# *Raman Spectroscopy of Thin Films*

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## Abstract

Raman Spectroscopy is a powerful experimental technique to analyze the vibrational modes of thin films. Using Raman Spectroscopy, we have investigated zirconia in order to decipher their vibrational modes and to explore the quality of sample. The zirconia was deposited on silicon substrates, treated with either Oleic Acid or Trioctylphosphine oxide (TOPO), and then calcined at specific temperatures. Using a combination of results from 632 nm and 532 nm laser spectroscopy, we found that the zirconia underwent crystal phase transformation around 700 to 900 degrees Celsius. The spectra of the zirconia treated with TOPO showed strong signs of both monoclinic and tetragonal crystal structure, results which were verified by X-ray diffraction as well.

We also used Atomic Force Microscopy to explore the topography of the zirconia samples. From these images we were able to calculate the root mean square, which is the average roughness of the surface.

## Background

### Raman Spectroscopy

- The Raman Effect, otherwise known as Raman Scattering, is the inelastic scattering of a photon due to excited vibrational modes of a material.
- By shooting a laser at a thin film, we can excite new vibrational modes of a material. Since the exciting laser is influenced by the vibrational modes, the photons can lose or gain energy.
- While the Rayleigh Scattering is by far the dominant phenomena, Raman Scattering still occurs. This shift only occurs within one per millions of the reflected photons, and is thus unobservable to the naked eye.
- A Raman Spectrometer is able to filter out a lot of those reflected photons, and graph a spectrum of the shifts. This is only possible through excitation with a single wave length, as notch filters can be optimized.

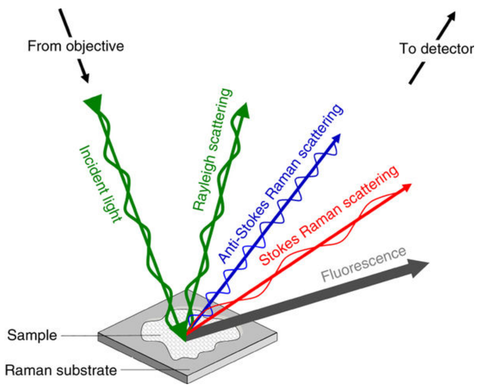



Diagram of Raman [1]

### Atomic Force Microscopy

- Atomic Force Microscopy (AFM) uses a cantilever to measure force on the surface of a material.
- As the cantilever runs across the top of the material, fluctuations in the surface height will apply different forces.
- Piezoelectronics are able to move the sample at finely tuned increments, while a laser is reflected off of the cantilever. The position of the the laser is recorded by a photodiode .
- By comparing the displacement of the laser with the displacement of the sample by the piezoelectronics, we are able to create a topography of the sample.

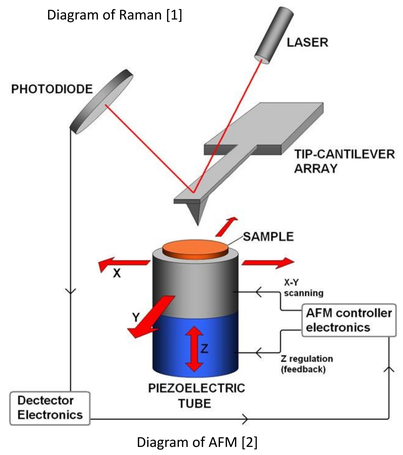
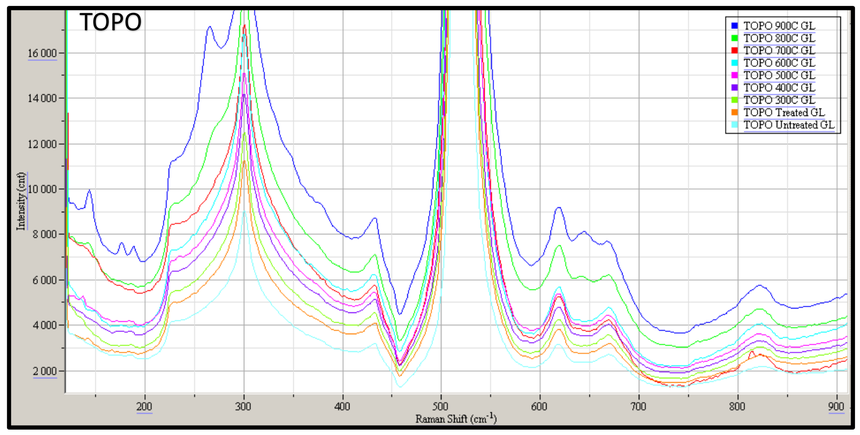


