Abstract
Titanium dioxide (TiO$_2$), a wide-bandgap semiconductor, has in recent decades been the subject of intense scientific study due to its photoactive properties. Although TiO$_2$ has been thoroughly researched in projects regarding applications of those properties, few, if any, have focused on how the electrical and structural properties change over long term exposure to damaging high energy radiation. This type of radiation can alter the atomic structure of the material which leads to changes in characteristic properties. Our present study seeks to understand the long and short term effects that exposure to high energy radiation has on TiO$_2$.

We exposed thin films of TiO$_2$ to a $^{137}$Cs (661.8 keV) γ-radiation source for varying amounts of time. After irradiation, the structural, optical, and electrical properties were fully characterized to examine the impact of radiation exposure on this technologically important material.

Introduction
TiO$_2$, commonly referred to as titania, is not a relatively new material. It has been in use for several decades largely as a pigment in paints, plastics, and even toothpastes (Nowotny 2011). The comparatively high index of refraction of the material often presents itself in a desired white hue. After its photoactive properties were first observed in 1972 (Fujishima & Honda), TiO$_2$ has been researched extensively for application purposes (Chen et al. 2007). These characteristic properties make it a promising candidate in many applications such as a photocatalyst for purposes in water splitting, or as a key elemental component in solar cells such as the Grätzel dye-sensitized solar cells (O’Regan & Grätzel 1991). Research focused towards incorporating TiO$_2$ into technology stems largely from the cost and scarcity of other materials current in use. For example, Indium, a popular material in high efficiency solar cells, is about as rare and expensive as silver. Titanium, comparatively, is lower cost and naturally more abundant (Nowotny 2011).

Little research, if any at all, has directed attention towards the effects of high energy radiation specifically on TiO$_2$. It is necessary that if TiO$_2$ is to be utilized as a photoactive ingredient in applications where high energy radiation is present (e.g. space) that the effects of the radiation on the material are understood.

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Methods

Before the films were grown, substrates were prepared. Films were grown on two different substrates: BK7 glass and Si (100) wafers. The samples were then placed in a reactive DC sputtering machine where the films were grown. Films were grown in vacuum at room temperature with oxygen and inert argon flowing through the vacuum chamber. A 99.995% pure Ti target was used as the Titanium source. Upon the completion of film growth, the new films were annealed at 500°C for approximately an hour.

Film morphology was then briefly checked to ensure that a homogeneous and uniform film had been grown as desired. This was done by taking atomic force microscopy images (Fig. 1) and profilometry measurements. The profilometer was also used to measure the thickness of the films.

Before samples were damaged, baseline tests were conducted. The first tests conducted on the films before irradiation were optical tests. Reflectance of the film, compared with an aluminum mirror baseline, was conducted from 190-1100 nm using a UV-Vis near-IR spectrometer. Percent transmission was measured next from 190-3300nm also using a UV-Vis spectrometer. During the transmission test, the BK7 glass with film was measured in tandem with a control BK7 glass that had no film. This allowed the control to be subtracted from the film glass so only the film properties were analyzed. Both reflection and transmission test were done without the Si substrate film as the Si wafers are not transparent in the regions being observed.

Using the transmission data and the mathematical Tauc Relationship $a h \nu = (h \nu - E_g)^{1/2}$, an approximate bandgap of the material was determined by linear interpolation of the resulting curve. The approximated bandgap of the material was where the linear portion of each curve crossed the energy axis (Fig. 4).

The other optical property studied was the index of refraction. This was done using a spectroscopic ellipsometer. Data were fit using the Cauchy model with an Urbach tail, and were constrained to be Kramers-Kronig consistent.

The second round of tests were conducted to examine the structural properties of the film. An X-ray diffractometer (XRD) could examine crystal structure and help confirm that the films were $\text{TiO}_2$. XRD would determine if continued radiation exposure altered the lattice constants of the crystal. Shifts and changes to characteristic peaks would signify damage to the atomic lattice of the films. The XRD measurements conducted were at a grazing incidence angle of approximately 3.5° which is common when analyzing thin films. The relatively small angle helps to ensure that the film is being analyzed and not the substrate beneath it. X-ray photoelectron spectroscopy (XPS) was also used to quantify the amounts of titanium and oxygen in the film. XPS showed the local binding environments of the film elements and how they were changing over time as the film was damaged.

After all baseline tests were conducted. The samples and the control were placed in a Cs$^{137}$ irradiator with the films facing the Cs source. The irradiator emits characteristic Gamma-radiation...
(γ-radiation) at 661.8 keV. Samples were placed in the irradiator for varying amounts of time before being taken out, having its properties tested again, and going back in the irradiator. By periodically testing the films, trends over time could be observed.

