

In-Situ Investigation of the Growth of Silver Oxy-Iodide Popsicles (Part I)

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The main purpose of this experiment was to determine the relative locations of AgI and Ag₂O in films grown by oxidizing iodide-covered silver metal, and compare them to those grown by conversion of Ag₂O to AgI. We also planned to quantify observed changes in the structure or compactness (density) of the oxide grown atop silver iodide and explore the mechanism by which the oxide and iodide are separately stripped under cathodic polarization [1-4].

We began by performing neutron reflectometry (NR) on a number of samples that have been pre-screened with X-ray reflectometry. Two samples, labeled 20 and 21, were chosen for further investigation where NR would be carried out in-situ while the samples underwent electrochemical reactions. Figure 1 is the example of the quality of data obtained with these samples. Here, the experimental NR data (red points) for Sample #21, are plotted together with calculated reflectivity from a least-squares fitted model (inset table). The successful fitting verifies that the as prepared samples are of sufficient quality.

Figure 2 shows the overlay of the NR curves recorded from Sample #20 in three different conditions: in solvent (D₂O), in D₂O/KOH (0.1M) and, after anodic oxidation at +0.25 for 120s. The comparison between the reflectivities in D₂O with and without KOH (red and black curves) shows that the presence of the KOH does not make an observable change in the silver film. However, after anodic oxidation (blue curve) a significant amount of the silver metal is lost. As the Pilling-Bedworth ratio (the volume of the oxide divided by the volume of the metal used to create the oxide) is larger than one for silver, this missing thickness is somehow surprising. If the oxide layer remained at the surface after anodization, the overall film thickness should not be lower than the initial thickness of the silver film unless part of the Ag metal is dissolved in the solution. The data in Figure 2 indicates that the anodization is accompanied by Ag dissolution.

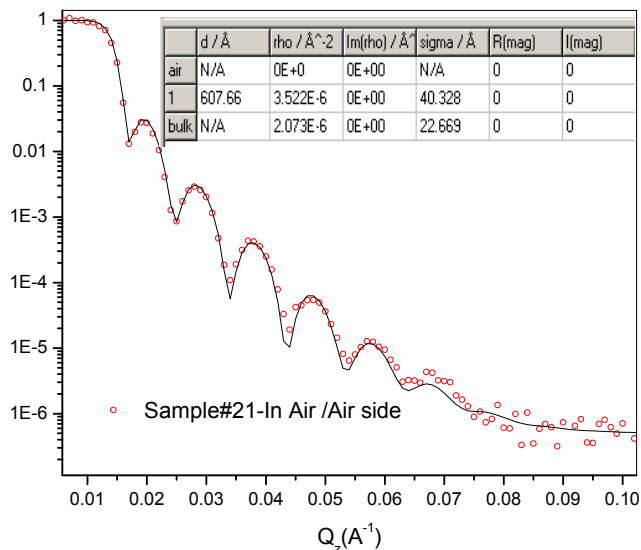


Figure 1 NR of silver film sample #21 prepared on Si wafer by sputtering technique (red points). Inset table shows the parameter used by Parrat32 to fit (black curve) experimental data points.

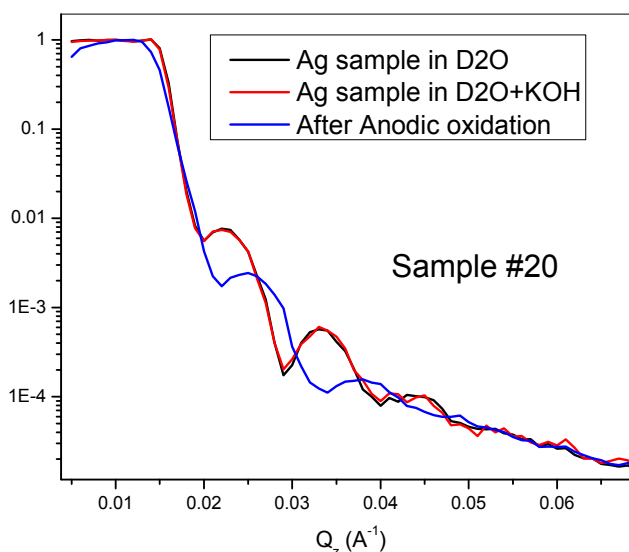


Figure 2 Overlay of the NR curves from the sample #20 before and after anodic oxidation measured in different solvents. Red curve shows the NR of the as prepared sample #20 after it was placed in D₂O. Black curve is the NR measured after KOH was added for the final concentration of 0.1M. The blue curve is measured in D₂O/KOH (0.1M) after oxidizing at +0.25 for 120s.

Figure 3 shows the comparison between the NR curves of sample #20 in D₂O after anodic oxidation, after sample being exposed to KI (1x10⁻³M for 20 minutes) and after the second cathodic stripping voltammetry (CSV). This figure shows two important results; I) The oxide layer is stable in 0.1M KOH solution and II) Under this experimental condition there is no observable difference between NR curves before and after KI addition.

