage bone cell adhesion.
- However, the influence of nanostructure on the biological response mechanism is not well understood.

How can we understand the biological response mechanism?

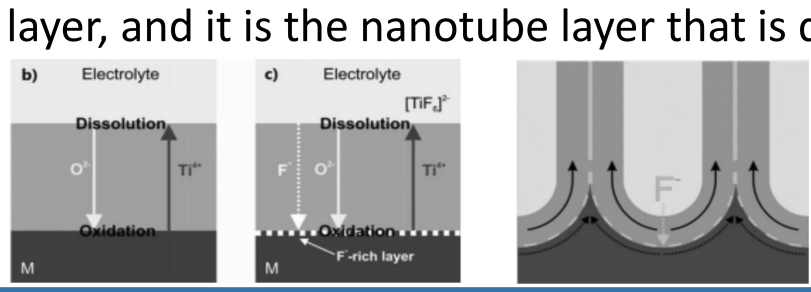
- Transparent TiO_2 nanotubes may enable live-cell imaging of cell interaction with nanotubes.

How is transparency achieved?

- Physical vapor deposition (PVD) of a thin (500nm-1 µm) titanium film on glass substrates.

What is the problem?

- Often in the fabrication of transparent samples, a nanoporous surface layer remains; this layer is not representative of the nanotube layer, and it is the nanotube layer that is desired for study.



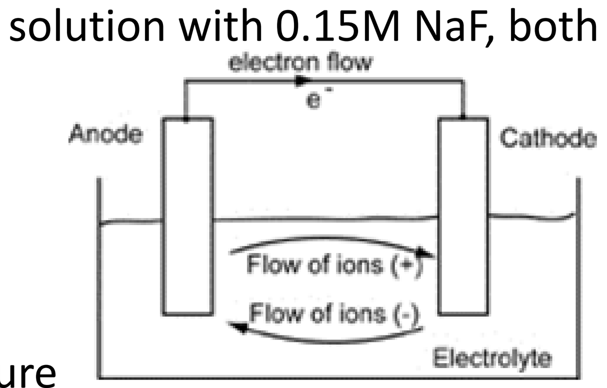
[3] Widely accepted diagram for the mechanism of nanotube formation

Project Objective

This research focuses on developing a repeatable method for removing nanoporous surface layers from TiO_2 nanotubes.

Experimental Procedure

1. Opaque titanium: cut and polish disks ½ in. in diameter, 2mm thick. Transparent titanium: PVD of titanium over glass cover slips.
2. Anodize titanium samples in a 2-electrode electrolytic cell where Ti acts as the anode.
   - ❑ Two electrolytes used; ethylene glycol with 0.15M NH4F with 2.5 wt. % water and a 0.44 M H_3PO_4 aqueous solution with 0.15M NaF, both typically with a volume of 100mL.
   - ❑ Anodization voltage was typically 90V
3. Nanopore removal methods
   a) Longer anodization times
   b) Two-step anodization
   c) Etching by extended fluorine exposure
   d) RF plasma etching
4. Use scanning electron microscopy to characterize surface topography

