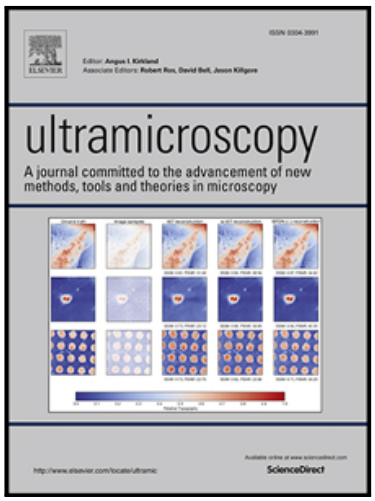

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Correlative Raman Spectroscopy and Focused Ion Beam for Targeted Phase Boundary Analysis of Titania Polymorphs

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Abstract

Site-specific preparation of specimens using focused ion beam instruments for transmission electron microscopy is at the forefront of targeting regions of interest for nanoscale characterization. Typical methods of pinpointing desired features include electron backscatter diffraction for differentiating crystal structures and energy-dispersive X-Ray spectroscopy for probing compositional variations. Yet there are situations, notably in the titanium dioxide system, where these techniques can fail. Differentiating between the brookite and anatase polymorphs of titania is either excessively laborious or impossible with the aforementioned techniques. However, due to differences in bonding structure, Raman spectroscopy serves as an ideal candidate for polymorph differentiation. In this work, a correlative approach utilizing Raman spectroscopy for targeted focused ion beam specimen preparation was employed. Dark field imaging and diffraction in the transmission electron microscope confirmed the region of interest located via Raman spectroscopy and demonstrated the validity of this new method. Correlative Raman spectroscopy, scanning electron microscopy, and focused ion beam is shown to be a promising new technique for identifying site-specific preparation of nanoscale specimens in cases where conventional approaches do not suffice.

Keywords: Raman spectroscopy; focused ion beam; transmission electron microscopy; correlative; site-specific preparation; polymorphs

Abbreviations: TEM, transmission electron microscopy; FIB, focused ion beam; EBSD, electron backscatter diffraction; EDS, energy-dispersive X-ray spectroscopy; RISE, Raman imaging-scanning electron, SEM scanning electron microscopy; SAED, selected area electron diffraction

1. Introduction

Transmission Electron Microscopy (TEM) serves as one of the most powerful techniques for nanoscale structural characterization. With spatial resolutions better than 50 pm, imaging of nanoscale structural features and atomic positions is feasible.[1,2] However, specimen volumes are often restricted to less than 10 μm^2 due to specimen geometry requirements. Limited specimen volumes necessitate site-specific specimen preparation such that the nanoscale structural features are available for analysis, primarily using Focused Ion Beam (FIB) techniques. Secondary analysis tools have become useful prior to FIB specimen preparation procedures in order to select regions of interest for TEM characterization. Electron Backscatter Diffraction (EBSD) can distinguish between regions of varying crystal structure and Energy-Dispersive X-ray Spectroscopy (EDS) can be used to differentiate regions of dissimilar chemical composition. These two techniques are commonly used for locating regions of interest in the FIB instrument.[3-6] However, these techniques have limitations when the regions of interest are chemically identical and structurally similar.

One such case is differentiating polymorphs of titanium dioxide (TiO_2), specifically rutile, anatase, and brookite. Anatase ($I4_1/amd$) forms in a tetragonal structure with corner-sharing octahedra (Fig. 1a). Brookite ($Pcab$) is slightly distorted from anatase into an orthorhombic structure and exhibits both corner- and edge-sharing octahedra (Fig. 1b). This distortion is subtle enough that structural variations between the brookite and anatase polymorphs are difficult to detect with EBSD. With identical chemical compositions and similar diffraction patterns, neither EDS nor EBSD will be sufficient for differentiating brookite and anatase.

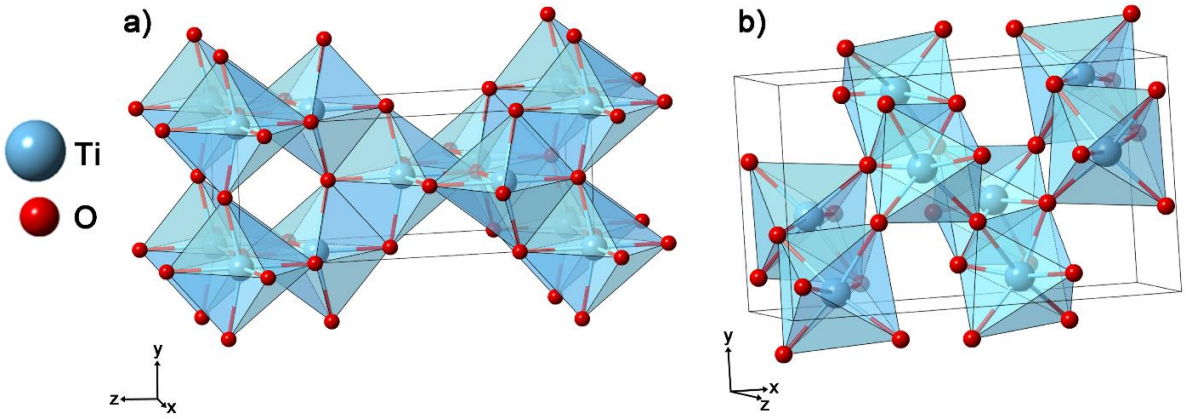

Figure 1. Crystal structures of TiO_2 polymorphs; (a) anatase and (b) brookite.

Fortunately, Ti–O bonding varies significantly between the two polymorphs. Measurable differences in vibrational modes within each structure allow for Raman spectroscopy to be a superior method of polymorph differentiation in this system. A unique correlative imaging technique termed Raman imaging-scanning electron (RISE) microscopy was introduced by TESCAN and WITec in 2014.[7] The integration of confocal Raman microscope into a FIB-SEM workstation enables the acquisition of Raman and electron images of the same area within the same instrument. This configuration is well-suited for precisely locating an anatase-brookite boundary with the confocal Raman microscope for TEM specimen preparation with the FIB-SEM workstation. For this study, two separate instruments were used to complete the work presented here due to the configurations of available instruments.

2. Experimental

The titanium oxide films were deposited by pulsed laser deposition from a TiO_2 target (99.998% Materion) onto Eagle XG glass (Corning) substrates at room temperature. A Lambda Physik KrF laser was used with a laser repetition rate of 10 Hz and the energy density of approximately 2.2 J/cm^2. A partial pressure of oxygen of 1 mTorr was maintained during deposition. After deposition, the films were post annealed at 400°C for 90 seconds in a nitrogen atmosphere.

Secondary electron micrographs were acquired with a TESCAN MIRA3 field emission scanning electron microscope (SEM) operating at a 5 kV accelerating voltage and 14 mm working distance over 1024 x 768 pixels with a 100 µs pixel dwell time.

A WITec confocal Raman imaging system integrated in the MIRA3 SEM was used to collect Raman images consisting of two-dimensional arrays of Raman spectra. In this study, an area of 30x30 µm^2 was analyzed by acquiring an array of 100x100 complete Raman spectra, with an integration time of 0.13 s/spectrum. A 532 nm excitation laser in combination with an UHTS300 spectrometer equipped with a grating of 1800 g/mm were used for these investigations. All Raman spectra were background corrected using the shape function of the WITecProject software and distinct peaks were attributed to each titania polymorph using the filter manager of the WITec Project software. Regions of interest were located and tracked while transferring samples between instruments using TESCAN's X-Positioner tool.

Sample preparation for TEM was done with a TESCAN LYRA3 FIB workstation equipped with a SEM via *in situ* methods described by Giannuzzi in ref. [8]. Specimens were further ion milled at 2 kV and 77 pA to remove Ga ion beam damage and achieve a final thickness of approximately 80 nm.

Transmission electron micrographs were acquired with an FEI Co. Talos F200X transmission electron microscope with scanning capabilities operating at an accelerating voltage of 200 keV. Structural characterization was conducted by acquiring selected area electron diffraction (SAED) patterns on an FEI Co. Ceta 16M pixel CMOS camera at a camera length of 410 mm. Platinum from the FIB was used to calibrate the camera constant, allowing SAED reflections to be accurately measured and indexed. Dark field imaging was conducted using an objective aperture to acquire images only from electrons diffracted by crystallographic planes specific to each polymorph.

3. Results and Discussion

3.1 Correlative Raman-FIB

A TiO_2 thin film sample, confirmed by X-ray diffraction to contain brookite and anatase, is selected for site-specific TEM preparation via the technique discussed here. The film is first imaged using the TESCAN MIRA3 field emission SEM to identify a region of interest. Using the confocal Raman imaging system integrated with the MIRA SEM, a 100 x 100 spectral array is generated by collecting and joining single spectra within the region of interest. The pixel size is 0.3 x 0.3 µm, below the diffraction limit of the used setup. After background correction, a cluster analysis is performed on the 2-D spectral array. Two main cluster of Raman spectra are identified corresponding to the brookite and anatase phases of TiO_2. Within each phase, small changes in peak intensities are observed as presented in Fig. 2a and 2b, respectively. Such small changes of Raman band intensities are related to different orientations of the brookite phase and varying porosity of the anatase phase.[9,10] These four spectra are used as a basis for

