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In-Situ 4D-STEM Study of Amorphous Titanium Oxide for Water Splitting Application

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Photoelectrochemical (PEC) water splitting produces hydrogen and oxygen byproduct out of water and sunlight [1]. Silicon with nano-structured surface, called black silicon, is used as a photoanode in PEC cells, where it absorbs photons and generates charge carriers to initiate redox reactions on the surface of electrodes [2]. ultra-thin amorphous titanium oxide (a-TiO_2) grown by atomic layer deposition (ALD) on the Si substrate is able to protect b-Si surface from corrosion. At the same time, a-TiO_2 film does not interfere in light absorption due to its light transparency, and it can provide charge conductivity for PEC reactions [3]. Variations in ALD conditions lead to variations in PEC performance through the mechanisms which have been unknown so far. It's believed that local orderings such as medium range ordering (MRO) play a key role in controlling a-TiO_2 film properties. Calculation of normalized intensity variance, V(k), from nano-diffractions acquired by four dimensional scanning electron microscopy (4D-STEM) is a powerful method to detect type and degree of medium range ordering in this amorphous system [4]. Furthermore, combination of 4D-STEM technique and in-situ heating experiment could provide useful information about evolution of MROs as a function of temperature, which has been the aim of this work.

DENS Solution heating holder was used to run the heating experiment on a-TiO_2 films in a precisely temperature-controlled environment [5]. Each homogeneous amorphous film experienced a heating cycle as shown in Fig. 1a, followed by implementation of 4D-STEM. In 4D-STEM technique, a nano-sized (~1.5nm) converged probe was scanned over the amorphous region of interest, and a high dynamic range pixelated detector (EMPAD) collected thousands of nano-diffractions from the scanned positions (Fig 1.b and c) [6]. Subsequently, normalized intensity variance was calculated over nano-diffractions to analyze the MRO type and degree of ordering (Fig. 1c). As a result, Fig. 2a shows the change in MRO degree as a function of in-situ temperature, where MRO degree increases to 400°C. However, a decrease in the peaks amplitude is observed after 400°C, where the homogeneous crystallization is dominant, suggesting the amorphous system relaxes during crystallization, and evolution of MRO is occurring prior to crystallization. Also, mono-chromated electron energy loss spectroscopy (EELS) was carried out on amorphous and crystalline areas of the film experienced 430°C heating cycle. Crystal field splits are observed for L_2 and L_3 Ti edges, also the shape of the peak at 458.7 to 461.3 eV confirms the formation of Anatase phase from amorphous matrix (Fig 2. b) [7].

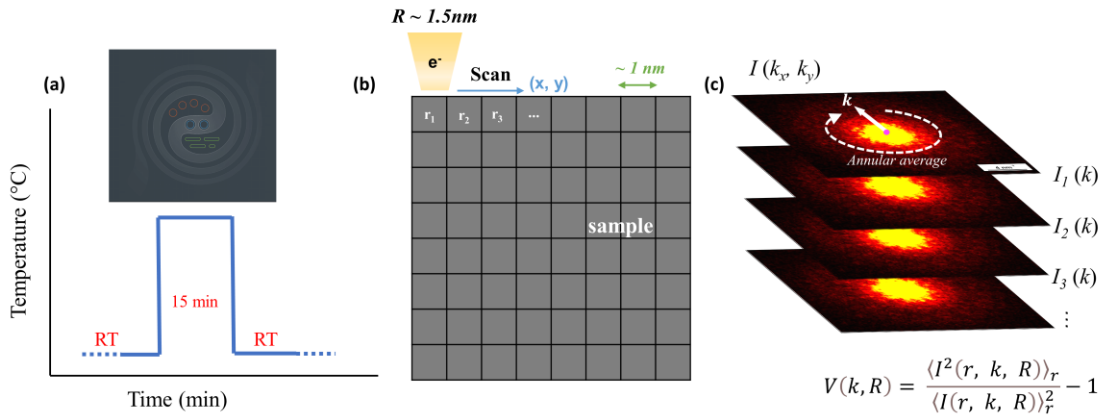

Figure 1: a) in-situ heating cycle and DENS Solution heating chip [8], b) 4D-STEM schematics, and c) V(k) calculation from 4D-STEM nano-diffractions.

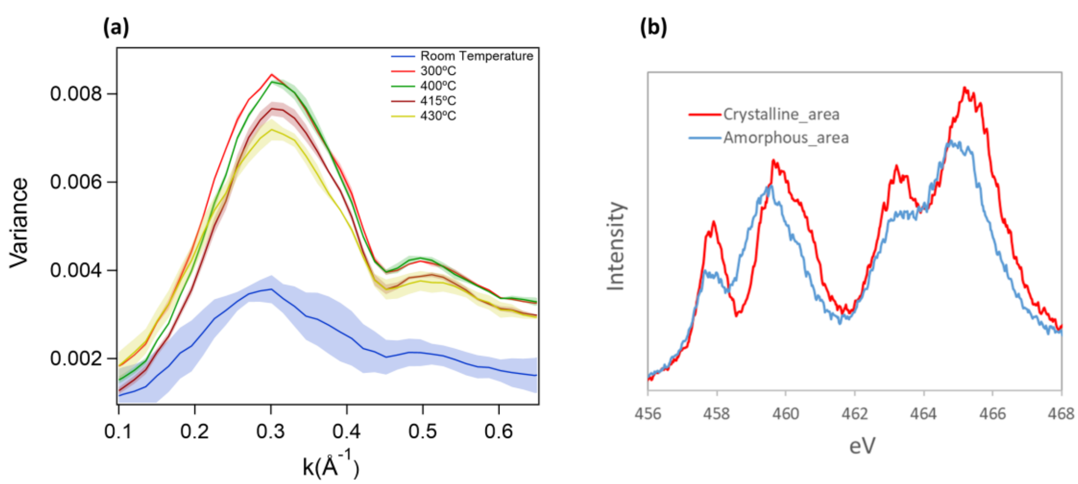

Figure 2: a) V(k) plots of the films a function of in-situ heating temperature, and b) EELS L_2L_3 Ti edges for the film experienced 430°C cycle.

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