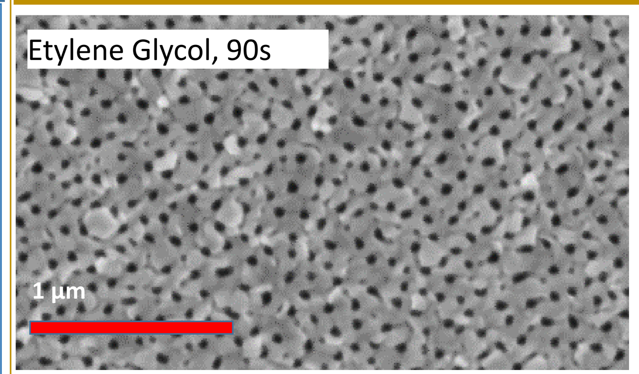


Results

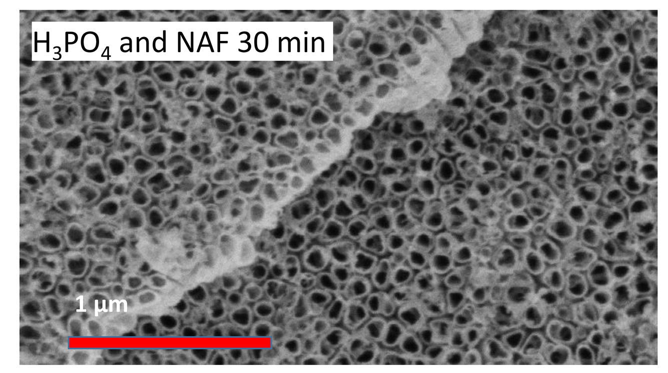
Top: Opaque samples before and after anodization
Bottom: Transparent samples before and after anodization

- Opaque samples are used for initial testing of nanopore removal methods.
- If a method works on opaque samples, it is attempted on transparent samples.

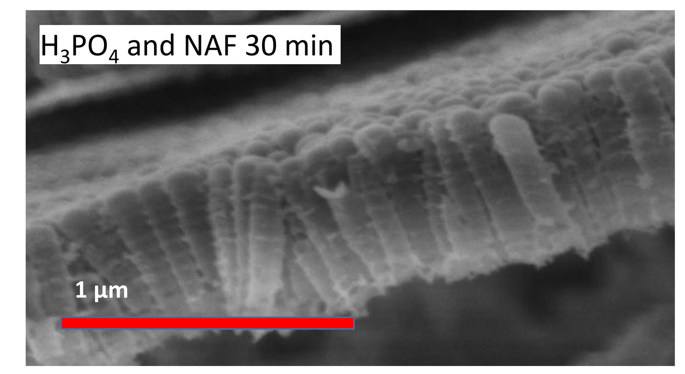
Surface Characterization



Nanoporous surface on titanium



Nanotubular surface on titanium



Nanotube cross-section

- Sample images provided are from opaque samples because there is negligible difference in appearance of nanoporous regions between opaque or transparent samples.
- TiO_2 nanopores are characterized by completely enclosed by dense TiO_2 and are in a non-uniform pattern
- TiO_2 nanotubes are characterized by a pore region separated by thin TiO_2 walls separated by intertube void space

Increased Anodization Time

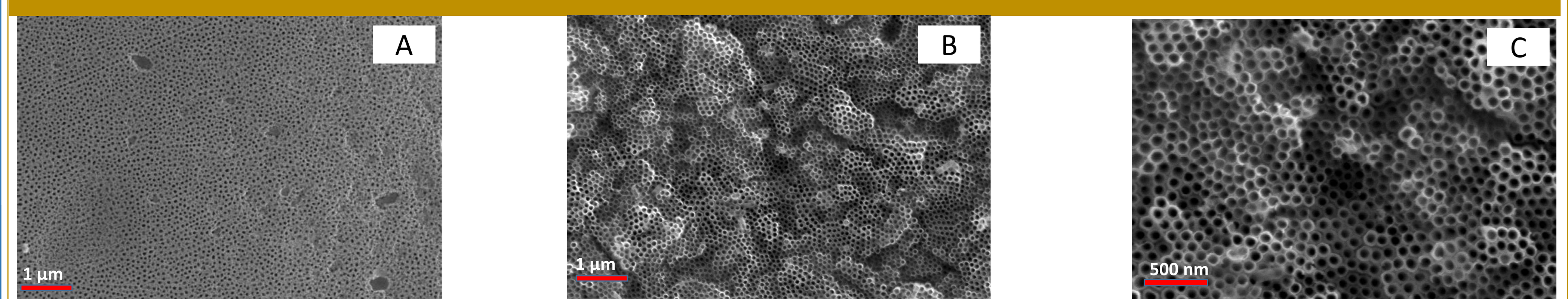
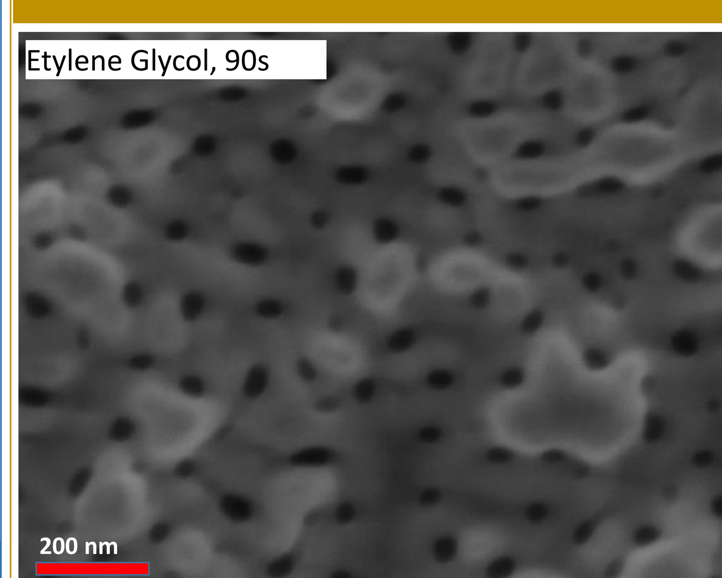


