Performing ATR-SEIRAS with ITO-Coated Wafers from Jackfish SEC

1 Purpose

This document aims to provide a description of a basic adsorption/desorption experiment for users new to ATR-SEIRAS measurements. It provides a specific protocol for depositing a surface-enhancing gold nanoparticle film on the ITO-coated wafers offered by Jackfish, and provides a means for assessing the level of surface enhancement using a pyridine derivative (4-methoxypyridine, MOP) which adsorbs reversibly under potential control and which provides a convenient spectroscopic handle with three strong mid-IR peaks. The described procedure is adapted from [1].

2 Precheck

Confirm that your VeeMAX is aligned by following the alignment procedure in the VeeMAX user manual. Select an appropriate angle on the VeeMAX. Table 1 provides a list of recommended starting-point VeeMAX settings for different ATR elements.

Table 1: Recommended angle of incidence starting points for SEIRAS of films supported on an ITO underlayer.

ATR Element	Recommended VeeMAX setting (starting point)
60 degree face-angled crystal	40°
35 degree microgrooved wafer	55°
55 degree microgrooved wafer	35°

Confirm that the alignment and throughput of the VeeMAX is acceptable by installing the ATR element and its holder in the VeeMAX top plate. First, record a background spectrum with the dry ATR element. Next, pipette a drop of water in the centre of the element and confirm that the ATR spectrum of the water appears as expected. Most acquisition settings can be adjusted as needed. The spectra presented in this document were collected using the parameters in Table 2.

Table 2: Recommended FTIR acquisition parameters.

Setting	Recommended starting value
J-stop aperture diameter	2 mm
Spectral resolution	8 cm^{-1}
Number of coadded scans	32

3 Preparations

The instructions in this guide make use of the following aqueous stock solutions (suggested volumes in parentheses):

- 0.1 M solution of 4-methoxy pyridine (MOP) (2 mL)
- 0.5 M solution of $KAuCl_4$ (2 mL). This solution should be shielded from light and stored in the refrigerator.
- 0.05 M solution of NaF (100 mL)

4 Preparing Deposition Solution in Jackfish Cell

1. Assemble your Jackfish cell according to the instructions in the manual. Fill the cell with 0.05 M NaF and take note of the volume of electrolyte required. Begin purging the cell with inert gas. Connect the potentiostat leads to the counter, reference, and working electrodes of the cell. Purge for ten minutes.
2. Spike the electrolyte in the cell with enough of the 0.5 M $KAuCl_4$ solution to yield a concentration of approximately 2.5×10^{-4} M. Continue purging the cell with inert gas. As the gold salt mixes into the solution, the open circuit potential should rise to approximately +0.8 V (all potentials in this document are reported vs Ag/AgCl, sat. KCl). The potential should rise to a stable value within five minutes of purging.
3. Spike the electrolyte in the cell with a volume of the MOP stock solution to yield a concentration of approximately 1.0×10^{-4} M. Continue purging the cell for two minutes.

5 Cycling to Electrodeposit Au

1. Set up the potentiostat to cycle the potential from -1 V to +1 V at a scan rate of 20 mV/s for a total of three cycles. During the negative polarization, the gold salt will be reduced to form a gold nanoparticle film on the ITO. On the second and third cycles, you should observe an increasing gold oxidation peak at the upper limit and a gold oxide reduction peak around +0.55V.

6 Monitoring IR Enhancement

1. Apply a constant potential of -900 mV. At this potential, MOP will desorb from the surface of the working

electrode. Wait five seconds and initiate a collection of the background spectrum while continuing to hold the potential. Turn the cell off (return to open-circuit potential) after the background has been collected.

2. Apply a constant potential of +300 mV, and after five seconds, collect the "sample" FTIR spectrum while continuing to hold the potential. This potential will cause the MOP to adsorb to the working electrode surface. Turn the cell off after the FTIR scans have completed.

3. Plot the potential difference spectrum as an absorbance: $A = -log_{10}(SB_{samp}/SB_{ref})$, where SB_{ref} is the single beam of the collected background spectrum and SB_{samp} is the sample single beam. In the resulting spectrum, you may observe bands corresponding to MOP (Table 3.) Note that the signal is low after the first set of three deposition cycles, and the bands may not be visible above the noise floor.

Table 3: Assignment of three selected bands in ATR-SEIRAS spectrum of MOP.

Band position of ATR-SEIRAS spectra (this work)	Band position (pure liquid in transmission) [2]	Band assignment [2]
1612	1597	Ring vibration (8a)
1508	1507	Ring vibration (19a)
1304	1289	COC (asymmetric stretch)

7 Continuing Deposition and IR Monitoring

Repeat the steps in Sections 5 and 6 as required (these steps will hereafter be referred to as a "round of deposition"). Generally, the level of enhancement as measured by the intensity of the MOP bands will increase as the deposition proceeds, reach a maximum, and then decrease as the gold film becomes too thick. Concurrently, there are changes in the spectral line shapes, with the general trend of increasing bimodality as deposition proceeds, with a possible return to a conventional lineshape after prolonged deposition cycles. A judgment will have to be made as to what is deemed to be an acceptable signal intensity and deviation from ideal line shape. In addition to observing the MOP bands, it can be helpful to monitor the detector counts after each round of deposition, as declining detector counts indicates a decline in throughput. Declining detector counts will eventually lead to an unacceptable signal-to-noise ratio.

Figure 1 shows six ATR-SEIRAS spectra; each spectrum was collected after another round of deposition, for a total of six rounds. The bands become more intense as deposition proceeds, however the bands also become increasingly bimodal. Deposition can be halted once the desired level of performance has been achieved.

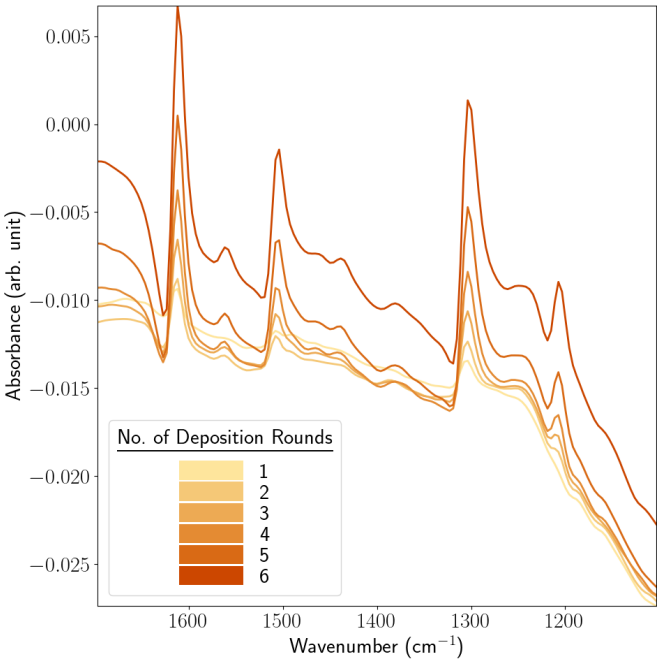


Figure 1: ATR-SEIRAS spectra of MOP after an increasing number of Au deposition cycles.

8 Preparing for Experiments

Once the deposition is complete, the cell can be emptied of the plating solution, rinsed, and refilled with a fresh solution of 0.05 M NaF. The cell does not necessarily need to be fully disassembled to be rinsed.

Some trace MOP will remain adsorbed on the gold film. This issue can be addressed by refilling the cell with 0.05 M NaF after rinsing and then applying -0.9 V while bubbling with the long bubbler for five minutes. Much of the residual MOP will desorb and be driven into the bulk solution. The cell can again be emptied and rinsed. Collecting a potential difference ATR spectrum in a fresh 0.05 M NaF electrolyte can confirm that MOP is below the limit of detection.

Be aware that the enhancement factor of the electrodeposited film will be reduced somewhat after rinsing (as compared to the final spectrum collected with the electrodepo-

sition solution). Presumably this is due to the loss of weakly bound gold structures during rinsing.

9 Limitations and Suggestions for Improvements

The procedure provided in this document is intended to serve as a reliable method for producing a SEIRAS-active gold film, but it has not been highly optimized. The following comments are provided to raise awareness of some potential limitations of the procedure and how it might be improved for a particular application.

- The gold/MOP electrolyte is not fully stable, as evidenced by purple colloidal gold deposits which may be visible on the glassware following deposition. It is important to maintain consistent timing of all the steps (and waiting periods between steps) to obtain reproducible results.
- Mixing the solution by purging with inert gas or stirring will affect the deposition rate.
- Pyridine derivatives are often shape-directing ligands for gold nanoparticles. Although the concentration recommended here is low compared to the concentration utilized when a shape-directing effect is desired, the presence of MOP may affect the morphology of the deposited gold.
- It may not be possible to fully displace the MOP from the surface of the gold such that it does not interfere with the chemical system that you desire to study. After becoming familiar with the deposition procedure, it may be desirable to substitute or omit the IR probe molecule from the deposition solution, provided that a film with a consistent enhancement factor can be produced without IR monitoring during the deposition.
- Conceptually, it is helpful to separate the gold deposition from the in-situ assessment of the IR surface enhancement. Of course, the gold salt is present during both steps, and thus gold deposition will also occur during the cathodic polarization of the electrode in the second step.

10 Document Version History

Date	Revision Description
Nov 2, 2026	Initial Release

References

(1) Andvaag, I. R.; Morhart, T. A.; Clarke, O. J. R.; Burgess, I. J. Hybrid Gold-Conductive Metal Oxide Films for Attenuated Total Reflectance Surface Enhanced Infrared Absorption Spectroscopy. *ACS Applied Nano Materials* **2019**, *2* (3), 1274–1284, DOI: 10.1021/acsanm.8b02155.

(2) Spinner, E.; White, J. C. B. The Vibration Spectra of the Cations of Methoxypyridines. *Journal of the Chemical Society (Resumed)* **1962**, *165*, 3115–3118, DOI: 10.1039/JR9620003115.