Results
Optical transmission data (Fig. 2) shows a steady increase in percent transmission right around the 350 nm mark during the initial radiation period before leveling out and decreasing after the 80-hour mark. Why transmission initially increased is unknown. One theory points towards the radiation initially working as a form of radiation annealing for the crystal structure of the film, helping it lock in a more energetically favorable configuration before further damaging the film. Annealing for an extended period of time may have reduced that effect. Another possible explanation comes from specific electron transitions between the valence and conduction bands happening at the 350 nm edge feature of the film being altered by the radiation process. The specific electron transitions that occurred are not known. The ultra-violet (UV) and infrared (IR) regions show no significant changes or trends to percent transmission. No significant changes in percent reflection were present from the observed data. The changes to index of refraction (Fig. 3) also saw no significant changes with continued radiation exposure.

(Fig. 4) shows the linear interpolation of the Tauc relationship as well as the plotted bandgap vs. time relationship. Largely mirroring the optical transmission results, the bandgap steadily increased before leveling out and decreasing, approaching a plateaued region. Although changes to the bandgap are seen, the relative change is fairly insignificant, ranging from 3.85 eV at the lowest and peaking at 3.99 eV.

Fig 2: Transmission curves of arbitrary time intervals of radiation exposure.

Fig 3: Index of refraction of TiO₂ film.

Fig 4: (Left) Tauc relationship curves with linear interpolations to the energy axis (eV). (Right) The intersections of the linear portions with the energy axis plotted with respect to irradiation time.
Titania exists naturally as three crystalline polymorphs known as rutile, anatase, and brookite (Wei & Chang 2011). XRD data confirms through the characteristic peaks in (Fig. 5) that anatase form TiO$_2$ had been grown. Anatase is the phase most suited and studied for photoactive applications (Hanini et al. 2013). XRD data is shown to become slightly more erratic over continued irradiation with a slight widening of the characteristic peaks. This is representative of a decrease in symmetry in the crystalline lattice of the TiO$_2$ due to damage from the radiation process. However, these changes are not highly significant.

XPS data further confirmed the presence of titanium and oxygen within the films. Both Ti $2p$ and O1$s$ peaks were thoroughly examined for changes in binding energy and intensity. No changes were seen in the Ti $2p$ peaks. The O1$s$ peaks did, however, present the emergence of a shoulder on the left side of the peak (Fig. 6). Table 1 displays the area ratio under the normal lattice peak and the emerging interstitial peak. The reduction of the ratio over time and the visibly growing shoulder are indicative of oxygen vacancies within the crystal lattice. This shows there was enough energy from the gamma radiation to physically remove oxygen atoms from the crystal lattice. It is expected that oxygen would be more effected and have greater changes in the lattice as oxygen has an atomic weight roughly three times less than that of titanium.

**Conclusion**

Experimental results suggest TiO$_2$ is a relatively “radiation hard” material that is able to resist changes from exposure to high energy radiation. Transmission of light through the film was minimally altered, particularly in the UV and IR regions. XPS and XRD data support limited damage to the crystalline structure of the films over time. TiO$_2$, regardless of specific photoactive application, is a suitable candidate for material applications in high radiation environments.

The study can be further improved and extended if desired. Films can be further irradiated to ensure that deterioration of the characteristic properties has plateaued or stopped with prolonged irradiation. Extended times would also indicate if any interesting features are introduced. Further, it is desired to examine how the electrical properties of the film are altered with respect to radiation exposure time, particularly the conductivity/resistivity of the film. A four-point resistivity
measurement tool would be recommended for the conduction of this portion of the experiment. Repetitions of this experiment would help to further confirm previous results and observations.

References
Chen, X., & Mao, S. “Titanium Dioxide Nanomaterials: Synthesis, Properties, Modifications, and Applications.” Chemical Reviews 107.7 (2007): 2891-2959.
Hanini, F., Bouabellou, A., Bouachiba, Y., et. al. “Structural, Optical and Electrical Properties of TiO₂ Thin Films Synthesized by Sol-gel Technique.” IOSR Journal of Engineering IOSRJEN 3.11 (2013): 21-28.
Fujishima, A., & Honda, K. “Electrochemical Photolysis of Water at a Semiconductor Electrode.” Nature 238.5358 (1972): 37-38.
Nowotny, J. “Oxide Semiconductors for Solar Energy Conversion: Titanium Dioxide”, (2011):9781439848395.
Oregan, B., & M. Gratzel. “A Low-cost, High-efficiency Solar-cell Based ON Dye-sensitized Colloidal TiO2 Films.” Nature 353.6345 (1991): 737-740.
Wei C., & Chang, C. “Polycrystalline TiO2 Thin Films with Different Thicknesses Deposited on Unheated Substrates Using RF Magnetron Sputtering.” Materials Transactions 52.3 (2011): 554-559.