Image A: Nanoporous surface. Electrolyte: ethylene glycol. Image B: Nanotubular surface after increasing the anodization time of the sample shown in Image A. Image C: Closer view of the nanoporous surface in Image B.

- Increased anodization time subjects the nanopore layer to field-assisted chemical dissolution, which eventually leads to complete removal of nanopores and exposure of nanotubes.
- This method is successful on opaque samples, but due to the thinness of the titanium layer on transparent samples, too much titanium is often etched away causing nanotube delamination.

Extended Fluorine exposure



SEM top-down image after one hour of additional exposure to fluorine

- While increasing the anodization time was too aggressive, it was thought that increasing the sample's exposure to fluorine would etch away the nanoporous surface.
- After anodization, current was turned off while the sample remained in the housing with the magnetic stir bar spinning at 600 rpm for one hour.
- SEM shows no change in surface morphology with nanopores still present.

Two-Step Anodization

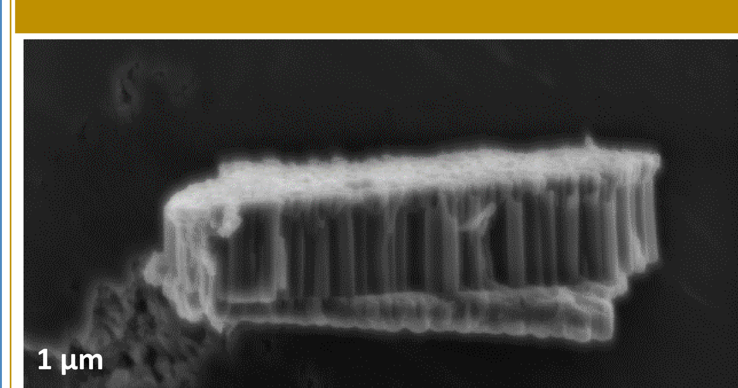


Image taken after a second anodization
Ethylene glycol, 90V
Anodized 5 min, sonicated 10 min, anodized 30 min

