

DEMONSTRATION OF AN IN-SITU ELECTROCHEMICAL RBS SYSTEM TO STUDY ELECTRODE-ELECTROLYTE INTERFACES

Adrian Hightower¹, Bruce Koel¹, and Thomas Felter²

¹Department of Chemistry, University of Southern California, Los Angeles, California, 90089-0482

²Lawrence Livermore National Laboratory, Livermore, California 94550

ABSTRACT

An *in-situ* electrochemical Rutherford backscattering (ECRBS) system has been demonstrated that enables the investigation of electrode and solution composition, along with kinetics of nuclide adsorption and desorption, at an electrode-electrolyte interface (EEI) under potential control. In contrast to other *in-situ* electrochemical diffraction or spectroscopy techniques, ECRBS can provide quantitative elemental analysis over an area of $\sim 0.25 \text{ mm}^2$. The probe depth of the RBS ion beam allows observation of the EEI through a thin film electrode window assembly ($\sim 200 \text{ nm}$). The depth resolution of RBS (1-10 nm) allows for measurement of nuclide concentration of the surface and near-surface layers. In this first report, we seek to demonstrate elemental characterization using ECRBS by measuring iodine adsorption on a polycrystalline gold electrode as well as gold dissolution. We believe ECRBS will bring new insight to a wide range of electrochemical processes, in particular to investigations of corrosion, electrodeposition, and electrocatalysis.

INTRODUCTION

We demonstrate in this report an *in-situ* electrochemical Rutherford backscattering (ECRBS) system with the goal of characterizing the composition of the electrode-electrolyte interface (EEI) under potential control and enabling new investigations of the kinetics of nuclide adsorption and desorption. Historically, it has been extremely challenging to design experiments that directly correlate electrochemical performance of an EEI to an atomistic model. The advent of numerous *in-situ* electrochemical diffraction and spectroscopy techniques has greatly expanded our understanding of the EEI, however until recently, elemental and atomic level characterization of surfaces could only be accomplished with techniques working in ultrahigh vacuum (UHV) conditions [1-3]. The new technique, ECRBS, is an *in-situ* method that can probe the EEI under potential control. We believe that ECRBS will further the understanding of a wide range of electrochemical processes, in particular corrosion, electrodeposition, and electrocatalysis.

In contrast to other *in-situ* electrochemical diffraction or spectroscopy techniques, ECRBS can provide quantitative elemental analysis. *In-situ* electrochemical Fourier transform infrared spectroscopy

(FTIR), scanning tunneling microscopy (STM), and surface X-ray diffraction (SXS) provide information on bonding, topography, and crystalline phases at the EEI, respectively [4-7]. The analysis area for a given ECRBS scan is $\sim 0.25 \text{ mm}^2$ and is primarily dictated by the size of the UHV window. The probe depth of the RBS ion beam allows observation of the EEI through a thin film electrode window assembly ($\sim 200 \text{ nm}$). The depth resolution of RBS (1-10 nm) allows for measurement of nuclide concentration of the surface and near-surface layers.

Ion beam techniques have been applied previously to investigate liquid-solid interfaces with reasonable success. Morita *et. al.* were able to study lead adsorbed on SiO_2 using an *in-situ* RBS system that utilized a 5.5-micron Si window [8]. 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 [9]. They also identified bubble formation at regions of beam impact that was likely due to water radiolysis, but found that these bubbles could be eliminated with sufficient circulation of the solution.

Adsorption of aqueous iodine on a polycrystalline Au electrode served as a benchmark in testing our ECRBS system. The adsorption of iodine ordered-monolayer phases on Au electrodes has been studied extensively by cyclic voltametry [10-12], surface X-ray scattering (SXS) [13, 14], STM [15-20], and electrochemical quartz crystal microbalance (ECQCM) [21, 22] techniques. Iodine adlayers on single crystal gold surfaces demonstrate potential-dependent phase transitions [20, 23] and are known to have a strong impact on the underpotential deposition of metal ions [19, 24]. In the results reported herein, we seek to demonstrate elemental characterization using ECRBS by measuring iodine adsorption on a polycrystalline gold electrode and measuring partial gold dissolution.

EXPERIMENTAL

Our initial results were obtained from a sealed UHV electrochemical cell with a 0.5 mm x 0.5 mm, 150-nm thick Si_3N_4 window. A schematic drawing of this cell is shown in Figure 1. The UHV electrochemical cell was placed directly in the RBS chamber (base pressure of 2×10^{-8} Torr). The working electrode was a 10-nm Au film that was sputtered onto the Si_3N_4 window (SPI Supplies). The Si_3N_4 window was mounted on 200- μm thick Si frame and rated to withstand a pressure differential of 1 atm. A Pt wire (125- μm diameter) was used as a pseudo-reference electrode and the ultradense amorphous carbon (UDAC) substrate served as the counter electrode. A 7 mM KI solution was prepared from 18 $\text{M}\Omega\cdot\text{cm}$ water (B&J Brand) and analytical grade reagents (Alpha Aesar). It was decided for these first experiments to postpone the use of more conducting electrolytes (H_2SO_4 or HClO_4) in order to simplify analysis of the RBS results. Unfortunately, this limits the analysis of electrochemical measurements. A 1.5 mL liquid well is formed with a vacuum grade epoxy resin (Torr Seal®). The three electrodes are interfaced to an ACM Gill AC potentiostat via coaxial UHV feedthroughs.

A 2.3-MeV He^+ ion beam at a current of 40 nA and a spot size of 0.4 mm^2 was used. The RBS spectra were acquired using an Ortec Ion-Implanted-Silicon Charged-Particle detector set at $2\theta = 164^\circ$ relative to the incident ion beam. Spectra were obtained over 1024 channels with a resolution of $< 20 \text{ keV}$. RBS spectra were normalized to the total number of detected ions. Measured spectra were

compared to simulations produced by the Rutherford Universal Manipulation Program (RUMP) code. Electrodes were held at a given, constant potential while a RBS scan was performed. The average scan time used to obtain a RBS spectrum was about 10 minutes.

RESULTS

Figure 2 displays the ECRBS spectra of a polycrystalline Au electrode in 7 mM KI solution obtained at open circuit and held at a minor reducing potential of -0.5 V. One can observe distinct peaks for gold and adsorbed iodine with edge onsets at 2.16 and 2.07 MeV, respectively. Plateaus approximately 0.1 MeV wide can be observed at 1.36 and 0.75 MeV for the Si and N components, respectively, of the 150-nm thick Si_3N_4 window. Ions backscattered from the 200- μm thick Si-window substrate and the UDAC mask produce counts below 1.36 and 0.6 MeV, respectively. The unwanted Si background (0 - 1.36 MeV) counts indicate a slight misalignment of the UDAC mask, He ion beam, and silicon frame. Minor peaks from K and O can be observed at 1.63 and 0.91 MeV, respectively.

In order to observe the dissolution of the Au electrode, the cell was driven to anodic potentials of 1.5 V. Several RBS spectra of the Au electrode are shown in Figure 3. Figure 3A shows a reduction and redistribution of the area under the 2.16 MeV Au peak. Figure 3B shows the silicon, oxygen nitrogen and carbon onset regions (0.62 MeV) in greater detail. The unwanted Si background (0 - 1.4 MeV) arises from the 200- μm thick Si-window frame. Since the backscattered yield depends on the atomic number squared, light elements are easily obscured by the presence of the Si background. More accurate mask alignment should reduce this significantly, making it easier to quantify light elements, such as oxygen.

DISCUSSION

An increase in iodine concentration at the electrode surface, as indicated by the increase in area under the I peak in the RBS spectra, was observed when a reducing potential of -500 mV versus a Pt pseudo-reference electrode was applied. There is a relatively small amount of adsorbed iodine initially despite electrode exposure to the solution for 15 minutes prior to the RBS measurement. Iodine monolayers are known to spontaneously form on clean Au electrodes within minutes of exposure. We attribute the slow adsorption kinetics of I on the Au electrode to the presence of contaminants on the electrode surface. Once a potential was applied to the electrode, an iodine monolayer formed within the time required for one RBS scan (10 minutes). The size of the mask opening, and therefore the amount of the incident beam that actually hits the electrode, is not precisely known. Therefore we can compare the measured areas of the iodine and gold peaks to RUMP simulations assuming an initial smooth, 10-nm thick Au electrode. Our measurements yield an iodine surface concentration of 1.3 ± 0.3 nmol/cm² for the

adsorbed monolayer agreeing with the value of 1.04 nmol/cm^2 reported by Rodriguez et. al [25] within the rather large uncertainty in initial Au electrode thickness.

Analysis of the ECRBS spectra for iodide oxidation on a polycrystalline Au electrode is complicated by the use of a Pt pseudo-reference electrode (Pt wire). This made the determination of the onset potentials of Au dissolution difficult. The application of 1.5 V forms an iodine film whose thickness increased with each successive scan. This formation was accompanied by a large initial dissolution of Au, as indicated by the decrease in area of the 2.16 MeV Au peak. Further scans showed a redistribution of the Au peak to lower energies indicating a roughening of the Au electrode. Though these observations are consistent with previous studies [10, 26], this was a demonstration experiment only and we are cautious to draw definitive conclusions about the electrochemistry itself. The ECRBS studies were carried out over the course of one hour with 1.5 ml of stagnant electrolyte. The system is susceptible to radiolysis and formation of bubbles near the electrode surface would complicate interpretation of the RBS spectra. Nevertheless, we can clearly observe the coordinated formation of an iodine layer as well as the dissolution of the gold electrode. Improvements in the technique in later experiments will include addition of a standard reference electrode, incorporation of a mechanism for electrolyte circulation, and better electrochemical characterization.

Figure 4 displays scanning electron microscopy images of the initial 10 nm-thick sputtered Au electrode and the electrode after the ECRBS study. The electrode is initially homogeneous, but after the ECRBS experiments contains altered regions $\sim 300\text{-nm}$ in size that arise from radiolysis and/or gold dissolution. Subsequent energy dispersive X-ray spectroscopy (EDX) measurements could not detect iodine at the electrode surface.

The depth resolution of ECRBS (1-10 nm) is relevant for measuring aspects of diffusion in electrodes and electrolytes and phase transitions in electrode materials as a function of potential, but provides limited information regarding adsorbed monolayers at the electrode surface. Channeling and blocking experiments in ECRBS utilizing single-crystal metal electrodes may be one approach to increasing this capability. Medium Energy Ion Scattering (MEIS) techniques employ lower energy ion beams ($\sim 100 \text{ keV}$) and can have much better depth resolution (0.5-1 nm). Thus, *in-situ* electrochemical MEIS may offer a better avenue for quantitative elemental analysis of electrode surface species than ECRBS. To our knowledge, no such experiment has been made previously.

CONCLUSION

An *in-situ* electrochemical Rutherford backscattering (ECRBS) system has been demonstrated with the goal of developing a new *in-situ* elemental analysis technique for investigating electrochemical processes at the electrode-electrolyte interface (EEI) under potential control. Iodine accumulation of $1.3 \pm 0.3 \text{ nmol/cm}^2$ at a polycrystalline Au electrode under a reducing potential was directly measured by ECRBS. The coordinated formation of an iodide layer and dissolution of the gold electrode was also directly observed by ECRBS. We have suggested changes that will improve the technique, and we point

out that a similar approach utilizing Medium Energy Ion Scattering (MEIS) should be possible in order to characterize electrode adlayers with submonolayer resolution.

ACKNOWLEDGEMENTS

The authors thank Merck & Co., Inc and the United Negro College Fund for their financial support. Work at LLNL was performed under the auspices of the U. S. Department of Energy by the University of California, Lawrence Livermore National Laboratory under Contract No. W-7405-Eng-48.

