

Demonstration of an *in situ* electrochemical RBS System to Study the Electrode-Electrolyte Interface

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An *in situ* electrochemical Rutherford Back Scattering (ECRBS) system has been developed to investigate the kinetics of nuclide adsorption and desorption at electrode-electrolyte interfaces. We believe this technique will have broad applications to the fundamental studies of corrosion, electrodeposition, and electrocatalysis. The adsorption of aqueous iodine on a polycrystalline Au electrode served as a preliminary test.

The probe depth of an RBS ion beam (~0.1–5 μm) allows for the observation of the liquid solid interface through a thin film window assembly. The depth resolution of RBS (~5–20 nm) allows for some estimation of nuclide concentration as a function of depth. In contrast to other *in situ* electrochemical scattering or spectroscopy techniques, ECRBS techniques can provide elemental analysis over a large sample area (~0.25 mm^2).

Ion beam systems have been applied to the investigation of liquid-solid interfaces with reasonable success. Morita et. al. were able to study lead desorption on SiO_2 using an *in situ* RBS system through a 5.5 μm Si window [1]. Bouquillon et. al. were able to resolve Pb in aqueous solutions at concentrations less than 10 ppm through a 100 nm Si_3N_4 window [2]. They also identified bubble formation at regions of beam impact. These bubbles, likely due to water radiolysis, could be totally eliminated with sufficient circulation of the solution.

Initial results have been obtained from a sealed UHV electrochemical cell with a 0.5 mm x 0.5 mm, 150 nm thick Si_3N_4 window (Figure 1). The UHV electrochemical cell was placed into the RBS chamber that operated at a base pressure 2×10^{-8} torr. A 10 nm Au film was sputtered onto the Si_3N_4 window and used as a working electrode. A 5 mil Pt wire was used as a pseudo reference electrode and an ultra dense amorphous carbon (UDAC) substrate served as a counter electrode. A 1.5 mL liquid well was formed with a vacuum grade epoxy resin (Torr Seal®). The three electrodes were interfaced to an ACM Gill AC potentiostat via coaxial electrical feedthroughs.

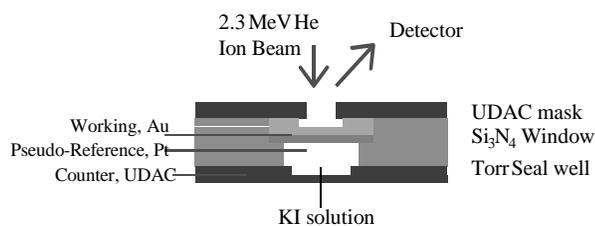


Fig. 1. Schematic of the UHV electrochemical cell incorporated into the RBS chamber.

A 2.3 MeV He ion beam at a current of 40 nA and a spot size of about 0.4 mm^2 was used for RBS. The RBS spectra were acquired using an Ortec Ion-Implanted-Silicon Charged-Particle detector set at 18°. Spectra were obtained over 1024 channels with a resolution of 3 keV per channel. Measure spectra were compared to theoretical results from Rutherford Universal Manipulation Program RUMP simulations.

We chose to study iodine adsorption on polycrystalline gold because the species' large atomic numbers improved RBS signals. The adsorption of iodine on electrodes surfaces has been well studied and is known to have a strong impact on the underpotential deposition of metal ions [3]. Single crystal studies of iodine on gold have shown the structure of the I/Au(111) adlayer to be strongly potential dependent [4].

Figure 2 displays the ECRBS spectra of a polycrystalline Au electrode in 7 mM KI solution held at open circuit and minor reducing potentials. Distinct peaks for Au and adsorbed I can be observed at 2.16 MeV and 2.07 MeV respectively. Plateaus approximately 0.1 MeV wide are observed from the 150 nm Si_3N_4 window at 1.36 MeV and 0.75 MeV respectively. The increasing tails at 1.36 MeV and 0.6 MeV that extend to 0 MeV are due to the beam interactions with the 0.2 mm thick Si window frame and the UDAC mask respectively. Lastly, minor K and O peaks are observed at 1.63 MeV and 0.91 MeV.

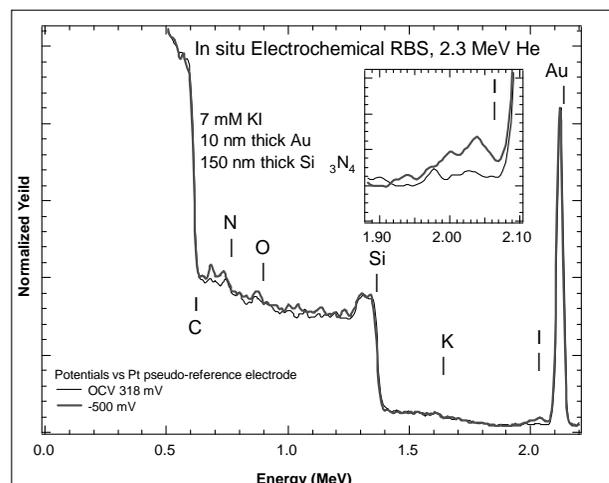


Fig. 2. RBS spectra of polycrystalline Au electrode in 7 mM KI held at open circuit potential and -500 mV.

An increase in I concentration indicated by the area under the RBS spectra at the electrode surface is observed when a reducing potential, -500 mV vs Pt pseudo reference electrode, was applied and persisted at higher potentials.

Future work will include the addition of a standard reference electrode, mechanisms for electrolyte circulation, alternative electrodes materials, and further electrochemical characterization of electrodes.

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