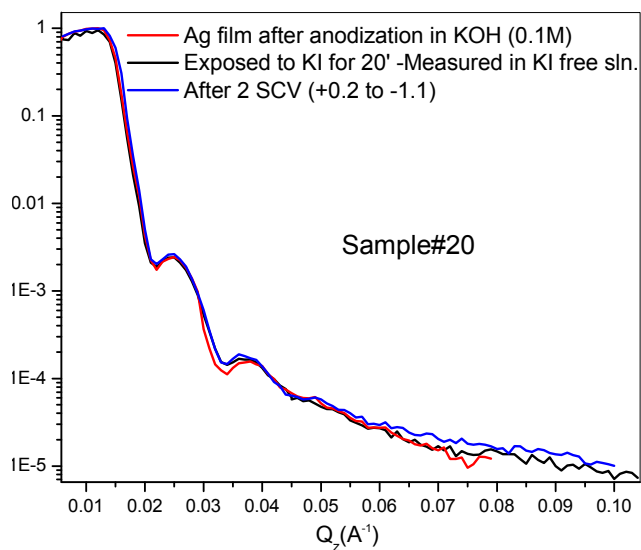


Figure 3 Overlay of the NRs obtained from the silver film (sample #20) after anodic oxidation at +0.25V for 120s in KOH/D₂O (0.1M) solution. Red curve shows the NR of the oxidized Ag film recorded in KOH/D₂O solution. Black curve is NR measured after exposure to 1x10⁻³M of KI for 20 minutes followed by draining and refilling the EC by fresh KI free D₂O/KOH (0.1M) solution. Blue curve shows the NR from the same sample after the second cathodic stripping voltammetry.

Figure 4 shows the overlay of the SLD profiles obtained from the square fitted data analysis for the sample#20 at five different conditions including: an empty electrochemical cell (EEC), after anodic oxidation in solution (D₂O/KOH 0.1M), after anodic oxidation in argon (dried condition) and, after being exposed to KI in iodine free solution (D₂O/KOH 0.1M). After anodic oxidation, one extra layer (so-called silver oxide) between silver and electrolyte must be added to the model to be able to fit the experimental NR data properly. As seen in this figure, other than the decrease in the metal thickness due to the dissolution of Ag during anodization, there are two other interesting significances. First, the roughness of the Silver oxide/electrolyte interface is very large and, second, a

small decrease in the SLD of the oxide layer after addition of KI. Under the experimental conditions we chose, the Ag/oxide and oxide/electrolyte interfaces became so rough that it was not possible to observe any other changes of the sample.

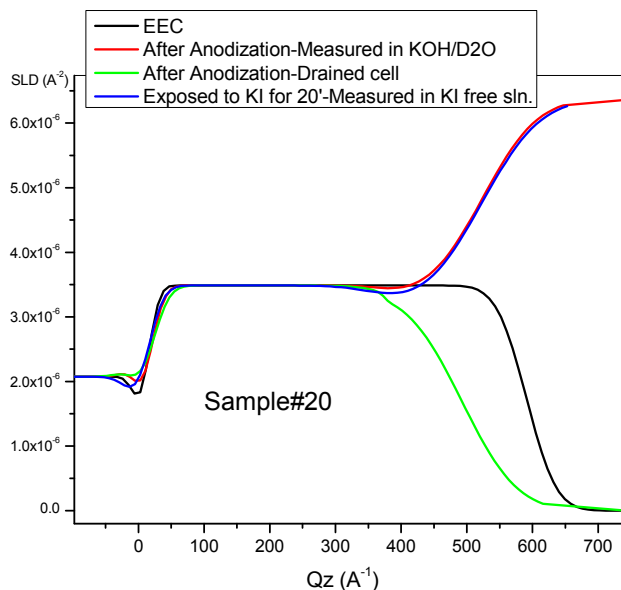


Figure 4 The SLD profiles of the silver sample #20 at different experimental stages, measured in empty electrochemical cell (EEC) (black), after anodic oxidation in KOH/D₂O (0.1M) solution (red), after anodic oxidation in argon (green) and, after being exposed to KI for 20 minutes measured in fresh KOH/D₂O solution (blue).

References

- [1] E. Krausmann and Y. Drosinos, "A model of silver-iodine reactions in a light water reactor containment sump under severe accident conditions", *J. Nucl. Mater.*, **264** (1999) 113-121.
- [2] X. Zhang, S. Stewart, D.W. Shoesmith, and J.C. Wren, "Interaction of aqueous iodine species with Ag₂O/Ag surfaces", *J. Electrochem. Soc.*, **154** (2007) F70-F76.
- [3] X. Zhang, D.W. Shoesmith, and J.C. Wren, "Galvanically coupled process for the conversion of Ag₂O to AgI", *Corr. Sci.*, **50** (2008) 490-497.
- [4] V.I. Birss and G.A. Wright, "The kinetics of silver iodide film formation on the silver anode", *Electrochim. Acta*, **27** (1982) 1439-1443.