the analysis of the 2D spectral array. Each spectrum from the 2D spectral array is written as a linear combination of the four Raman spectra, resulting in a weighting factor for each pixel of the 2D array. As these four phases are unique, with unique Raman spectra, only one spectrum contributes to a specific pixel in the 2D array. This analysis method of 2D spectral arrays results in distribution images of the identified chemical/structural species.[11] By overlaying these images using the colors of the spectra, a color-coded Raman image is generated, highlighting the distribution of the titania polymorphs within the region of interest (Fig. 2c). By overlaying this Raman image on the SEM micrograph, of the region of interest, the RISE image, (Fig. 2d), the precise location of each polymorph can be identified and tracked for TEM preparation. Furthermore, by analyzing the position of the Raman band at 145 rel.1/cm, a stress map is generated as shown in Fig. 3a. The lamella like structure visible in the SEM image (Fig.3b), matches the stress map of the brookite phase obtained by Raman imaging.

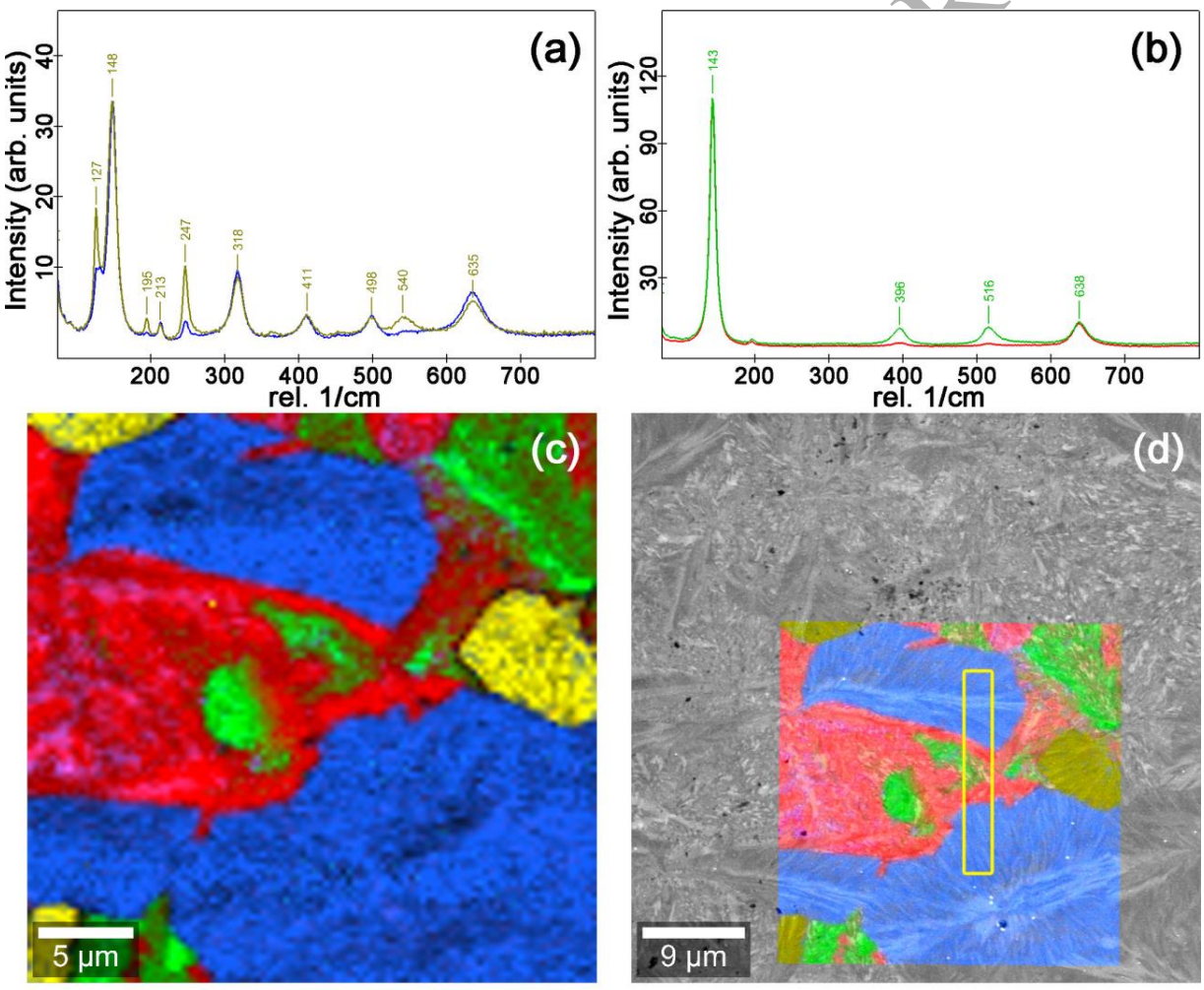

Figure 2. Raman spectra extracted from cluster analysis for (a) brookite (blue, yellow) and (b) anatase (red, green). (c) Color-coded Raman image, and (d) RISE image of the region of interest indicating areas of brookite and anatase. Region of interest for TEM specimen preparation is outlined by yellow box.

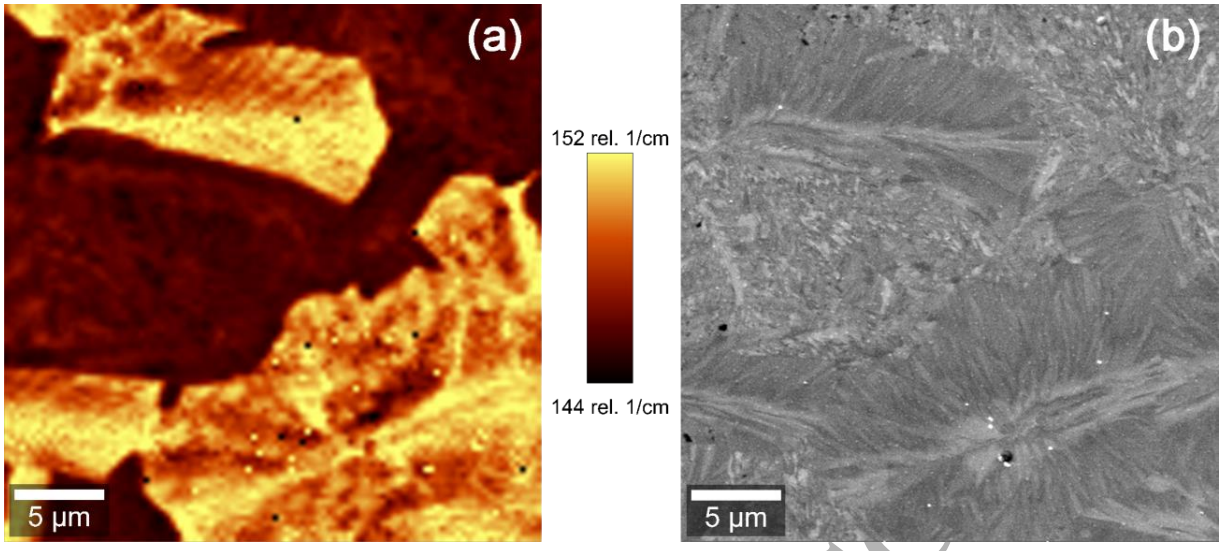

Figure 3. (a) Stress map of the brookite phase and (b) high resolution SEM image of the same region of interest, revealing a lamella-like fine structure.

