Monitoring of Actinide Concentrations in Molten LiCl-KCl Salt using Alpha Spectroscopy

Fuel Cycle Research Development

Lei R. Cao
Ohio State University

Collaborators
University of Utah

Mike Reim, Federal POC
Mark Williamson, Technical POC
Final Progress Report

Title “Monitoring of Actinide Concentrations in Molten LiCl-KCl Salt using Alpha Spectroscopy”

NEUP Project 15-8074

Start: October 1st, 2015

End: December 31st, 2018

Project Investigators: Dr. Lei R. Cao¹, Dr. Thomas E. Blue¹, and Dr. Michael F. Simpson²

National Laboratory Collaborator: Dr. Guy Fredrickson³

Students involved: Neil Taylor¹, Nora Alnajjar², Joshua Jarrell¹, Silvia Padilla², Milan Stika², Sha Xue¹, and Eric Moore¹

¹. Nuclear Engineering Program, Department of Mechanical and Aerospace Engineering
   The Ohio State University
  2. Department of Metallurgical Engineering
     University of Utah
  3. Idaho National Laboratory

March 6th, 2019
Executive Summary

This project addresses the need for real time monitoring of actinide concentrations for spent fuel reprocessing utilizing alpha spectroscopy. This project specifically focuses on spent fuel reprocessing with the pyroprocessing technique that uses high temperature molten salt. Pyroprocessing uses molten salt such as lithium chloride and potassium chloride to separate out uranium and plutonium from spent fuel. To prevent any possible diversion of high purity plutonium in this process, monitoring of the actinide concentrations within the refinery are essential for safeguards and non-proliferation efforts. Alpha spectroscopy enables the identification and quantification of actinide isotopic concentrations. However, current assay methods involving intrusive sampling and ex-suit measurement require weeks to provide accurate information. A near real-time and in-situ measurement system is required to quickly quantify actinide isotopic concentrations within the salt. Semiconductor radiation detectors provide a compact, high energy resolution option for completing these measurement needs. Silicon carbide (SiC) has been shown to operate effectively at high temperatures and high chemical stability in the molten salt environment. 4H-SiC Schottky diode alpha particle detectors were fabricated and tested to determine their alpha spectroscopy capabilities. The detectors need to operate at the elevated temperatures, survive the molten salt environment, be radiation hard, and have sufficient energy resolution under all these conditions to determine isotopic concentrations. Along with the detector, a method of producing samples of the actinides in the salt is required. To produce a thin film of the actinides on the detector, which is a necessity for alpha spectroscopy, electrodeposition can be used. Electrodeposition uses an electric potential difference to selectively deposit uranium or other actinides from the salt using an anode and cathode. Deposition of the material directly onto the sensor would produce a thin film of material that would enable materials accountability measurements to be taken in real time.

4H-SiC Schottky diodes were successfully fabricated to perform alpha spectroscopy. Devices were fabricated using a variety of metal contact structures and passivation layers. The process was optimized to achieve the best energy resolution, as this would allow for the most accurate isotopic concentration measurements. The devices were successfully tested up to the elevated temperatures of a pyroprocessing environment at 550 °C and survived exposure to the harsh molten salt. The radiation hardness of the detectors was evaluated using a Co-60 gamma irradiator (25 kRad/hour) and a mixed neutron and gamma field of The Ohio State University Research Reactor. The
detectors were packaged in such a way to minimize the effects of temperature and immersion in the molten salt while still operating and allowing for electrodeposition of material on the surface. Electrodeposition was tested on several coupons of various materials corresponding to the metals chosen for the contacts on the devices. Deposition of U, Th and U/Th were performed successfully on the coupons and deposition parameters were chosen to best electroplated uniform thin layers. Packaged detectors were submerged in a molten salt eutectic mixture with U and electrodeposition of U was achieved on the surface of the detectors. The detectors were cleaned and then tested for alpha spectroscopy capabilities. Packaged detectors were able to determine isotopic concentration information regarding the $^{234}$U.
Objective versus Accomplishment

Objectives

- Design, fabricate and characterize alpha particle detectors
- Develop techniques for actinide electrodeposition onto the detectors
- Test detectors and electrodeposition technique in representative environment

Accomplishing

- 4H-SiC based charge particle detectors were designed, fabricated, and tested for alpha spectrum acquisition. The best energy resolution achieved for 5.486 MeV alpha particles was at ~ 0.6%. Sensors were tested at up to 500 °C as well as in a molten salt environment. The results proved that they were working properly with only a slightly degraded resolution. Rad-hardness evaluation of those fabricated sensors were performed with a Co-60 gamma irradiator (~ 20 kRad/hour) and in a mixed neutron-gamma field at a near-core location at The Ohio State University Research Reactor. All the tested sensors have survived the high radiation field with acceptable performance at post-irradiation.

- The electrodeposition techniques were developed for thorium, uranium, and the mixed thorium-uranium deposition that were successfully demonstrated on nickel substrate, which is the surrogate for the alpha particle detector. XRD, SEM-EDXS, and ICP-OES were used to characterize the deposition phases, thickness, and composition. Eventually the methods were developed to deposit uranium onto a Pt electrode of those SiC sensors immersed into molten salt. The concentration of the actinides could be determined based on the measured current flow and the time of deposition.

- Device packaging was developed for SiC sensors to be sealed into stainless steel casing with mineral insulating cable and standard BNC connectors. Actinides dissolved in molten salt was electrodeposited onto the surface of the fully packaged 4H-SiC alpha detectors. Alpha spectrum from Uranium was collected with the same 4H-SiC detector after electrodeposition and the isotopic ratio of $^{234}\text{U}/^{238}\text{U}$ was successfully determined.

