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# 4D-STEM Determination of Atomic Structure of Amorphous Materials for Renewable Energy Applications

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Hydrogen production using photoelectrochemical (PEC) water splitting is a promising method to sustain a renewable energy source [1]. In a PEC cell [2], a photoelectrode, such as a nanostructured silicon, captures solar energy and generates charge carriers that lead to hydrogen reduction (Fig. 1a). It has been found that ultrathin amorphous $TiO_2$ (a-$TiO_2$) films grown by atomic layer deposition (ALD) on Si photoanode can protect Si from corrosion as well as providing proper charge conductivity [3]. Moreover, it has been hypothesized that local nanoscale atomic ordering in a-$TiO_2$ plays a key role in determining the film properties. In this work, we present the fluctuation electron microscopy (FEM) and angular correlation (AC) analyses of nano-diffraction patterns acquired via four-dimensional scanning transmission electron microscopy (4D-STEM) that provide information about the type and symmetry of medium range orderings (MRO) in a-$TiO_2$. The experimental results are then used as an input to the StructOpt optimization [4] to determine the possible structures of MRO that may be critical to film properties.

In our 4D-STEM experiment, about ~100,000 nano-diffraction patterns were recorded using an Electron Microscopy Pixel Array Detector (EMPAD) from a-$TiO_2$ film, as shown in Fig. 1b and 1c. Normalized intensity variance (V) [5] and AC [6] were calculated from the patterns to extract the type and structural symmetry of MROs within the sampling volumes. The 2-fold and 4-fold symmetries are visible from the experimental AC results as shown in Fig. 2b and 2c. From the modeling side, possible structures of MROs were simulated using StructOpt algorithm. The optimization was constrained by energy (E) generated with COMB potential [7] as well as experimental V. The inclusion of V in the simulation made substantial improvement in generating realistic MRO (Fig. 1f). To evaluate the symmetry of modeled MROs from two models (Fig. 1d and e), a few hundred nano-diffraction patterns were simulated by multi-slice algorithm [8] from the models, which took into account multiple scattering in conjunction with insignificant thermal scattering using absorptive model [9] (Fig. 2a), as well as different model orientations. After that, AC was calculated from the simulated patterns, which was then compared to the experimental AC data. The averaged AC results show some similarities in terms of 2-fold symmetries, while showing some discrepancies in terms of the higher order symmetries (Fig. 2d and 2e). Direct incorporation of experimental AC data into StructOpt is currently underway, and it is expected to generate a better match to the experimental data, which in turn will provide more realistic MRO models.

In summary, our result demonstrates that the implementation of angular correlation analysis along with multi-slice simulation is a powerful method to study the symmetry and 3D information of models of amorphous materials. The comparison of AC calculations between simulated models and experiment provides us high fidelity in validating the models in terms of the realistic structure of medium range ordering.

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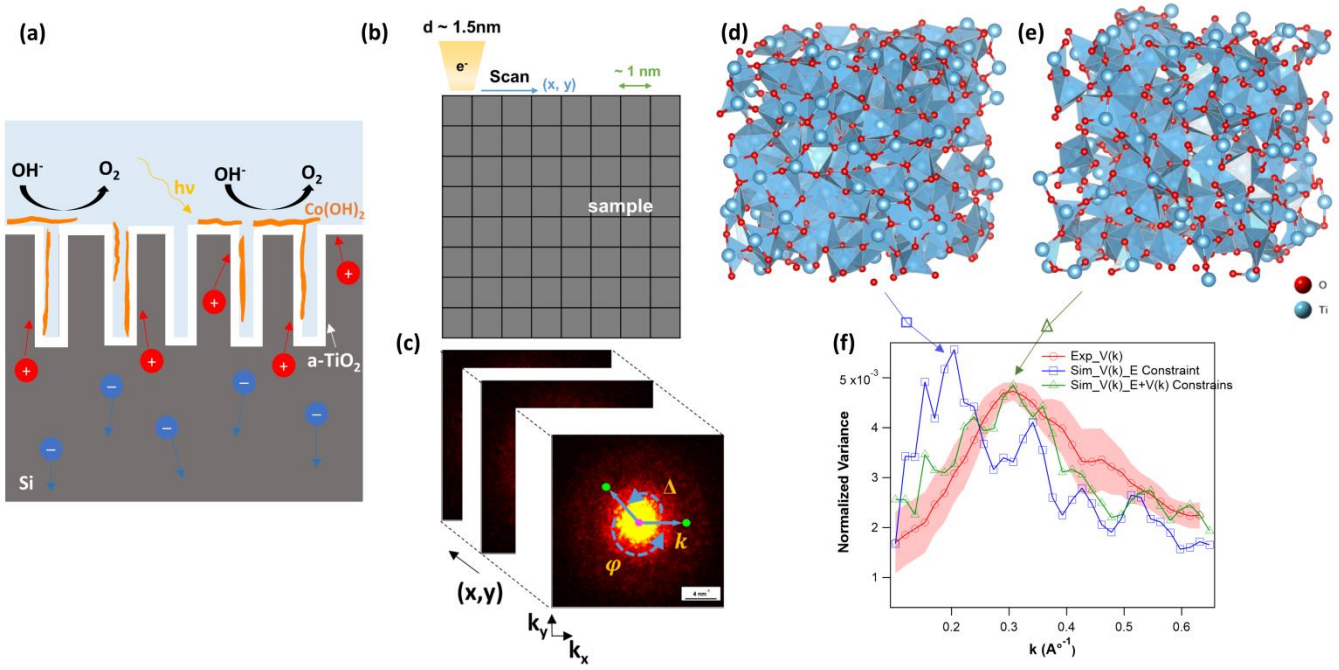