REFERENCES

1. Somorjai, G.A., *Introduction to Surface Chemistry and Catalysis*. 1994, New York: Wiley-Interscience.
2. Hubbard, A.T., *Electrochemistry at Well-Characterized Surfaces*. Chemical Reviews, 1988. **88**(4): p. 633-656.
3. Soriaga, M.P., *Ultra-High Vacuum Techniques in the Study of Single-Crystal Electrode Surfaces*. Progress in Surface Science, 1992. **39**(4): p. 325-443.
4. Iwasita, T. and F.C. Nart, *In situ infrared spectroscopy at electrochemical interfaces*. Progress in Surface Science, 1997. **55**(4): p. 271-340.
5. Lin, W.F., P.A. Christensen, and A. Hamnett, *The electro-oxidations of methanol and formic acid at the Ru(0001) electrode as a function of temperature: in-situ FTIR studies*. Physical Chemistry Chemical Physics, 2001. **3**(16): p. 3312-3319.
6. McHardy, R., W.H. Haiss, and R.J. Nichols, *An STM investigation of surface diffusion on iodine modified Au(111)*. Physical Chemistry Chemical Physics, 2000. **2**(7): p. 1439-1444.
7. Samant, M.G., et al., *Grazing-Incidence X-Ray-Diffraction of Lead Monolayers at a Silver (111) and Gold (111) Electrode-Electrolyte Interface*. Journal of Physical Chemistry, 1988. **92**(1): p. 220-225.
8. Morita, K., et al., *An in situ RBS system for measuring nuclides adsorbed at the liquid-solid interface*. Radiation Physics and Chemistry, 1997. **49**(6): p. 603-608.
9. Bouquillon, A., et al., *In situ dynamic analysis of solids or aqueous solutions undergoing chemical reactions by RBS or PIXE with external beams*. Nuclear Instruments & Methods in Physics Research Section B-Beam Interactions with Materials and Atoms, 2002. **188**: p. 156-161.
10. Chen, A.C., et al., *Iodide adsorption at the Au(111) electrode surface*. Journal of Electroanalytical Chemistry, 1999. **467**(1-2): p. 342-353.
11. Hamelin, A., *The Crystallographic Orientation of Gold Surfaces at the Gold Aqueous-Solution Interphases*. Journal of Electroanalytical Chemistry, 1982. **142**(1-2): p. 299-316.

12. Bellier, J.P. and A. Hamelin, *Experimental Study of Gold Monocrystal Surfaces with Crystallographic Orientation 111 in Aqueous Halide Solutions*. Comptes Rendus Hebdomadaires Des Seances De L Academie Des Sciences Serie C, 1975. **280**(25): p. 1489-1492.
13. Wang, J., et al., *In-situ X-Ray-Diffraction and X-Ray-Reflectivity Studies of the Au(111) Electrolyte Interface - Reconstruction and Anion Adsorption*. Physical Review B, 1992. **46**(16): p. 10321-10338.
14. Ocko, B.M., G.M. Watson, and J. Wang, *Structure and Electrocompression of Electrodeposited Iodine Monolayers on Au(111)*. Journal of Physical Chemistry, 1994. **98**(3): p. 897-906.
15. Gao, X.P., et al., *Sensitivity of Electrochemical Adlayer Structure to the Metal Crystallographic Orientation - Potential-Dependent Iodide Adsorption on Au(100) in Comparison with Other Low-Index Surfaces*. Journal of Physical Chemistry, 1994. **98**(33): p. 8086-8095.
16. Itaya, K., et al., *In situ scanning tunneling microscopy of organic molecules adsorbed on iodine-modified Au(111), Ag(111), and Pt(111) electrodes*, in *Solid-Liquid Electrochemical Interfaces*. 1997. p. 171-188.
17. Itaya, K., *In situ scanning tunneling microscopy in electrolyte solutions*. Progress in Surface Science, 1998. **58**(3): p. 121-247.
18. Tao, N.J. and S.M. Lindsay, *In-situ Scanning Tunneling Microscopy Study of Iodine and Bromine Adsorption on Au(111) under Potential Control*. Journal of Physical Chemistry, 1992. **96**(13): p. 5213-5217.
19. Yamada, T., N. Batina, and K. Itaya, *Interfacial Structure of Iodine Electrodeposited on Au(111) - Studies by LEED and In-situ STM*. Surface Science, 1995. **335**(1-3): p. 204-209.
20. Yamada, T., N. Batina, and K. Itaya, *Structure of Electrochemically Deposited Iodine Adlayer on Au(111) Studied by Ultrahigh-Vacuum Instrumentation and in-Situ STM*. Journal of Physical Chemistry, 1995. **99**(21): p. 8817-8823.
21. Gu, N.Y., L. Niu, and S.J. Dong, *Simultaneous determination of both the calibration constant in an electrochemical quartz crystal microbalance and the active surface area of a polycrystalline gold electrode*. Electrochemistry Communications, 2000. **2**(1): p. 48-50.
22. Lei, H.W., H. Uchida, and M. Watanabe, *Electrochemical quartz crystal microbalance study of halide adsorption and concomitant change of surface excess of water on highly ordered Au(111)*. Langmuir, 1997. **13**(13): p. 3523-3528.
23. Batina, N., T. Yamada, and K. Itaya, *Atomic-Level Characterization of the Iodine-Modified Au(111) Electrode Surface in Perchloric-Acid Solution by In-Situ STM and Ex-Situ LEED*. Langmuir, 1995. **11**(11): p. 4568-4576.
24. Ogaki, K. and K. Itaya, *In-Situ Scanning-Tunneling-Microscopy of Underpotential and Bulk Deposition of Silver on Gold (111)*. Electrochimica Acta, 1995. **40**(10): p. 1249-1257.
25. Rodriguez, J.F., T. Mebrahtu, and M.P. Soriaga, *Determination of the Surface-Area of Gold Electrodes by Iodine Chemisorption*. Journal of Electroanalytical Chemistry, 1987. **233**(1-2): p. 283-289.
26. Schneeweiss, M.A. and D.M. Kolb, *Oxide formation on au(111) - An in situ STM study*. Solid State Ionics, 1997. **94**(1-4): p. 171-179.