After Raman imaging, the sample is transferred to the TESCAN LYRA3 FIB-SEM workstation. The region is relocated by using TESCAN's X-positioner tool to navigate in the SEM using correlated external image data. With the polymorph map now laid out in the FIB-SEM workstation, structural features of the film can be purposefully targeted for TEM specimen preparation. Conventional *in situ* FIB lift-out methods are then conducted to prepare a thin cross-section of the film containing a boundary between regions of brookite and anatase.[8]

3.2 Confirmation in Transmission Electron Microscopy

Dark field TEM imaging is conducted to confirm the presence of the boundary between the two polymorphs. Selected area electron diffraction is first used to locate regions of brookite and anatase by identifying reflections specific to each polymorph. An area that exhibited diffraction conditions of both brookite and anatase structures (Fig. 4a) is located for dark field imaging. Micrographs are acquired by using an objective aperture to isolate diffracted electrons unique to each polymorph. By way of dark field imaging, regions of the film corresponding to either polymorph are highlighted. Bright field imaging is also utilized by isolating only directly transmitted electrons to acquire an overview of the film microstructure (Fig. 4b). Diffracted electrons from the brookite (020) planes (d = 2.725Å), indicated by the blue box in Fig. 4a, are used to image the brookite region of the film (Fig. 4c). Diffracted electrons from the anatase ($\bar{1}03$) planes (d = 2.432Å), indicated by the red box in Fig. 4a, are used to image the anatase region of the film (Fig. 4d).