In summary, all the tasked specified in this project were completed with a fully achieved accomplishment for all the stated objectives.
Milestone 1: Sensor is fabricated with capability to obtain alpha spectrum

Detector Fabrication Process

Each detector is fabricated from a silicon carbide (SiC) wafer with a nitrogen doping concentration of $1.0 \times 10^{18}$ cm$^{-3}$ in the bulk layer and $5 \times 10^{14}$ cm$^{-3}$ in the epitaxial layer. The thickness of the SiC wafer is approximately 320 $\mu$m. Each detector substrate consists of a square wafer section measuring 7.59 mm by 7.59 mm. Each wafer section is cleaned prior to the deposition of metal contacts to either side of the section. First, an ohmic contact is deposited to the bulk substrate side of the wafer section, followed by a thermal annealing process in an inert argon environment. Following the thermal annealing process, the wafer is again cleaned and a metal contact is applied to the epitaxial layer. The wafer sections are then annealed once more in order to form the appropriate metal-semiconductor interaction at the epitaxial surface.

![Diagram of Detector Composition](image.png)

Figure 1. Diagram of Detector Composition

The cleaning process of the wafer sections consists initially of an industry standard RCA process. The RCA cleaning process is commonly used in semiconductor fabrication. The process consists of an organic contaminant removal, followed by an oxide removal, and an ionic deposit removal step. The final steps in the cleaning process are a repeat of the oxide removal step and then drying using nitrogen gas.
The ohmic contact is deposited on the entirety of the bulk layer of each wafer section. The composition of the contact is 100 nm of nickel covered with a 10 nm inert capping layer of platinum. Following the deposition of the bulk side contact, the wafer section is placed in an inert argon atmosphere thermal annealer. The wafer section is then heated to 870 °C in order to form an ohmic contact at the nickel and bulk layer interface.

Following the ohmic contact anneal, a second cleaning process is performed in order to remove any contaminants from the epitaxial layer surface. This cleaning process is less aggressive than the initial RCA cleaning process. The wafer sections are cleaned in an acetone wash, followed by an isopropyl alcohol wash. Any oxides that may have been deposited are then removed by a hydrofluoric acid rinse. The sections are then washed in deionized water and dried with nitrogen. All cleaning steps in this procedure are performed at room temperature.

Table 1. Initial Wafer Cleaning Procedure

<table>
<thead>
<tr>
<th>Clean</th>
<th>Solution</th>
<th>Temp</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Clean</td>
<td>H₂O₂:NH₄OH:DI (1:1:5)</td>
<td>80 °C</td>
<td>15 min</td>
</tr>
<tr>
<td>DI Rinse</td>
<td>Room</td>
<td></td>
<td>2 min</td>
</tr>
<tr>
<td>Oxide Clean</td>
<td>HF: DI (1:50)</td>
<td>Room</td>
<td>15-20 sec</td>
</tr>
<tr>
<td>DI Rinse</td>
<td>Room</td>
<td></td>
<td>10-15 sec</td>
</tr>
<tr>
<td>Ionic Clean</td>
<td>HCl:H₂O₂:DI (1:1:5)</td>
<td>80 °C</td>
<td>15 min</td>
</tr>
<tr>
<td>DI Rinse</td>
<td>Room</td>
<td></td>
<td>2 min</td>
</tr>
<tr>
<td>Oxide Clean</td>
<td>HF: DI (1:50)</td>
<td>Room</td>
<td>15-20 sec</td>
</tr>
<tr>
<td>DI Rinse</td>
<td>Room</td>
<td></td>
<td>10-15 Sec</td>
</tr>
<tr>
<td>Dry with N₂ gun</td>
<td>Room</td>
<td></td>
<td>As needed</td>
</tr>
</tbody>
</table>

Table 2. Second Cleaning Procedure

<table>
<thead>
<tr>
<th>Clean</th>
<th>Solution</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organic Clean</td>
<td>Acetone</td>
<td>2 min</td>
</tr>
<tr>
<td>Organic Clean</td>
<td>IPA</td>
<td>2 min</td>
</tr>
<tr>
<td>DI Rinse</td>
<td>DI</td>
<td>2 min</td>
</tr>
<tr>
<td>Oxide Clean</td>
<td>HF:DI (1:50)</td>
<td>30 sec</td>
</tr>
</tbody>
</table>

The ohmic contact is deposited on the entirety of the bulk layer of each wafer section. The composition of the contact is 100 nm of nickel covered with a 10 nm inert capping layer of platinum. Following the deposition of the bulk side contact, the wafer section is placed in an inert argon atmosphere thermal annealer. The wafer section is then heated to 870 °C in order to form an ohmic contact at the nickel and bulk layer interface.

Following the ohmic contact anneal, a second cleaning process is performed in order to remove any contaminants from the epitaxial layer surface. This cleaning process is less aggressive than the initial RCA cleaning process. The wafer sections are cleaned in an acetone wash, followed by an isopropyl alcohol wash. Any oxides that may have been deposited are then removed by a hydrofluoric acid rinse. The sections are then washed in deionized water and dried with nitrogen. All cleaning steps in this procedure are performed at room temperature.
Following the second cleaning step, a circular metal contact is deposited on the epitaxial layer. The contact composition is 100 nm of nickel capped with 10 nm of platinum. The preferred circular contact diameter is currently being explored in order to optimize detector performance. Increasing the contact diameter increases the sensitive area of the detector and allows for shorter counting times in radiation spectrum measurements. However, increasing the diameter leads to an increase in the undesirable leakage current, thus an optimization between these two characteristics must be determined. Currently the three diameters being explored are 1.5, 3.0, and 5.0 mm with 3.0 mm appearing to be the optimal of the three. The wafer section is then annealed in an inert argon atmosphere at 650 °C in order to form a Schottky barrier at the nickel and epitaxial layer interface. Figure 2 shows a completed detector.

**Figure 2. Fabricated Pt-Ni Contact SiC Detector on plastic holder. The circular Schottky contact is apparent on the surface of the wafer section.**

**Alpha Spectroscopy with Fabricated Detectors**

To measure an alpha spectrum, a bias voltage is applied across the detector electrical contacts. This bias voltage forms a charge depleted sensitive region within the detector which allows for the collection of charge liberated by incident ionizing particles. Shown below in Figure 3 is the observed alpha spectrum collected using a 3 mm contact SiC detector operating at -200 volts of bias voltage. The alpha source used was a 1.88 μCi $^{241}$Am source. All alpha measurements were made in <50 mtorr of atmosphere in order to reduce alpha energy attenuation due to air. Negligible
energy loss compared to detector resolution occurs as the alpha particles pass through the inert capping layer and Schottky contact.

Figure 3. Alpha Spectrum from $^{241}$Am Measured with Ni-Pt SiC Detector at -200V bias

The energy resolution was found to be 1.85% for the predominant $^{241}$Am alpha particle energy of 5.485 MeV at 20° Celsius. The above measurement was performed with a counting time of 1000 seconds. Currently, measurements of the alpha spectrum from a low activity (approximately 1 Bq) electroplated thorium source are being performed using a SiC detector. The thorium has been electroplated from a molten salt and will serve as an intermediate step to measurement of actinides electroplated directly to the surface of the detector.

The thorium spectrum has so far been measured using a partially depleted in-house fabricated SiC detector. The resulting spectrum is shown in Figure 4. The spectrum shape follows the theoretical prediction for a partially depleted detector output, having a cutoff energy value corresponding to the energy lost by an alpha particle passing entirely through the thickness of the depleted region.
Figure 4. Measured Thorium Alpha Spectrum using 4H-SiC Detector

The daughter progeny of the $^{232}\text{Th}$ decay series was measured using a Canberra surface barrier silicon detector. The in-growth of daughter activities was measured approximately six months after the electrodeposition of the thorium sources. Figure 5 shows the resulting alpha spectra. The in-growth of the daughter activities and their specific energies match those predicted in the $^{232}\text{Th}$ decay series.

Figure 5. Thorium Source Spectra with Daughter in-growth ~6 months after Electrodeposition
Milestone 2: Initiated U/Th co-deposition tests on BDD coated cathodes

At University of Utah, researchers first experimented with pure nickel plates as an alternative to boron doped diamond (BDD) coated cathodes. Nickel is cheaply available, electrically conductive, and chemically stable in contact with molten electrorefiner salt at typical operating temperatures.

Initial electrochemical deposition on these coupons was performed using LiCl-KCl-ThCl₄ or LiCl-KCl-UCl₃. The first test was completed using LiCl-KCl-UCl₃-ThCl₄. The salt contained 2 wt% UCl₃ and 1 wt% ThCl₄. Two different cathodes were used for deposition—a tungsten rod and a nickel coupon. Cyclic voltammetry was performed using the tungsten rod that indicated different peaks for U³⁺ reduction and Th⁴⁺ reduction, as shown in Figure 6 below. U³⁺ reduction occurs as -2.25 V, and Th⁴⁺ reduction occurs at -2.35 V. The difference in reduction potentials is consistent with the known standard reduction potentials. The other “wave” visible is U⁴⁺/U³⁺ oxidation/reduction that occurs at about -1 V.

![Figure 6: Cyclic voltammetry using tungsten rod to identify U and Th peaks](image)

Next, the tungsten rod was replaced with the cathode assembly that holds two nickel coupons. A repeating chronoamperometry run was performed with the potential toggled between -2.4 V and -2.135 V. The run appeared to work as expected with the cumulative charge passed consistent with a 1-micron thick U/Th deposit. XRD, SEM-EDXS, and ICP-OES was later used to characterize the deposition phases, thickness, and composition.
Milestone 3: Deposited conducting film on sensor

Diamond Growth Process

A diamond film was grown on a 4H-SiC substrate using microwave plasma chemical vapor deposition (MPCVD). The diamond film will function as a protective layer in addition to being an electrical contact from the molten salt environment the alpha detector is intended to function in. The diamond layer is planned on being doped with boron using ion beam implantation to make the diamond conductive. This document will cover the steps for growing diamond on 4H-SiC and the results of the growth, including confirmation of diamond growth using Raman spectroscopy and scanning electron microscope (SEM) images.

The SiC wafer has a nitrogen doping concentration of $1.0 \times 10^{18}$ cm$^{-3}$ in the bulk layer and $5 \times 10^{14}$ cm$^{-3}$ in the epitaxial layer. The thickness of the SiC wafer is approximately 320 µm and the outer dimensions of the entire square wafer measured to be 7.59 mm by 7.59 mm. The diamond film was grown on the epitaxial side of the wafer.

The diamond growth was performed in an ASTEX AX5200M 1.5 kW CVD reactor. Diamond growth is performed by using “recipes”, as referred to in the field of chemical vapor deposition. In the context of this project, the diamond growth is considered to be a heteroepitaxial growth since the diamond is being deposited on a substrate other than diamond; the substrate being 4H-SiC in this project. In order to grow diamond on a non-diamond substrate, a nucleation step is necessary. A nucleation step serves the purpose of creating diamond nucleation sites, sometimes called seeds, on the substrate which creates the foundation for the diamond film to begin growing.

One method of creating nucleation sites is called bias enhanced nucleation (BEN). This process is a recipe performed in the CVD reactor where a bias is applied to the substrate during diamond growth conditions for a brief amount of time. This creates a high density of nucleation sites on the substrate. The bias is then set to 0 volts and a growth step is performed where the final diamond film is then grown to confluence.

The recipe for the BEN step that resulted in sufficient nucleation sites for diamond growth on 4H-SiC is the following:

- MW Power = 700 W
- Temperature = 840 °C
• Pressure = 20 Torr
• Bias Voltage = 400V
• H₂ flow rate = 300 sccm
• CH₄ flow rate = 15 sccm
• Duration = 30 mins.

After the BEN step was complete, a growth step was performed directly afterward without taking the sample out of the CVD reactor. The growth step is a different recipe from the BEN recipe. The growth step which resulted in diamond film growth on 4H-SiC was the following:

• MW Power = 1300 W
• Temperature = 705 °C
• Pressure = 50 Torr
• H Flow Rate = 300 sccm
• CH₄ Flow Rate = 3 sccm
• Duration = 3 hours

After the growth step was complete, the substrate was taken out of the chamber and the diamond growth was complete.

**Diamond Thin Film Growth Confirmation**

To confirm the growth of diamond on the SiC wafer, Raman spectra were taken at various points on the surface of the substrate after the CVD growth. If the growth conditions were not sufficient, then amorphous carbon and graphite can be deposited on the substrate surface as opposed to diamond. A location on the surface of the substrate where Raman spectroscopy was performed can be seen in Figure 7.
Figure 7. A location on the post-CVD SiC substrate.

The dark grey material deposited on the surface of the substrate is the diamond. The location that the Raman spectrum measurement was taken at can be seen by the green laser dot in the middle of the picture. The resulting Raman spectrum at this location can be seen in Figure 8.

Figure 8. The Raman spectrum of diamond on 4H-SiC.

The growth of diamond has been confirmed by the sharp Raman peak at 1334 cm\(^{-1}\) which is characteristic of diamond, as seen in Figure 8. Raman measurements were taken at various other locations on the substrate and the characteristic diamond peak was present in all spots confirming diamond thin film growth on SiC.
To have insight into the grain size and thickness of the diamond thin film, SEM images were taken of the diamond film on the micrometer scale. Some images can be seen of the surface morphology of the diamond on SiC in Figure 9, Figure 10, and Figure 11.

Figure 9. An SEM image of the surface morphology of diamond on 4H-SiC.

Figure 10. An SEM image of the surface morphology of diamond on 4H-SiC.
It can be seen in Figure 11 that the grain size of the diamond is around 4-5 μm. Figure 9 shows a location on the substrate where diamond grains grew to confluence and there are no gaps in between the diamond grain. This is a location where, upon doping, the diamond film would be made conductive and electric current would be allowed to flow through the diamond film functioning as an electrical contact. In summary, a diamond thin film has been successfully grown on 4H-SiC, the material that will serve as the basis for the alpha particle detector.
Milestone 4: Sensor showed no degradation at up to 500 °C

Heated Alpha Spectrometry

Each detector is fabricated from a silicon carbide (SiC) wafer with a nitrogen doping concentration of $1.0 \times 10^{18}$ cm$^{-3}$ in the bulk layer and $5 \times 10^{14}$ cm$^{-3}$ in the epitaxial layer. The thickness of the SiC wafer is approximately 320 µm.

The ohmic contact is deposited on the entirety of the bulk layer of each wafer section. The composition of the contact is 100 nm of nickel covered with a 10 nm inert capping layer of platinum. A circular metal contact is deposited on the epitaxial layer. The composition is 100 nm of nickel capped with 10 nm of platinum. The preferred circular contact diameter is currently being explored in order to optimize detector performance. Increasing the contact diameter increases the sensitive area of the detector and allows for shorter counting times in radiation spectrum measurements. However, increasing the diameter leads to an increase in the undesirable leakage current, thus an optimization between these two characteristics must be determined. Figure 2 shows a completed detector.

To establish a vacuum environment to avoid attenuating the alpha particle energies measured by the detector and eliminate convective cooling of the detector surface, all measurements were performed in a custom bell jar. The bell jar was evacuated of air and maintained at a pressure below 1 mtorr. This ensures that negligible cooling occurs on the detector allowing for a uniform temperature profile in the detector, and that the incident alpha particles are not attenuated before reaching the detector surface.

Alpha Spectroscopy at Elevated Temperatures

To measure the energy resolution of the detector at elevated temperatures, an Inconel RF substrate heater was used. The SiC detector was placed on the heater with a collimated $^{241}$Am alpha source placed over top of the detector. The substrate heater was controlled using a Bluewave Semiconductor Temperature controller and a custom Labview program. The detector was heated in 100 °C increments from room temperature to 500 °C. At each point, the detector was irradiated with the alpha source and the resulting energy spectrum collected using a DSA-2000 multichannel analyzer.
The energy resolution was found to be 0.93% for the predominant $^{241}$Am alpha particle energy of 5.485 MeV at room temperature ($25^\circ$ C). The measurement shown below in Figure 13 was performed with a counting time of 1000 seconds. The detector energy resolution while operating
at 100 °C was 1.13%.

The alpha spectra collected at each remaining temperature are shown in Figure 14. The shift to the higher channel number follows the predicted increase due to the increased average thermal energy of bound electrons resulting in an increase in the number of charge carriers freed per unit energy lost by ionizing radiation. This increase manifests as a shift to higher channel number in the multichannel analyzer.

Figure 13. Measured Thorium Alpha Spectrum using 4H-SiC Detector
Figure 14. The approximately stable detector resolution, varying by roughly a factor of 2 from 25 °C to 500 °C shows little degradation in detector response versus temperature.

Figure 15 shows the trend of increasing channel number with increasing temperature. The close fit to the predicted response indicates that the detector operation has not degraded with increasing temperature.
Figure 15. The linear relationship between Centroid position and temperature is predicted by the measured W-value for 4H-SiC versus temperature.

Milestone 5: Optimized electrodeposition of actinides

Thorium electrodeposition

The electrodeposition of thorium on a nickel substrate (surrogate to alpha detector’s Schottky contact) was optimized by the use of the repeating chronoamperometry (RCA) technique. In contrast to simple constant controlled current (chronopotentiometry) or constant controlled potential (chronoamperometry) techniques, RCA is an advanced technique with periodically changing rate. The method alternates between two set potentials. The first one is of very cathodic voltage compared to the equilibrium potential, and of short duration – this period is hence called the pulse ($E_{\text{pulse}}$, $t_{\text{pulse}}$). The second one is of slightly anodic voltage compared to the equilibrium potential, and of longer duration – this period is hence called the relaxation ($E_{\text{relax}}$, $t_{\text{relax}}$). The evolution with time is depicted in Figure 16, where the convenient unit of deposition amount is the amount of charge $Q$ that was passed through the electrochemical cell.

During each pulse, a large amount of nucleation sites is created by the rapid influx of thorium atoms, and some growth also commences. Normally this growth would be of undesirable quality since deposits formed under high overpotentials are usually dendritic. However, the subsequent
application of the (anodic) relaxation period partially dissolves the deposit back into the solution. The most unstable portions of deposit dissolve first, while the relatively stable, ordered structures remain. By alternating these two modes, reasonably ordered growth of the deposit is achieved, as seen on Figure 17.

**Uranium electrodeposition**

The electrodeposition of uranium on a nickel substrate using RCA was also successful. Very similar parameters were used for the RCA, since uranium and thorium share similar redox potential. One difference was that U-Ni alloying effects were seen (Th-Ni binary phase diagram also permits some alloy formation, however this was not observed). Alloying is actually not detrimental since it promotes more compact deposit formation. Uranium and nickel were intimately mixed with initially no apparent layer on top of nickel. Pure uranium deposits on top of nickel were seen only after the nickel layer seemed “saturated” with uranium – see Figure 18.

The only issue with alloying is the potential complication in re-use of the surface, where the deposit needs to be completely stripped off the nickel before new measurement commences. The stripping experiment proved that the alloying does not present particular difficulty, since the surface was not considerably altered, and the alpha background from the residual uranium (0.5 wt%) would be very small. The surface after two depositions/strippings is depicted in Figure 19.

**Mixed thorium-uranium electrodeposition**

The ultimate objective was to mix the two actinides in a single salt and reliably deposit them onto a nickel substrate. This was again achieved using the RCA technique. Interestingly, the two elements affect each other in the mixture in an unexpected way (deposition time increase, morphology change).

Regarding deposition time, the deposition of the combined thorium-uranium deposit was slower than the deposition of equivalent amount of either thorium or uranium alone. This surprising fact could be explained by mutual diminishing of activities via reduction of respective activity coefficients. Regarding morphology of the deposit, the addition of thorium rendered the uranium tendency to form an alloy with nickel less favorable. In other words, stricter substrate/deposit regions were identified, with thorium-uranium layer on top of (mostly unalloyed) nickel substrate. This is best demonstrated in Figure 20.
Figure 16. The saw-toothed pattern of the deposition using RCA technique. Short cathodic pulses are alternated by longer anodic relaxations. Overall, net deposition is achieved.

Figure 17. SEM micrograph with EDS map overlay of thorium RCA deposit on nickel.
Figure 18. SEM-EDS overlay of uranium RCA deposit on nickel. Note the apparent bare spot on the left side of the figure: uranium is not absent from this spot, as indicated by the uranium map – an effect of alloy formation.
Figure 19. SEM-EDS overlay of nickel surface after two deposition/stripping cycles. Note the residual amount of uranium: 3.1 wt% translates to 0.5 at%.

At 500 °C (773 K), deposits from salt compositions ranging from 0.7 to 2.8 wt% ThCl$_4$ with 0.2-5.2 wt% UCl$_3$ were obtained. The RCA parameters for satisfactory deposits are as follows:

- $E_{\text{pulse}} = -2.4$ V (vs Ag/100%AgCl reference electrode)
- $t_{\text{pulse}} = 0.2$ s
- $E_{\text{relax}} = -2.10 \div -2.18$ V (depends on a particular run)
- $t_{\text{relax}} = 1.0$ s
- $Q = 9$ C

In summary, the thorium-uranium deposition was successfully demonstrated on nickel substrate, which is the surrogate for the alpha particle detector. If the Pt capping layer is employed on top of the nickel surface, the deposition parameters would need to be re-evaluated, since platinum and nickel are dissimilar substrates.
Figure 20. SEM-EDS overlay of thorium-uranium RCA deposit on nickel. Note the bare spot on the right side of the figure: uranium (and thorium) is absent from this spot, as indicated by the map – an effect of suppressed alloy formation due to thorium addition.
Milestone 6: Sensor showed no performance degradation in molten salts

Detector Molten Salt Testing Procedure

Figure 21. Argon Atmosphere Glovebox used for salt experiments

To test the detector performance degradation with exposure to the molten salt found in the INL electrorefiner a eutectic LiCl-KCl salt was heated and held between 500 and 600 °C for a period of one hour. A spectrum was collected using a DSA-2000 multichannel analyzer and Ortec 142B preamplifier in a vacuum bell jar with an $^{241}$Am source to provide a baseline of detector resolution and centroid position. The salt was heated in an inert argon atmosphere glovebox, shown in Figure 21. The salt was purchased from Sigma-Aldrich and 20 grams was added to a alumina crucible.
Figure 22. Alumina crucible used to hold LiCl-KCl salt at 500-600 °C

The alumina crucible containing the salt was placed into a Kerr Electro-melt furnace and heated to 550 °C. The heater is capable of holding a set temperature ±10% of the setpoint temperature. Thus, the temperature of the salt oscillated between 500 and 600 °C. The crucible was heated for 1 hour to ensure that the salt was uniformly heated and homogenous. After the salt was heated, the furnace lid was lifted and the detector was submerged into the liquid salt. The detector was suspended by a stainless-steel wire and clamp to maintain a constant depth in the liquid salt.

The detector was left in the molten salt for 1 hour, after which it was removed and left to cool still suspended by the clamp and wire in the argon atmosphere. This was to prevent rapid cooling from conduction from the detector coming in contact with an approximately 20 °C surface. The detector was left to cool for 3 hours, after which it was removed from the argon atmosphere glovebox and washed using deionized water and isopropyl alcohol. The detector was allowed to dry in air for approximately 8 hours. The detector was then placed in a vacuum bell jar and exposed to an $^{241}$Am alpha source. The system used to acquire the alpha spectrum was identical to the baseline spectrum acquired before exposure to the salt.
Alpha Spectroscopy Pre-and Post-Salt Exposure

A bias voltage of -200 volts was applied to the detector to create a depleted region greater than the range of the $^{241}\text{Am}$ alpha particles in 4H-SiC. This allows for the full energy of the incident alpha particle to be deposited in the charge depleted region of the detector. Figure 24 shows the spectra both before and after exposure to the molten salt. As illustrated in the below figure, the detector resolution was not significantly degraded. The resolution prior to molten salt exposure was 1.36%, following molten salt exposure this rose to 1.7%. This increase in energy resolution does not represent a significant change in detector performance, with the resolution remaining below the approximately 2% energy resolution required to accurately discriminate between special nuclear material isotopes.
Figure 24. Alpha Spectrum from $^{241}$Am Measured with Ni-Pt SiC Detector at -200V bias
Milestone 7: Tested sensor in molten LiCl-KCl for concentration of actinides

Figure 25. Packaged detector in stainless-steel housing as sent to the University of Utah

To test the detector’s ability to collect a spectrum from an actinide source deposited onto the detector surface by electrodeposition, a detector was packaged as above in Figure 25. The detector was placed inside of a stainless-steel capsule and held in place with ceramic adhesive. Electrical connections were established using conductive silver solder. Electrical connection from the detector was established using a mineral insulated cable and an MI cable to a BNC adapter.
A LiCl-KCl-UCl₃-ThCl₄ salt comprised of 1 wt% U and 1 wt% Th was placed in the furnace shown in Figure 26 and heated to 500°C to liquify the salt. A deposition voltage was established across the detector surface relative to a reference electrode and a BNC connection and a controlled current was flowed across the electrodes. Repeated chronoamperometry, the technique of repeatedly varying the deposition voltage to ensure a uniform deposition, was employed to deposit Th and U on the detector surface. After deposition, the detector was removed from the salt and allowed to cool. The detector in its packaging was sent to The Ohio State University for spectroscopic measurements and received as shown in Figure 27. The detector was then placed in a bell jar and shielded with a Faraday cage. The measurement equipment and setup used to collect the alpha spectra was identical for the pre and post deposition measurements.
Figure 27. The detector and packaging as received at The Ohio State University. The upper and lower housing separated during electrodeposition and was reattached for alpha spectroscopy measurements.

**Alpha Spectroscopy of the Electrodeposited Source**

A bias voltage of -50 volts was applied to the detector to create a depleted region. This bias voltage is insufficient to fully deplete the epitaxial region of the detector. However, this voltage was chosen as the maximum voltage which would not result in a breakdown of the electric field in the detector. This allows for only a fraction of the full energy of the incident alpha particle to be deposited in the charge depleted region of the detector. Figure 28 shows the spectra resulting from an 8-hour counting experiment. The background noise was subtracted. As illustrated in the below figure, the detector resolution was significantly degraded, likely in part due to the partially depleted epitaxy. The incident alpha particles would thus not be able to deposit all of their energy in the charge depleted region, and the capacitance of the detector would increase. Both effects would lead to degraded detector resolution. Additionally, the combination of Th and U alpha emitters results in a more complex spectrum resulting in an overlap of the alpha spectra at partial depletion of the detector. Finally, the source thickness will further broaden the alpha spectrum peaks, degrading the apparent resolution. Modifications to the detector packaging, including improved insulation
between the electrodes used to bias the detector and the addition of a passivation layer may improve the detector resolution after electrodeposition.

![Graph](image.png)

*Figure 28. Alpha spectrum from the electrodeposited Th/U source measured with the packaged detector on which it was deposited. The detector was operated at -50V bias.*

Despite the poor performance of the spectrum, this is the first ever spectrum acquired after a packaged sensor has been successfully immersed into molten salt for electrodeposition. This is considered as accomplishment of the milestone by demonstrating a working sensor instrument that can survive molten salt, with salt deposition being successful. Further optimization will be presented at a later stage.
Milestone 8: Evaluated the radiation hardness of the fabricated sensor

We have fabricated silicon carbide detectors and evaluated their radiation hardness with a cobalt-60 (60Co) gamma irradiator and at a near-core location of a research reactor sector, which presents further evidence suggesting the application of SiC in an intense radiation environment.

Device fabrication
Several Schottky type SiC detectors were fabricated in the clean room facility at The Ohio State University Nanotech West. The 0.5 cm × 0.5 cm square bulk SiC wafers doped with $1.0 \times 10^{18}$ atoms/cm$^3$ of nitrogen with a 300 μm thickness were purchased from Cree, Inc. On top of the bulk SiC is a SiC epitaxial layer with a thickness of 21 μm, which is doped with $5 \times 10^{14}$ atoms/cm$^3$ of N. A circular Schottky electrode of 3 mm diameter is deposited on the epilayer side, which consists of 100 nm nickel and 300 nm platinum. The Ohmic contact electrode is 100 nm Ni and 10 nm Pt. The device is placed in a dual in-line chip carrier and pressed by a V-shaped probe with its inflection point touching the circular Schottky electrode of the device. Both ends of the V-shaped probe were soldered to the pad on the chip carrier as the Schottky electrode connection. The Ohmic contact is attached to the conducting base of the chip carrier, which is soldered with a wire for external circuit connection. The structure of the Schottky SiC detector and the packaged device are shown in Figure 29(a) and (b), respectively. This electrode connection method is easier to implement than wire bonding, which is more expensive and also puts devices at risk of damage by the high bonding temperature used in the gold and Pt wire bonding process. The $^{241}$Am spectrum acquired with a SiC sensor at varying bias voltage is shown Figure 29(c). A $^{241}$Am spectrum was also acquired with a SiC detector at varying temperature, as shown in Figure 29(d).
Radiation hardness testing

During the gamma irradiation, the SiC detector was exposed to an intense gamma background while measuring a weak $^{241}\text{Am}$ alpha source. The strong gamma background was provided by a $^{60}\text{Co}$ irradiator with a dose rate of $\sim$20 krad/h at the OSU Nuclear Reactor Lab (OSU-NRL). A $^{241}\text{Am}$ source (0.88 $\mu\text{Ci}$ in this test) and a SiC detector were sealed into a customized aluminum box, which provides electromagnetic shielding as well as a dark environment, as shown in Figure 30(a). The SiC detector was positioned 1.0 cm away from the center of the $^{241}\text{Am}$ source. The entire Al box was placed inside a $^{60}\text{Co}$ irradiator. A series of 5 min pulse-height spectra were acquired by the SiC detector biased at $-80$ V. In the neutron response tests, the SiC detector sealed in an Al box (without $^{241}\text{Am}$ source) was placed at a near-core location through Beam Port #1 at OSU-NRL, as shown in Figure 30 (b, c, d). The SiC detector was mounted on a phenolic board installed on a high-density polyethylene (HDPE) plug with a shallow spiral side slot for cabling. The entire plug, which is 2 m long, was inserted into a beam tube with a 0.5 mm thick cadmium (Cd) cap surrounding the segment where the detector box was located. The pre-amplifier that was placed outside the reactor was connected to the detector with a 4-meter long coaxial shielded cable going through the carved slots on the beam plug. The fast neutron flux is about $2.2 \times 10^7 \text{ cm}^{-2} \text{ s}^{-1}$ at the near-core location at the full power of 450 kWth. The SiC detector sealed in the Al box was
also exposed to an external neutron beam through Beam Port #2 at OSU-NRL, as shown in Figure 30(c), which has a thermal equivalent flux of $4.4 \times 10^6$ cm$^{-2}$ s$^{-1}$ and Cd ratio of 92, representing a fast neutron flux of $\sim 4.80 \times 10^4$ cm$^{-2}$ s$^{-1}$. A 0.4 mm Cd cover with 98.94% thermal neutron blocking ratio was used to identify the SiC detector response to fast neutrons alone. In all of the measurements, an Ortec-428 power supply was used to provide a bias voltage to the SiC detector, through an Ortec-142B preamplifier. The pulses from the preamplifier were shaped and amplified by an Ortec-575A amplifier and then digitized by an Ortec-926 ADCAM multichannel buffer. The pulse height spectrum from Ortec-926 ADCAM was acquired by the Ortec MAESTRO software.

![Figure 30](image_url)

*Figure 30. (a) SiC detector; (b) detector mounting board; (c) Beam port #1 and #2, where near-core and external irradiation take place, respectively; (d) a photo of high-density polyethylene (HDPE) beam plug with slots for wiring.*

**Gamma-ray Hardness result**

The gamma dose rate is strong inside of an electrorefiner, where this SiC device is intended to be used. The gamma-induced response of SiC detector should be investigated in the presence of a strong gamma background. For this case we exposed an operating SiC device when it was acquiring an alpha spectrum to a $^{60}$Co irradiator ($\sim 20$ krad/h). Figure 31 shows the pulse-height alpha spectrum acquired by a SiC detector with and without intense gamma-ray interference. The energy resolution of the 5.486 MeV main alpha energy, obtained at -80 V bias, has degraded from
2.8% under natural background to 10% when being exposed to the $^{60}$Co irradiator. The count rate of the full-energy-peak also decreased by about 15% in this condition. The degradation of the device performance may be caused by (1) defects introduced by gamma radiation that trap the charged particles produced by neutron interactions, (2) the increase of the dead time, and (3) the pulse pileup effect caused by the intense gamma radiation field. The intense gamma irradiation could cause trapping centers in the device which can degrade the performance of the detector as a secondary effect since the charge collection process will be compromised. Not only do the low amplitude of the gamma-induced pulses contribute to the low pulse-height response of the detector but they also broaden the peak of the neutron induced charged particle spectrum due to pile-up. The presented spectral response of the SiC detector demonstrates that the accompanying intense gamma irradiation can affect the collection of the charged particles, which is different from previous demonstrations when a mono-energetic neutron radiation field was applied. We conclude that even though a spectroscopic degradation is observed, SiC device still functions well under an intense gamma field.

![Image of a graph comparing alpha response spectrum with and without gamma irradiation](image.png)

*Figure 31. The alpha response spectrum with and without gamma irradiation provided by the $^{60}$Co irradiator.*

**Radiation hardness testing at near-core locations**
We also placed the SiC detector at a near-core location, as shown in Figure 30(c), to acquire first-hand performance evidence of SiC under an intense mixed neutron and gamma field. Firstly, a response spectrum of the SiC detector was obtained by operating the reactor at 10 $W_{th}$ power, which gave a 1-MeV equivalent flux (Si) of $2.2 \times 10^{7} \text{ cm}^{-2} \cdot \text{s}^{-1}$ at the detector’s location. Five minutes later, after the reactor shutdown, a near-core background spectra was measured by the SiC detector at the same location, which is obviously the pure gamma response. It is very clear from Figure 32 that the identical shape (channel 0 to ~ 50) from both spectra can be distinguished as the gamma-ray response, which is similar to the gamma response from the $^{60}$Co irradiator as shown in Figure 31. The neutron response spectrum has a similar shape as what has been acquired with the external neutron beam, which manifests a sharply declining plateau from channel ~30 to 95, attributed to Si, and then extends all the way from around channel 95 to 370 which is attributed mainly to carbon.

![Graph](image)

*Figure 32. The response spectrum obtained by exposing the SiC detector to the near-core radiation, while the reactor was operated at 10 $W_{th}$. After 5 min of the reactor shutdown, the near-core background response was measured as the black curve.*
Conclusion

We exposed the SiC detector to an intense $^{60}$Co source while still measuring a $^{241}$Am alpha spectrum to evaluate its gamma sensitivity. We also tested the device at a near-core location. Good performance with slightly degraded energy resolution at high temperature was validated. Intense gamma irradiation can cause degraded detector performance in terms of worsening resolution that may be due to pulse pileup and secondary trapping effects, which cannot be simply eliminated by increasing the lower limit detection (LLD) threshold. After the same SiC detector’s successive endurance of a $\sim 2$ h intense gamma irradiation, a 2 h external beam irradiation, and a 2 h near-core irradiation, it still performs in excellent condition and presents a stable spectral response. The experiments indicate that the SiC detector is highly radiation resistant, making it suitable for the proposed application in pyro processing for special nuclear materials accountancy.
Milestone 9: Sensor is able to measure actinides concentrations

Figure 33: Fully packaged 4H-SiC Schottky diode detector.