FIGURES

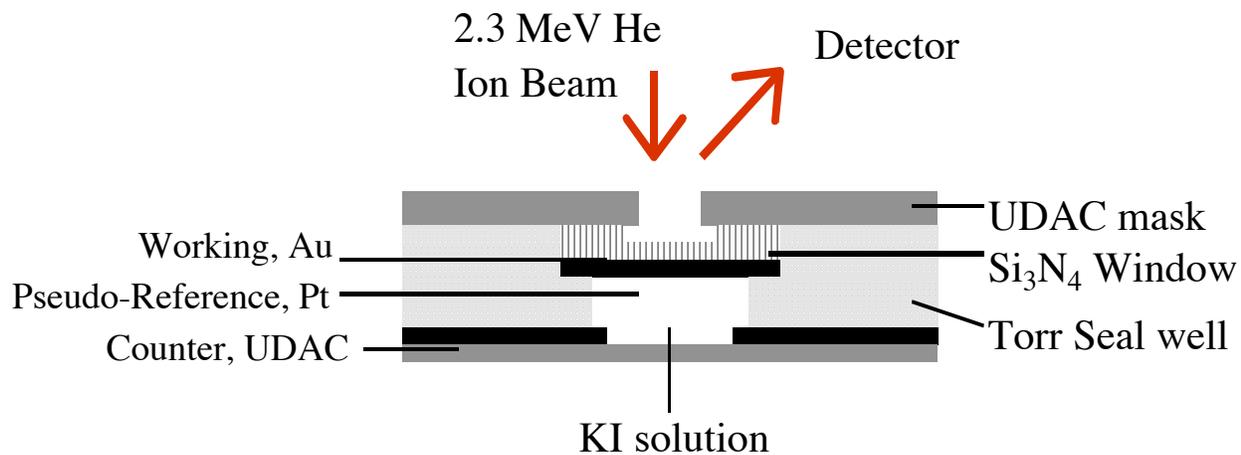


Figure 1. Schematic drawing of the UHV electrochemical cell used in ECRBS. The cell incorporates a 150-nm thick Si₃N₄ window, a 10-nm thick Au working electrode, a 125- μ m diameter Pt wire pseudo-reference electrode, a UDAC counter electrode, and a sealed 1.5 mL liquid well.

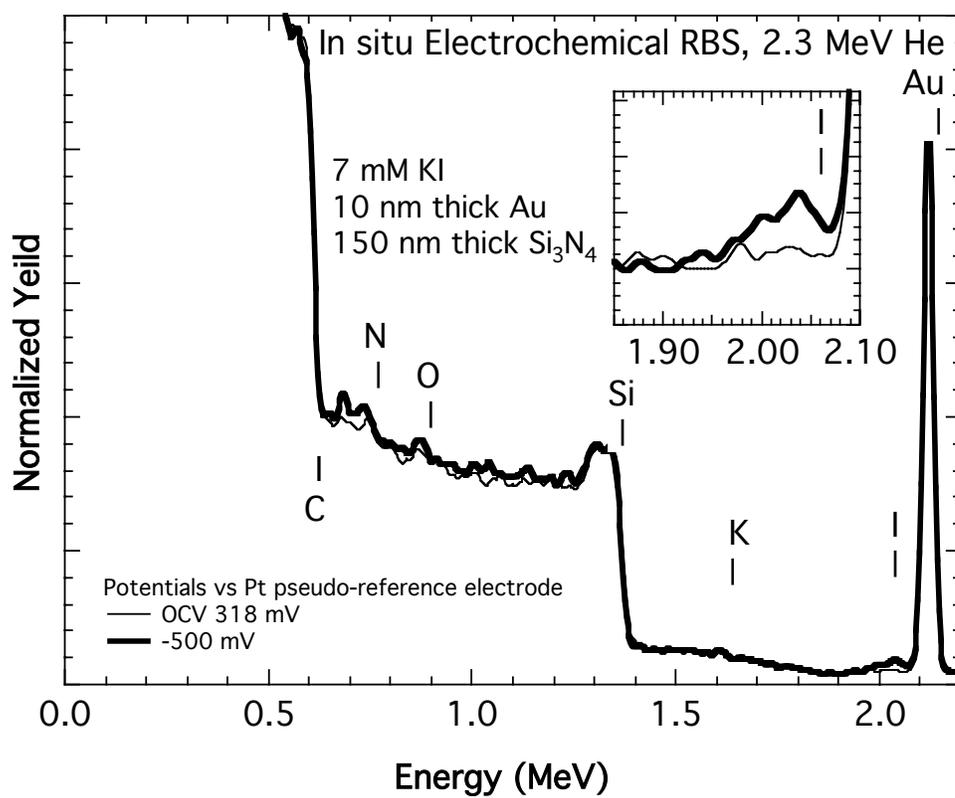


Figure 2. RBS spectra of a polycrystalline Au electrode in 7 mM KI held at open circuit and -500 mV.

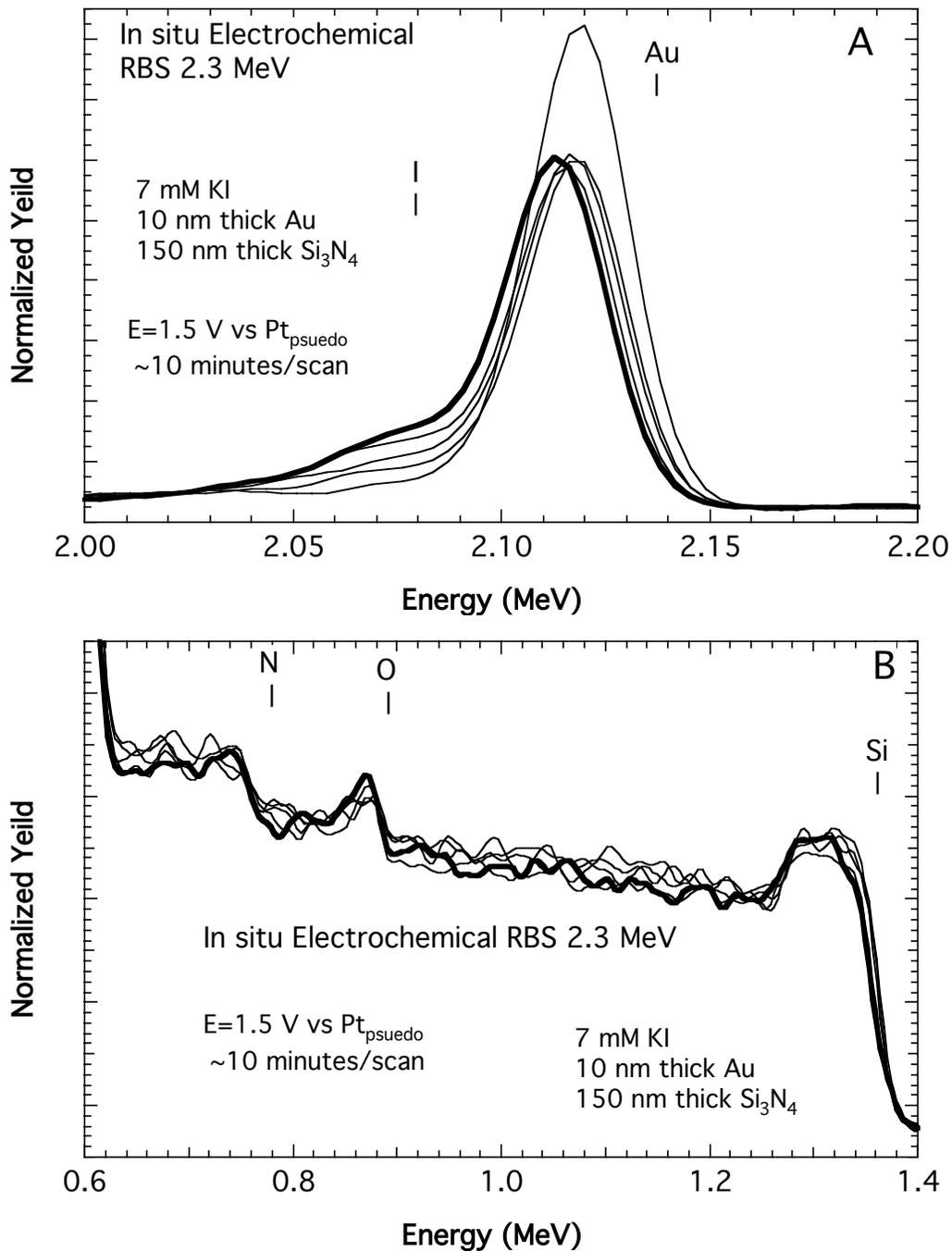


Figure 3 RBS spectra of oxidation of an Au electrode. Top image (A) shows broadening of the gold peak at 2.12 MeV indicative of roughening and formation of an adsorbed iodine layer. Bottom image (B) shows increase and sharpening of the oxygen peak at 0.87 MeV.

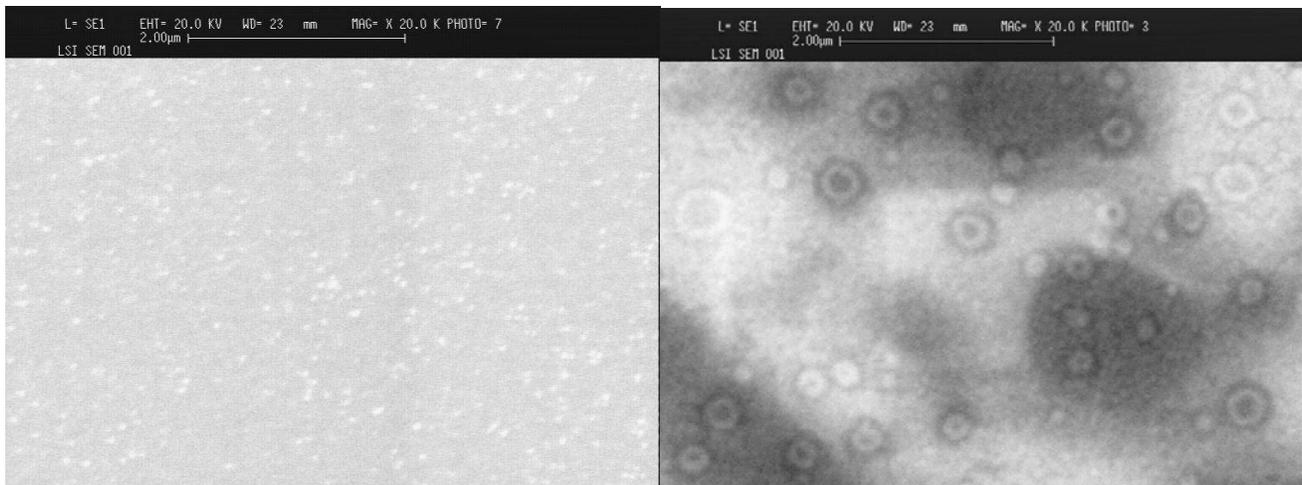


Figure 4. Magnified scanning electron microscopy images showing (left) initial 10-nm thick sputtered homogeneous Au film and (right) altered Au regions with a diameter of ~ 300 -nm after ECRBS experiments. The modified regions may arise from radiolysis and/or Au dissolution.