Project title: Chemical tomography of Co-doped Fe$_2$O$_3$ photoanodes for water splitting

Summary: Atom probe tomography was used to analyze the 3-D distribution of Co dopant atoms in a hematite (Fe$_2$O$_3$) photoanode for water splitting. For the first time, the feasibility of detecting a single monolayer of dopant was demonstrated in high-performance photoanodes fabricated at Argonne National Laboratory. This advance is significant because trace elements, which diffuse during annealing, play an important but not fully understood role in reducing the overpotential of metal oxide photoanodes. The outcome of the ISEN funded work will be incorporated into a proposal to DOE-BES that will establish structure/function relationships in nanostructures composite photoanodes of metal oxides by correlating atom probe tomography with scanning photocurrent microscopy.

Background and Motivation: the possibility of generating fuel from sunlight has focused considerable attention on the challenge of developing improved photoanodes for water splitting. Fe$_2$O$_3$ is an excellent photoanode candidate because it is abundant, chemically stable, and has a bandgap (2.2 eV) that can utilize a large portion of the solar spectrum. However, a large overpotential of ~0.5 V is required due to fast recombination via interface states and slow oxidation kinetics. Surface state passivation and protection against photocorrosion can be achieved by using thin surface layers. The protection layer, which is generally annealed after deposition, is also relatively stable under conditions necessary to drive water splitting. Slow oxidation kinetics can often be improved by the addition of a photocatalyst to improve water oxidation. For example, a single monolayer of Co deposited by atomic layer deposition (ALD) has been shown to be effective in reducing the overpotential relative to pure hematite. However, the limited spatial and chemical resolution of conventional characterization tools impedes a quantitative understanding of the structure function-relationship of doped photoanodes. Furthermore, typical processing regimens may lead to the diffusion of dopants from the substrate into the active layer.

Atom probe tomography (APT) could be a uniquely useful technique to analyze the nanoscale 3-D chemical composition of composite oxide photoanodes. Previously, there has been little APT analysis of oxides, and none to our knowledge of oxide photoanodes. However, recent developments in pulsed laser APT, in particular the addition of a UV laser to the NUCAPT facility, have extended the application space of APT to dielectrics.

Research objectives: The original research objectives targeted analysis of high-performance Fe$_2$O$_3$/Al$_2$O$_3$ composite photoanodes both before and after the water splitting reaction to determine whether a 3-D composition analysis might provide new insights into pinhole formation and breakdown. In the course of working with samples from Alex Martinson at Argonne National Laboratory, we revised the objectives to focus on detection of the photocatalyst distribution. The revised objectives of the research were to: (1) Fabricate standard doped photoanodes and special atom probe test structures on planar samples and silicon micro-post arrays to determine the sample geometry that would best enable atom probe tomography measurements. (2) Begin an electrochemical characterization effort at Northwestern to test the materials from Argonne and validate our measurement capabilities. (3) Establish optimized run conditions for atom probe tomography. (4) Establish the detection limit for Co dopants in Fe$_2$O$_3$ by atom probe tomography.
Results:

1. Determination of sample substrate and analysis target. Fe$_2$O$_3$ thin films were deposited by atomic layer deposition on n-type silicon substrates, and photoanodes were fabricated and tested at Northwestern University. Films with an Al$_2$O$_3$ capping layer were not sufficiently conductive to merit further testing. Instead, testing focused on cobalt doped samples. The best performing films have one nominal monolayer of cobalt doping incorporated at the end of the film deposition process, but the amount of cobalt had not been quantified prior to the studies. For optimal comparisons between water splitting experiments and atom probe analysis, atom probe samples were extracted from planar photoanodes using the lift out method.

2. Identification of appropriate capping layer and test sample. Prior to atom probe analysis, a metal capping layer needs to be deposited to protect against damage from focused ion beam milling during sample preparation. Several metals were tested to establish a compatible evaporation threshold with hematite; when the evaporation threshold of the metal and the metal oxide are significantly different, imaging artifacts and fracture at the interface are commonly observed. The capability to deposit Pt metal by ALD within the same deposition system used for the Fe$_2$O$_3$ was recently added. This enabled the cobalt doping to be encapsulated prior to exposure to atmosphere. For the final successful samples, 60 nm of chromium was sputter-deposited on top of 10 nm of ALD Pt.

3. Analysis of cobalt distribution. In order to benchmark the performance of APT, a test structure was designed that consisted of standard thicknesses of Fe$_2$O$_3$ separated by varying doses of the Co catalyst precursor (Figure 1). Atom probe tomography reconstructions clearly show three regions doped with Co of varying concentration within the Fe$_2$O$_3$ as expected from the ALD process. One-dimensional composition profiles (Figure 2) provide a quantitative measure of the Co distribution and show that the detection limit is well below 1%.

4. Implications and future work. This work shows, for the first time, and the possibility of detecting dilute catalyst species in metal oxide photoanodes. Several possible lines of investigation can now be seriously considered. First, the Martinson group at ANL has shown improved performance in crystalline Fe$_2$O$_3$. It would be interesting to see whether the catalyst in crystalline, polycrystalline, and nearly amorphous material is similar, or whether the catalyst segregates to e.g. grain boundaries. Second, many investigators have shown the benefits of utilizing nonplanar electrode geometries. APT has the unique ability to analyze dopant distribution in nanowires heterostructures, for example, and the Lauhon group has the capability to grow silicon nanowires. Finally, most optimized processes for photoanode fabrication involve annealing steps that may redistribute elements in the substrate and thin-film. It would be interesting to analyze anodes fabricated on fluorine-doped tin oxide to explore the role of unintentional dopants on performance.
Figure 1 Schematic of photoanode test structure and atom probe reconstructions showing distribution of Co dopant within Fe$_2$O$_3$ layer.

Figure 2 One-dimensional composition profiles of Co species detected during atom probe analysis. The detection limit appears to be well below 1%.
References:


