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.

**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$_3$PO$_4$ aqueous solution with 0.15M NaF, both typically with a volume of 100mL.
3. Anodization voltage was typically 90V.
4. Nanopore removal methods
   - Longer anodization times
   - Two-step anodization
   - Etching by extended fluorine exposure
   - RF plasma etching
5. Use scanning electron microscopy to characterize surface topography

**Results**
- Opalescent 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**
- Sample images provided are from opaque samples because there is negligible difference in appearance of nanoporous regions between opaque or transparent samples.
- TiO$_2$ nanotubes 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 intermittent void space.

**Increased Anodization Time**
- Increased anodization time subjects the nanopore layer to field-assisted chemical dissolution, which eventually leads to complete removal of nanotubes and exposure of nanopores.
- 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**
- 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.

**RF Plasma Etching**
- 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.

**Conclusion**
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**Future Work**
- 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.
- Surface characterization by using SEM.

**Acknowledgements**

**References**
[4] SEM images provided by Jevin Meyerink