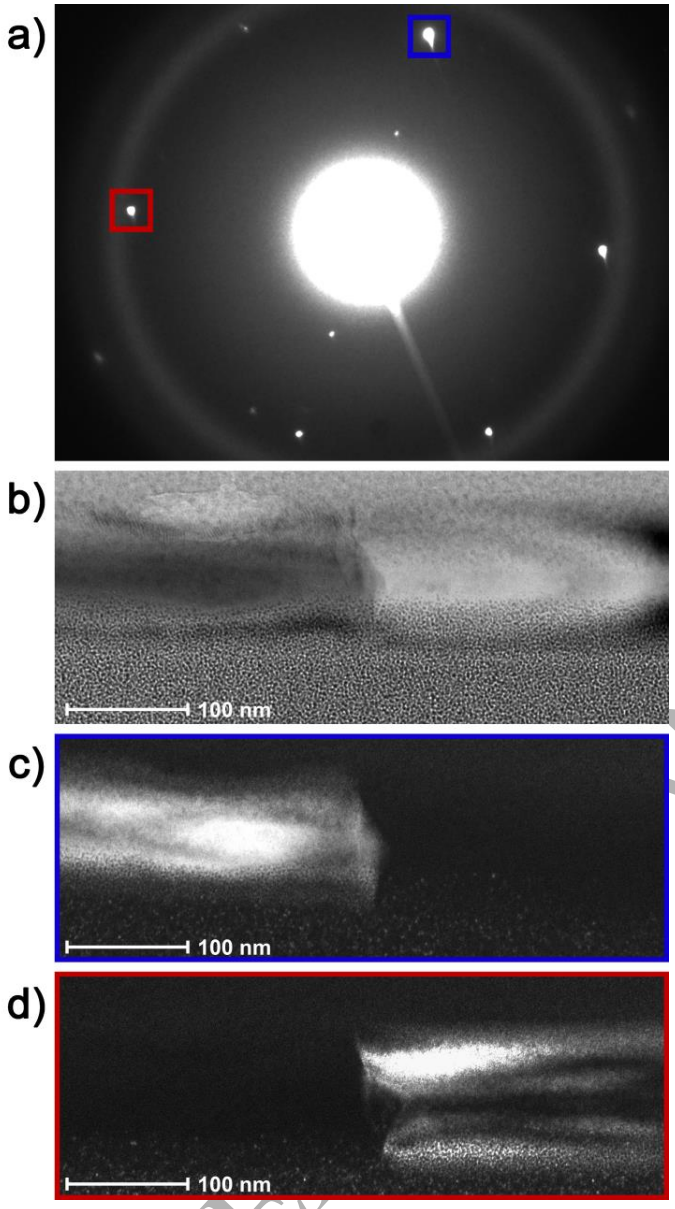

Figure 4. (a) Selected area electron diffraction pattern indicating polymorph-specific reflections for brookite (020) planes (blue) and anatase ($\bar{1}03$) planes (red), (b) bright field image, (c) dark field of brookite region, and (d) dark field image of anatase region.

As revealed by dark field imaging, the boundary between regions of brookite and anatase is successfully targeted at the mesoscale for subsequent imaging and microstructural analysis at the nanoscale. Further TEM characterization of this boundary at greater magnifications can be conducted to elucidate possible structural orientation relationships between the two titania polymorphs. This information could be vital in understanding growth and stabilization mechanisms of the brookite and anatase TiO_2 polymorphs. Additionally, this technique can be readily transferred to other material system to investigate specific phase boundaries, second phases, or interfaces.

4. Conclusions

Correlating Raman spectroscopy and focused ion beam for site-specific preparation of TEM specimens was discussed. Regions of a TiO_2 thin film containing two polymorphs, brookite and anatase, were mapped out using their distinct Raman spectra for differentiation. Overlaying these maps on SEM micrographs allowed for accurate identification of polymorph boundaries within the focused ion beam instrument. Specimens for TEM analysis were prepared from the region of interest pinpointed by Raman spectral mapping. Dark field imaging and SAED confirmed the presence of the boundary between the brookite and anatase polymorphs, proving that the region of interest can be targeted and maintained throughout the specimen preparation process.

Raman-guided FIB for site-specific preparation of TEM specimens is an exciting new technique that shows promise for the nanoscale characterization and microscopy community. This is especially true in situations where more common techniques such as EBSD and EDS lack the necessary resolution and/or capability to distinguish between polymorphs with similar structures and chemistries. Such areas include most Raman active materials: ceramics, semiconductors, organics and biomaterials, and geologic samples. Furthermore, this technique can just as easily be employed in targeted FIB preparation of specimens for atom probe tomography or micropillar nanoindentation of heterophase materials.

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