PROGRESS REPORT FOR ALNGRA10129

PROJECT TITLE: Investigation of arsenic film electrodedeposited on solid gold electrode

INVESTIGATOR(S)

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SCIENTIFIC OBJECTIVES

To investigate the chemical composition and thickness of arsenic film electrochemically deposited on a solid gold electrode from various electrolytes and deposition conditions using SIMS instrument.

DATA, PROGRESS REPORT and RESEARCH OUTCOMES

This report follows on from the two previous AINSE Grant investigations that have been carried out in 2007 and 2008 using the SIMS instrument. The final reports for those investigations have already been submitted. Those previous investigations were able to establish the following:

1. That the SIMS instrument is the appropriate instrument for this research project
2. Parameters, such as beam source, raster size, voltage, etc were optimised for the analysis of arsenic film deposited on the surface of the gold electrode
3. The sensitivity of the SIMS analysis determined that the surface of the solid gold electrode already contained arsenic impurities and therefore a gold film had to be deposited on top of the solid gold electrode in order to be able to obtain a signal from the electrodedeposited arsenic film
4. Elemental analysis of other species, such as Si, Cl and Au could provide additional information with regard to the quality of the electrochemically deposited arsenic film
5. In order to be able to determine the thickness of the arsenic film, a very thick layer of gold film needs to be deposited onto the solid gold electrode in order to eliminate the surface roughness of the solid gold electrode

The main aim of this AINSE Grant project was to continue the previous investigations and hopefully now be able to firstly establish the thickness of the electrochemically deposited arsenic film and secondly be able to determine the quality (i.e. thickness) of the arsenic film when deposited out of different electrolyte solutions, such as HCl, H₂SO₄, HNO₃ and CH₃COOH and using different deposition times and voltages.

Following is a summary of the main results that were obtained.

The first stage of this project involved obtaining a profile of the ‘bare’ gold electrode (Figure 1) prior to arsenic deposition. This step was particularly important in this case since the SIMS instrument was moved to another location and had a major upgrade and a new operator, so all the parameters had to be re-optimised.

The SIMS analysis of the bare gold electrode surface (Figure 2, shows SIMS analysis of three different areas on the same surface) which was only polished using various Al₂O₃ particle sizes down to 0.05µm, and had no arsenic or gold film on it, showed reasonably high counts initially for silicon (10⁴), which dropped down within 103 counts within 1000sec and stayed constant. The silicon presence is not surprising since the gold we are using in the electrode is 99.99% and typically that type of gold would contain up to 50ppm of silicon (per 9.2g of gold).
very high initial count of the silicon could be explained by the fact that the sand paper used to polish the electrodes contains silicon and thus silicon could be imbedded into the soft gold surface via the polishing process and so initially we get high levels of silicon and then they drop off and remain stable as the beam goes deeper into the electrode surface. The gold count is very low considering that this is sputtering from a solid gold surface, however, gold is known to be a poor emitter of gold ions and so perhaps that is why the count is so low (although in 2007/2008 I got 1000 times more counts with only using 2nA current, which is ten times less than what was used in this analysis). This is still a mystery since it was not possible to reproduce the results I obtained in 2007 and 2008 from solid gold electrode).

Arsenic detection started at around 200 counts and dropped off to around 12 counts. The arsenic we are seeing here is due to the impurities within the gold electrode (there is up to 30ppm of arsenic in the 99.99% gold). Chlorine counts were very low and that is to be expected since this electrode was not used for any electrochemical analysis so we would not expect to see much or any chlorine on the surface.

Figure 2 SIMS analysis of three different areas on the same surface of solid gold electrode, showing the sputtered areas on the surface of the electrode

The second stage of the analysis involved electrodepositing a very thick layer of gold film on top of the solid gold electrode and then electrodepositing an arsenic layer (Figure 3) and analysing it with the SIMS instrument to see if we could detect any arsenic film and also re-produce the data I obtained in 2008.

A very thick gold film (to eliminate the roughness of the gold electrode, as seen in pictures above, and to eliminate any arsenic signal coming from the gold electrode surface) was deposited for 1200sec from 100ppm Au standard in 1M HCl electrolyte solution at -700mV. Arsenic film was then deposited on top of that gold film out of 1ppm As(III) standard in 1M HCl electrolyte at -700mV for 960sec and this was analysed using SIMS. The thickness of the gold film was measured prior to the deposition of arsenic film with a profilometer to be approx. 1.5µm in thickness (Figures 4 and 5). Unfortunately, it was not possible to measure the thickness of the arsenic film using the profilometer at University of Western Sydney, because the weight of the stylus was too heavy to measure arsenic film. So the thickness of the deposited arsenic film at this stage was unknown.

Figure 3 Diagram showing the films on top of the gold electrode – not to scale
Figure 4  Stages of the stylus moving over the thick gold film electrodeposited on the gold electrode. The first picture shows the stylus on the left side of the crater (the crater was created by the SIMS instrument by bombarding the gold film with high energy Cs+ ions), as the stylus moves right towards the crater the topography of the surface is recorded (as shown in Figure 5 below).

Figure 5  Profilometry data shows the topography of the surface of the deposited gold film as the stylus moves across the crater. The crater appears to start at around 120µm and finishes at 490µm with a depth of approximately 1.5µm (ie the difference between depth at position at 120µm and depth at position 490µm). The large peaks seen within the crater are due to the very scratchy surface of the ‘bare’ gold electrode. As the stylus moves out of the crater the surface is smoother because of the gold film.

The SIMS data from the analysis of the arsenic film deposited on top of the gold film is presented in Figure 6 on the next page. A larger raster size had to be used in this analysis (500µm instead of 250µm as used for the ‘bare’ gold analysis), because the smaller raster size used before didn’t yield enough counts, so the only way to compare the data here with that obtained from the ‘bare’ gold electrode is to use ratios of the counts of the elements rather than actual counts. The silicon count is initially very high but then quickly drops off to almost nothing which would be consistent with expectations since there shouldn’t be any silicon within the arsenic and gold films. The arsenic count is substantial higher now and then drops off quickly to zero which agrees with expectations since the arsenic film is very thin and once the beam reaches the gold film there is no arsenic present. What is not clear is why gold counts are still rather low and decrease to zero as the beam goes deeper into gold film. Also, the chlorine results are puzzling. I expected high concentration of chlorine since both arsenic and gold films were deposited out of 1M HCl solution.

Comparing the ratios of the elements from the ‘bare’ gold electrode and those from arsenic film deposited on gold film we see the following:

Arsenic film on gold film:  Start ->  Au(1) : As(1.3) : Si (8.7) : Cl (0.03),  End ->  Au(1) : As(0.1) : Si (0.5) : Cl(0)
‘Bare’ gold electrode:  Start ->  Au (1) : As(0.3) : Si (8.9) : Cl (0.1),  End ->  Au (1) : As(0.1) : Si (6.2) : Cl(0.1)

Thus, it is clear from the ratios that indeed there was arsenic deposited on top of the gold film since the ratio of arsenic is higher than the ratio of arsenic found in the ‘bare’ gold electrode.
The arsenic film and gold films are visible, ‘sitting’ on top of the gold electrode if you compare the SIMS images of Figure 6 with those from Figure 2. The arsenic deposited on the gold film appears darker in colour than the gold film itself, which in turn appears dark orange and dull as compared to the ‘bare’ gold surface, as shown in Figure 7 below.

To observe a difference in the thickness of the arsenic film in the limited time available, rather than electrodepositing arsenic out of standard solution, I placed a drop of 1000ppm arsenic solution on top of the electrode which I first coated with gold film as before (Figure 8)
Figure 9 above shows SIMS data collected for the arsenic drop on gold film electrode, and again as before we can only compare the ratios, since the raster size had to be changed again here to 250µm. The results for this electrode are exactly what we were expecting to see. Arsenic count is very high and very slowly drops down but remains constant while the beam is still within the arsenic layer and at the same time we see that gold count is very low, almost zero, since there is no gold in the arsenic film. Silicon is low and gold is low (as expected), as is chlorine since the arsenic drop is from arsenic oxide solution, which didn’t contain any chloride ions. Unfortunately, this run didn’t get completed because even after 3000sec all counts remained the same indicating that we were still in the arsenic film layer. The arsenic layer must be very thick and since we were using very low current of 1nA so that we wouldn’t miss the arsenic film, it was taking a long time to get through the arsenic layer. Unfortunately, due to problems associated with beam dropping out and motor stage breaking it was not possible to complete this run. However, eventually we would expect that the arsenic count would drop down to nothing and then gold count should have increased. Comparing the ratios of counts for arsenic, it is clear that the largest count was obtained when 1000ppm drop of arsenic was placed on the gold film, as expected.

Arsenic drop on gold film:  Start -> Au(1) : As(48.5) : Si (3.0) : Cl (0.2),   End ->  Au(1) : As(43.3) : Si(1.4)  : Cl(0.2)
Arsenic film on gold film:  Start ->  Au(1)  : As(1.3) : Si (8.7) : Cl (0.03),  End ->  Au(1) : As(0.1)  :  Si(0.5)  : Cl(0.0)
‘Bare’ gold electrode:       Start ->  Au (1) :  As(0.3) : Si (8.9) : Cl (0.1),   End ->  Au (1) : As(0.1)  : Si (6.2)  : Cl(0.1)

Apart from depth analysis, it was also possible in this project to collect data on the distribution of arsenic on the surface of the electrode. This was only done on the electrode which had the 1000ppm arsenic drop on the gold film, due to instrument failure. Dr David Nelson, SIMS technician, was kind enough to run some surface images after I left UWS.

Surface imaging results are surprising (see Figure 10) as they clearly show how the arsenic layer has areas of high and low levels of concentration, so the distribution is not uniform as we would expect. This has implications for the depth analysis study, although this electrode had an arsenic solution drop simply evaporated on top of the gold film, which is different than electrodeposition. This imaging would need to be repeated with an electrode which had electrodeposited arsenic on it.

From the data obtained in this project, I have been able to determine the approximate thickness of the gold film deposited onto the gold electrode. Subsequent experiments using a number of different deposition times will be undertaken to discover the relationship with the thickness of the gold film. A direct relationship is expected.
Although, we could not determine the thickness of the arsenic film, the SIMS analysis showed a clear increase in arsenic count with higher concentration of arsenic deposited on the gold film. Subsequent experiments will try to relate the time taken for the beam at a particular current to ‘eat’ through the arsenic film to the electrodeposition time of arsenic. If beam time is found to be directly related to the thickness of the arsenic film, then I will be able to perform the tests I originally set out to do, i.e. vary deposition potential and electrolyte solutions.

Although the research outcomes originally proposed for this project were not achieved during this series of experiments, much valuable information was collected despite many external ‘hurdles’ which were encountered with this project. One major problem was that the air conditioning of the SIMS room broke and for two days the temperature in the room was rather warm and very humid (February 2011). This resulted in the Cs+ beam being misaligned and it took most of two days to align all the elements (As, Si, Cl, Au) needed for analysis. In addition, because the instrument had had a total upgrade since I used it in 2008, a lot of time had to be spent on optimizing all the parameters in order to be able to re-produce my previous set of data.

The information that I am hoping to obtain from this research project will help to understand the link between chemical profile of the electrode and arsenic deposition and thus provide valuable information how to obtain reliable and accurate results from using ASV to detect arsenic, in particular for infield measurements. This is become an important issue, since the disturbance of acid sulphate soils found in large sections of Australia can cause arsenic and other heavy metals to leach into groundwater. There is also a desperate need for an accurate and reliable infield arsenic detection method for countries such as Bangladesh and India, where millions of people are being poisoned by drinking arsenic contaminated groundwater.

| Signature of Investigator preparing the report for
| After signing this report please fax this page with your signature for our files |
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| M. Wajrak | Proj: ALNGRA10129 |
| Date: | 11.5.11 |

**PUBLICATIONS / REPORTS arising as a result of your work.**

No publications or grants have yet resulted from this particular grant, since the data was only collected in February 2011, however, as a result of the work done in this project and previous AINSE Grant projects, I have established collaboration with Prof Golimowski from Warsaw University in Poland, who is a well known electrochemist in Poland and I will be working with him and his research group during my study leave at the end of this year. I have been also invited to give a brief presentation on my arsenic research at the Bristol University in UK, in June this year.

Below I list conference presentations and publication that have resulted from my previous AINSE grants:

- Results from the 2007 AINSE Grant were presented at the 2nd International European Chemistry Conference in Turin, Italy, September 2008.
- Results from the 2008 AINSE Grant were presented at the 16th AINSE Conference on Nuclear and Complementary Techniques of Analysis, in Sydney, AINSE, Lucas Heights, November 2009.
- Results from the 2007 and 2008 AINSE Grants were presented at this year’s Australian X-ray Analysis Association, AXAA, Conference in Sydney, February 2011 and also published in the following paper:


**PhD STUDENTS**

No PhD students were involved in his project.