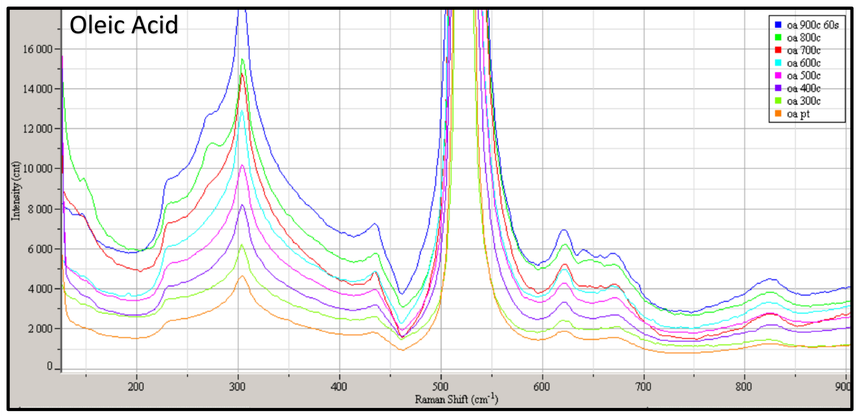

Diagram of AFM [2]

## Zirconia Samples

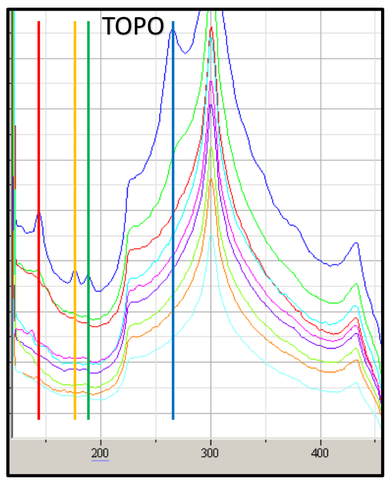
- Zirconium Dioxide (zirconia) is a compound with many emerging uses in industry
- Zirconia was spin coated on Silicon substrates, and then treated with either trioctylphosphine oxide (TOPO) or oleic acid (OA) .
- These chemicals affect the crystal phases of the zirconia. Zirconia can form in amorphous, monoclinic, tetragonal, and cubic structures. These phases are reached through exposure to temperature. Our samples were annealed for 168 hours at different temperatures ranging from 300C to 900C.

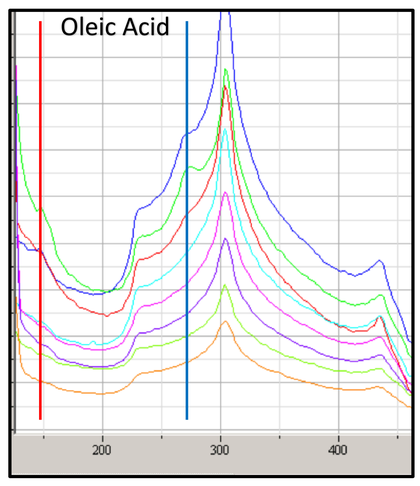
## Raman Spectra



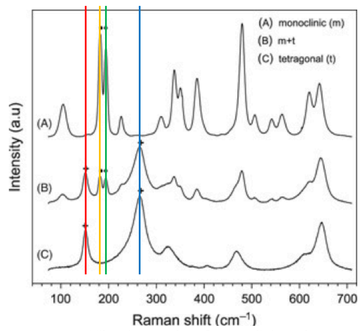




## Analyzing Spectra

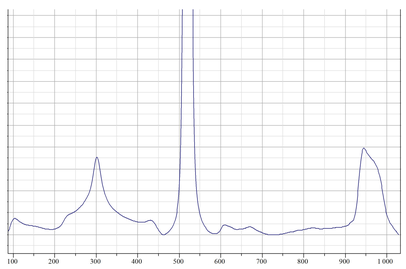



- Pictured above are portions of the Raman spectra for both TOPO and Oleic Acid
- Pictured to the upper right is a graph of general Raman spectra for zirconia, both monoclinic, zirconia, and mixed crystal structures
- Color coded are specific peaks at wave numbers corresponding to vibrational energy levels of specific crystalline structures
- At 146 and 260 $cm^{-1}$, tetragonal peaks exist.
- At around 180 and 190 $cm^{-1}$, a double monoclinic peak exists.
- The remaining peaks in the spectra (such as the one around 300) are from the silicon substrate.
- Pictured in the lower right is a spectrum of Silicon obtained in our lab. These peaks also appear in the above spectra because of the substrate.

