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# Correlative Raman Spectroscopy and Focused Ion Beam for Targeted Microstructural Analysis of Titania Polymorphs

John Mangum[1], Lisa H Chan[2], Lauren Garten[3] and Brian Gorman[1]

[1.] Department of Metallurgical and Materials Engineering, Colorado School of Mines, Golden, CO, USA
[2.] TESCAN USA Inc., Warrendale, PA, USA
[3.] National Renewable Energy Laboratory, Golden, Colorado, USA

Anatase and brookite, two of the less common titania polymorphs, are both employed in photocatalysis applications [1,2]. However, brookite, the less stable of the two, has been reported to exhibit greater photocatalytic activity than the anatase polymorph [3]. Recently, thin films of high brookite phase-fraction have been produced via pulsed laser deposition [4]. During crystallization of these films, we speculate that there may be a topotactic phase transformation influencing the growth of brookite from regions of anatase.

To attain a better understanding of the microstructure of the titania films, we prepared TEM specimens specifically targeting boundaries between regions of anatase and brookite. Typical approaches to grain boundary targeting in SEM, such as EBSD or EDS, are not feasible for this material system due to minute structural and the lack of compositional differences between the two polymorphs. However, the two polymorphs can be differentiated through Raman spectroscopy (Figure 1). A TESCAN MIRA3 FE-SEM with integrated Raman imaging alongside a TESCAN LYRA3 FIB-SEM and X-Positioner was used to pinpoint boundaries between the two polymorphs and subsequently prepare a TEM specimen containing anatase-brookite boundaries.

Two-dimensional Raman maps were acquired over various regions of the titania film and all spectra were background corrected and analyzed to correlate different Raman peak intensities. Brookite and anatase regions were color-coded based on distinct Raman peaks extracted from each spectrum in the map. These color-coded polymorph maps were overlaid on SEM images of the films to identify areas of interest for TEM specimen preparation (Figure 2). TESCAN's X-Positioner tool allows for precise site localization and navigation between all TESCAN instruments equipped with a SEM. Utilizing the X-Positioner, a FIB lift-out specimen was prepared from an area determined by Raman to contain a boundary between the anatase and brookite polymorphs.

The film sections prepared by correlative Raman, SEM, and FIB were imaged using an FEI Co. Titan 80-300 probe aberration corrected scanning transmission electron microscope. Atomic resolution micrographs were acquired across grain boundaries in the films (Figure 3). Fourier transform analysis of these micrographs confirmed the presence of the brookite structure on one side of the boundary. Due to structural similarities between the polymorphs, confirming the identity of the other side has proven to be difficult.

Correlative Raman spectroscopy and FIB has been shown in this work to be a very promising technique for targeting regions of interest in situations where little to no structural and compositional differences exist between the materials being characterized. Future work will consist of preparing additional specimens via Raman/FIB and more detailed TEM imaging and electron diffraction to fully characterize the boundaries between the $TiO_2$ polymorphs.

References:

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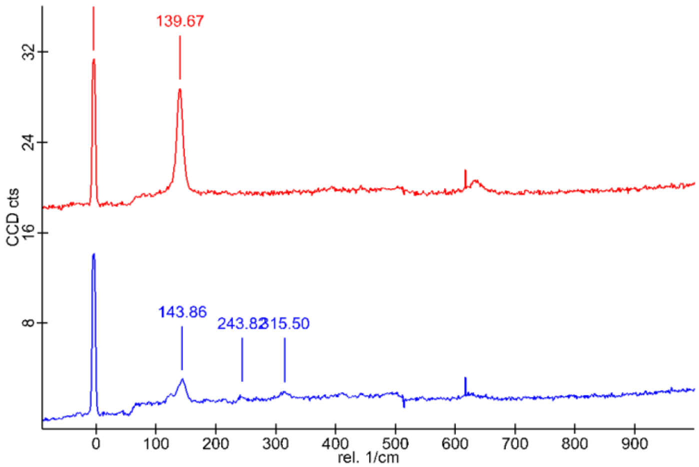


**Figure 1**. Measured Raman spectra of $TiO_2$ films, anatase (top) and brookite (bottom)

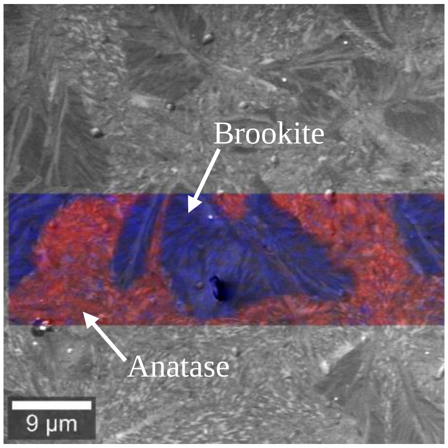


**Figure 2**. SEM micrograph of $TiO_2$ film overlaid with Raman map of anatase (red) and brookite (blue) regions.

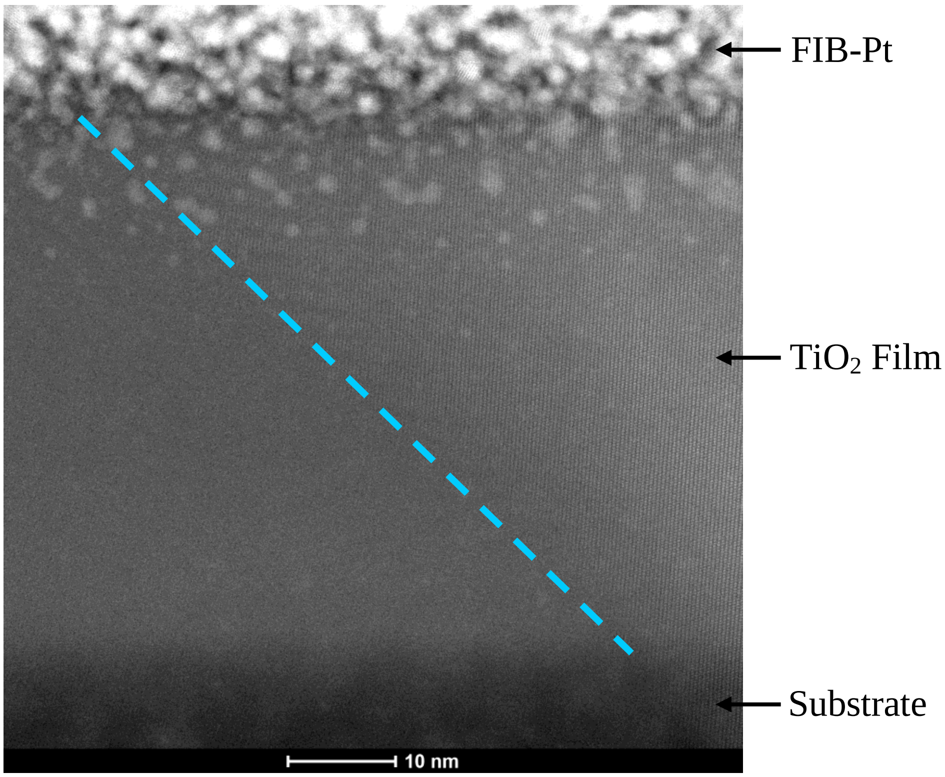


**Figure 3**. Atomic resolution STEM micrograph of grain boundary (dashed line) in $TiO_2$ film.

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