**Anatase crystalline phase discovery on ultra-thin layer $TiO_2$ films during low-temperature ALD on fluorine-rich carbon substrates**

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A novel approach to crystalline anatase phase in atomic layer deposition (ALD) of $TiO_2$ by deposited on a fluorine-rich carbon substrate using titanium (IV) isopropoxide (TTIP) and $O_2$ plasma. In films deposited at temperatures as low as 100 $^oC$ and with a thickness of only 4 nm, highly crystalline anatase phases have been observed. Furthermore, when deposited on glass or silicon substrates other than carbon, $TiO_2$ films consistently produce amorphous films under these conditions. This talk will highlight the unique substrate-driven crystallization of ALD $TiO_2$ and lays the ground rules for selective crystallization using surfaces with suitable initiation chemistries.

An ALD process using a Veeco® Fiji Gen2 ALD system was used to deposit $TiO_2$ on hydrophobic, polytetrafluoroethylene-coated carbon substrates (AvCarb GDS2230 from Fuel Cell Store). Temperatures of the ALD ranged from 100 $^oC$ to 200 $^oC$, and $O_2$ plasma (300 watts) and water were used as oxidants. Target film thickness ranged from 4 nm to 22 nm. To characterize the films, Raman, Fourier transform infrared spectroscopy (FTIR), and x-ray photoelectron spectroscopy (XPS) were used. AvCarb GDS2230 substrates with an $O_2$ plasma as an oxidant resulted in anatase $TiO_2$ films irrespective of thickness, even when deposited at temperatures below 100 $^oC$. However, the anatase phase is significantly weaker when $H_2O$ is used as the oxidant. An interfacial layer of ALD Al2O3 suppresses the growth of the anatase phase. Data from XPS indicates that Ti-F bonds form at the pre-deposition stages of films with anatase $TiO_2$. On non-fluorinated substrates, where the Ti-F bond does not exist, this structurally distinguishes amorphous $TiO_2$. This fluorine on the surface of the carbon paper serves as a directing agent [1-5] for the application of TTIP to PTFE in a flourolysis reaction, which drives the $TiO_2$ to crystallize into anatase films.

Fluorine doped crystallization in Ti-O systems has been reported in sol-gel and hydrothermal approaches to synthesize $TiO_2$ powders.[6, 7] Here, we report the first gas-phase analog of the above reaction mechanism to synthesize crystalline anatase $TiO_2$ films. With this strategy, surface initiation chemistries can be used to achieve area-selective and *in situ* crystallization of films.

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