

Effect of Amorphous Precursor Stoichiometry on Titania Polymorph Formation

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Certain structural polymorphs of titanium dioxide (TiO₂) are known to exhibit photocatalytic ability useful in applications pertaining to water splitting reactions and degradation of organics for water treatment.^[1,2] Among these polymorphs, the brookite structure has been shown to possess the greatest photoactivity under a variety of conditions.^[3,4] However, brookite is metastable and difficult to synthesize with respect to its polymorphic counterparts, rutile and anatase.

Over the last several decades, research efforts have produced brookite TiO₂ through many distinct synthesis procedures, ranging from hydrothermal syntheses to thin film deposition.^[4] Although these report the synthesis methods in detail, there is little to no evidence of exploring the underlying mechanism that stabilizes the brookite polymorph. This work aims to elucidate and understand that fundamental mechanism.

In our previous work, we found a range of pulsed laser deposition conditions that lead to high-fraction brookite films.^[5] These films are deposited in an amorphous state and preferentially crystallize in the brookite structure during subsequent thermal treatment. Raman spectroscopy is used to differentiate the polymorphs and characterize the overall phase fractions present in the films. Calculations of internal energy as a function of molar volume show a region of tensile stress in the TiO₂ system where brookite is favored over both anatase and rutile. If this region can be targeted through strain-inducing defects, such as oxygen vacancies, it may be possible to selectively stabilize the brookite phase during crystallization. Titania films were deposited under varying oxygen partial pressures to investigate the effect on amorphous precursor composition and resulting phase formation. Both Rutherford backscattering spectrometry (RBS) and electron energy-loss spectroscopy (EELS) reveal the as-deposited films are oxygen deficient with respect to stoichiometric TiO₂. EELS acquired from films deposited at a pO₂ of 1 mTorr show the Ti-L₃ peak at an E_{loss} of 460.4 eV and films deposited at a pO₂ of 0.7 Torr at an E_{loss} of 459.1 eV. This peak shift from higher to lower energy loss indicates an increase in Ti³⁺ character in the film - a result of oxygen deficiency. RBS determined the composition of these films to be Ti(1)O(1.932) and Ti(1)O(1.853), respectively, further supporting the EELS results. The 1 mTorr films form high fractions of brookite upon crystallization, while the 0.7 Torr films form rutile. We propose that the composition of the amorphous precursors directly affects the resulting crystalline TiO₂ phase via strain induced by oxygen vacancies.

References:

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