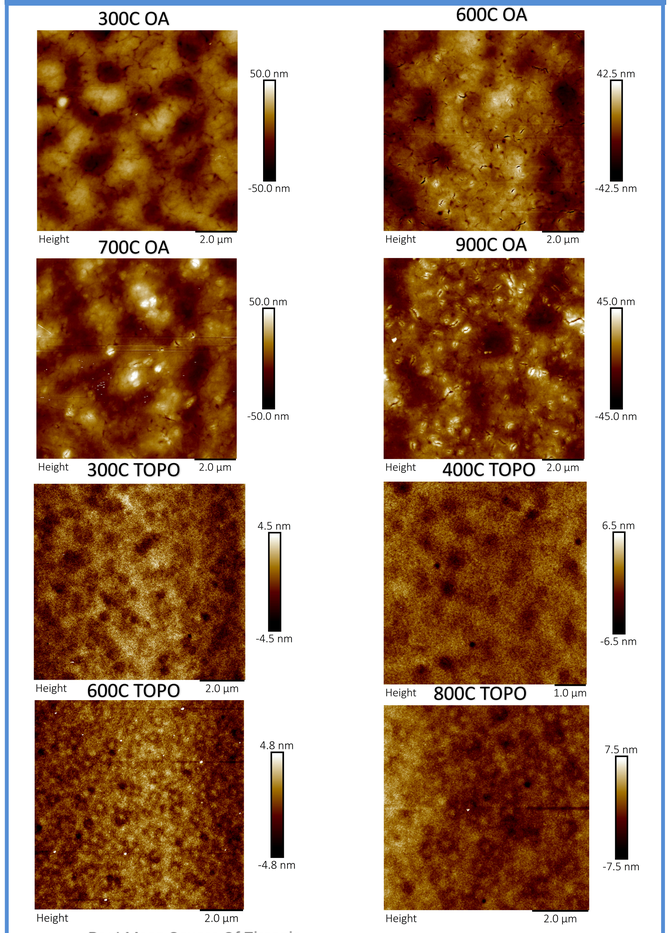



Vibration modes of monoclinic and tetragonal zirconia [3]

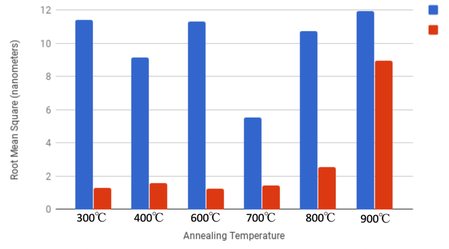


Raman Spectrum of Silicon in $cm^{-1}$

## AFM




Root Mean Square Of Zirconia




As the annealing temperature increases, shown in the AFM images, the individual crystalline sizes decrease. At high temperatures, the crystalline sizes corresponded to the expected zirconia nanoparticle sizes

## Conclusions

**TOPO Zirconia**

- From our data we found that TOPO zirconia began to undergo a phase transformation around 700C.
- At 900C, the TOPO zirconia has both monoclinic and tetragonal structure.
- This results were confirmed by X-ray diffraction.

**OA Zirconia**

- The Oleic Acid zirconia only showed a tetragonal crystal structure at higher temperatures.
- These results were also confirmed by x-ray diffraction.

**AFM**

- The crystal sizes in images we obtained corresponded to the nanocrystal sizes of zirconia.

## References

1. https://images.nature.com/full/nature-assets/nprot/journal/v11/n4/images_article/nprot.2016.036-F1.jpg
2. https://pharm.virginia.edu/files/2014/01/AFM2.jpg
3. A. Muñoz Tabares, José & J. Anglada, Marc. (2010). Quantitative Analysis of Monoclinic Phase in 3Y-TZP by Raman Spectroscopy. Journal of the American Ceramic Society. 93. 1790 - 1795

## Acknowledgments

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