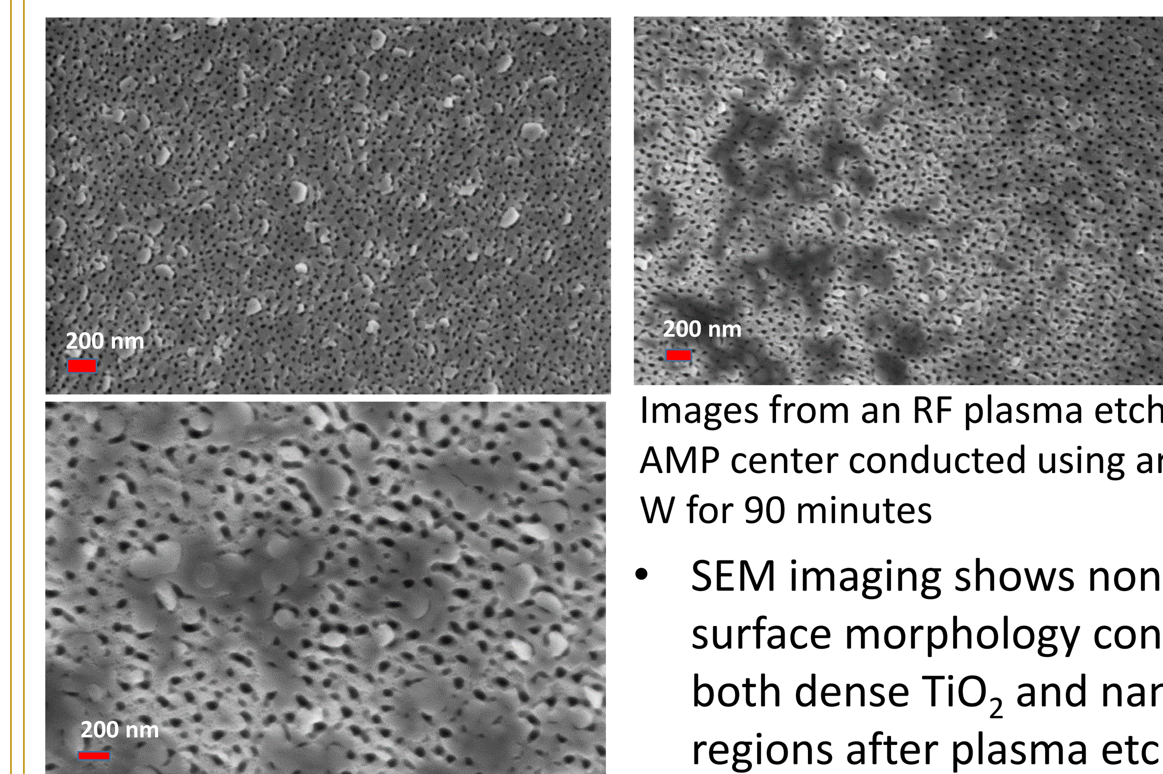
What is a Two-Step Anodization?

A sample is partially anodized to form the initial barrier layer and partial nanotubes. Those tubes are then sonicated off before the sample is re-anodized and a second layer is grown.

Results Obtained

- Successful formation of a second layer of nanotubes on opaque samples, as well as removal of the nanopore region for both samples
- TiO_2 nanotubes on transparent samples are still unstable and delaminate.

RF Plasma Etching



Images from an RF plasma etch done in the AMP center conducted using argon gas at 250 W for 90 minutes

- SEM imaging shows non-uniform surface morphology consisting of both dense TiO_2 and nanopore regions after plasma etching

Conclusion

- Anodizing samples for an increased period of time worked for the opaque samples, but due to a lack of titanium on the glass surface caused total nanotube delamination of tubes on transparent samples.
- Two-step anodization was tested with the hypothesis that if the initial barrier layer was formed and then removed (by sonication), nanotubes could be successfully fabricated, minus that initial layer. This method has so far only been tested on opaque samples
- RF plasma etching, previously described, had inconsistent nanopore removal, and in some areas no removal.
- Initial TiO_2 nanopore removal has been unsuccessful, but new methods have been proposed based on initial findings and can be found in future work.

Future Work

1. Perform a two-step anodization where the potential is reduced in increments to slow nanotube formation, but cause chemical dissolution of the nanopore region through prolonged exposure to electrolyte.
2. Surface characterization by using SEM.

Acknowledgements

Funding for this project was provided by the National Science Foundation, Grant number DMR-1460912. Thanks to Dr. Grant Crawford for his teaching and guidance. Thank you to SDSM&T Master's candidate Jevin Meyerink and Sturgis Brown High School student Holly Gerberding for their collaboration. Thank you to Dr. Kustas in the AMP center for providing PVD samples and to Dr. Boysen for help with communication and writing. A special thanks to the staff at SDSM&T for their help and cooperation.

NSF

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[2] Roy, Poulomi, Steffen Berger, and Patrik Schmuki. *Angewandte Chemie International Edition* 50.13 (2011): 2904-2939.

[3]http://www.lytron.com/Tools-and-Technical-Reference/Application Notes/Avoiding-Galvanic-Corrosion

[4]SEM images provided by Jevin Meyerink