**Figure 1.** (a) Schematic of PEC reactions on the interface of Si photoanode protected by a-TiO2 film [3], (b) 4D-STEM schematic, (c) 4D-STEM a-TiO2 nano-diffraction including AC along φ, averaged over Δ, for all scattering vector, k. Atomic models of a-TiO2 optimized by (d) energy, and (e) energy plus experimental V as a function of k. (f) Experimental V(k) with uncertainty range and simulated V(k)s of two model candidates for comparison.

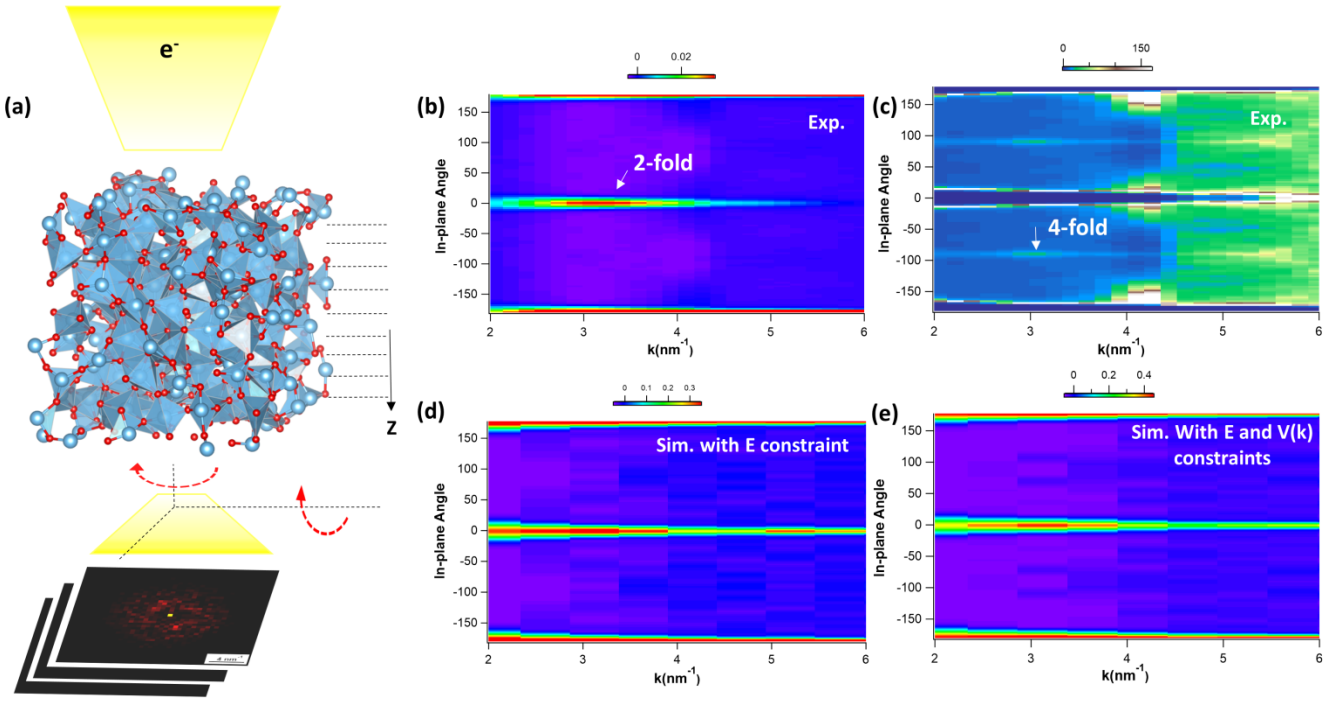


**Figure 2.** (a) Schematic of nano-diffractions' simulation by multi-slice algorithm from a model. (b and c) Experimental average and variance of AC, respectively, over all k. Simulated averaged AC for the candidate optimized by (d) energy only, and (e) energy as well as experimental V(k).

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