To test the detectors capability of determining actinide concentrations from a source electrodeposited on the surface of the detector the detector was packaged as shown above in Figure 33. The detector was mounted to a glass washer using a ceramic adhesive paste inside a stainless-steel housing. The capsule was electrically connected using a conductive silver epoxy. The housing was then covered in the ceramic adhesive to protect the housing from the molten salt. silver epoxy was used to connect the Schottky epitaxial contact to the MI cable sheathing and the MI signal cable was attached to the Schottky bulk side. The detector was brought to the University of Utah for electrodeposition.
LiCl-KCl with UCl₃ added to 2.0 wt% was heated to 500 °C to achieve a liquid homogeneous mixture, shown above in Figure 34. The detector was loaded into the furnace but held above the liquid salt for approximately 15 minutes to allow for a gradual heating of the detector. The detector was then submerged into the salt for the electrodeposition. A voltage relative to the reference electrode was applied to the Schottky contact of the detector by connecting the working electrode to the outer sheath of the MI cable. Repeated chronoamperometry was used to deposit uranium onto the surface of the detector. RCA is a technique that involves alternating between short cathodic pulses and longer relaxation periods to ensure an even deposition and reduce dendritic formation. The detector was withdrawn following electrodeposition.

Following deposition, the detectors were cleaned using DI water to remove any excess salt. The detectors were weighed before and after submersion to ensure that no significant uptake of salt from the detector. The detectors were then attached to the spectroscopy equipment to ensure deposition and detector operation. Figure 35 below shows the detector post electrodeposition. Five
detectors were brought, and one survived the electrodeposition to an extent that allowed for sufficient biasing to determine the isotopic concentration.

Figure 35. Fully packaged detector following immersion and electrodeposition in molten salt

Alpha Spectroscopy of Electrodeposited Source on Surface of Detector

The detectors were brought back to The Ohio State University for spectroscopy measurements. The detector had a bias voltage of 100 volts applied to the bulk Schottky contact side to induce a depleted region in the epitaxial layer of the detector. The voltage is sufficient to create a large enough depleted region to fully stop the maximum energy alpha particle emitted by the uranium source (4.775 MeV from $^{234}\text{U}$). This allows for the full energy of all the alpha particles to be collected by the detector. This voltage was also the maximum voltage which the detector could be biased before breakdown of the electric field in the detector. Figure 36 shows the resulting alpha spectrum from a 297-hour collection time.
Figure 36. Electrodeposited uranium source alpha particle spectrum on surface of fully packaged 4H-SiC detector biased at 100V for 297 hours.

From the above spectrum, two well-defined peaks can be seen associated with the $^{238}\text{U}$ and $^{234}\text{U}$ alpha particles. These peaks overlap due to the broadening caused by self-shielding of the electrodeposited source and the widening of the energy resolution of the detector being heated to 500°C for an extended period of time. The overlapping of these two peaks obscures the $^{235}\text{U}$ alpha peak. With this alpha spectrum, the area under each peak can be determined, and this is equal to the total number of counts for that isotope. From this spectrum it is possible to determine the activity ratio between $^{238}\text{U}$ and $^{234}\text{U}$ using the following equation $\frac{A_{^{234}\text{U}}}{A_{^{238}\text{U}}}$ $\approx 0.09$. 

A commercial Si detector was also used to benchmark the spectrum acquired by SiC. In this case, the electrodeposited SiC detector was used as a source for the commercially available Canberra silicon surface barrier detector (model PD 300-19-100 AM). The Si detector was placed in a vacuum chamber and evacuated to reduce the attenuation of the alpha particles in air. The spectrum above shown in Figure 37 shows the same two peaks of $^{234}$U and $^{238}$U. There is still overlap between the two peaks due to the broadening caused by the thickness of the source. From the activity ratios along with the specific activity of each isotope it is possible to determine the isotopic concentrations of the two isotopes within the electrodeposited source. Determining the isotopic concentration of the source will be representative of the isotopic concentration within the salt mixture. Table 3 below shows a summary of the isotopic weight percent and activity ratio of natural uranium, the spectra observed using the electrodeposited sensor and the Si detector.

Table 3 Activity Ratios and Isotopic Weight Percent of $^{234}$U

<table>
<thead>
<tr>
<th></th>
<th>Activity Ratio $^{234}$U/$^{238}$U</th>
<th>Isotopic Weight Percent of $^{234}$U</th>
</tr>
</thead>
<tbody>
<tr>
<td>Natural Uranium</td>
<td>~0.99</td>
<td>0.0053</td>
</tr>
<tr>
<td>SiC Detector</td>
<td>0.09</td>
<td>0.00047</td>
</tr>
<tr>
<td>Si Detector</td>
<td>0.10</td>
<td>0.00052</td>
</tr>
</tbody>
</table>
The activity ratio from these spectra are affected by the fact the $^{234}\text{U}$ peak is attenuated by the source thickness. This would result in a decrease of the activity ratio of the sample as some of the $^{234}\text{U}$ alphas are hidden by the $^{238}\text{U}$ peak. Previous uranium samples prepared at the University of Utah have been analyzed with samples of 1-micron thickness and have an activity ratio of ~0.30. Based on these and previous results, it would appear that these samples are two different sources as they have two different $^{234}\text{U}/^{238}\text{U}$ activity ratios.
Final Quad Chart

Monitoring of Actinide Concentrations in Molten LiCl-KCl Salt using Alpha Spectroscopy

OVERVIEW

Purpose:
Produce alpha particle spectroscopy devices to monitor nuclear material concentrations in electrochemical reprocessing environments by electrodeposition of actinides onto the detector surface.

Objectives:
- Design, fabricate and characterize alpha particle detectors
- Develop techniques for actinide electrodeposition onto the detectors
- Test detectors and electrodeposition technique in representative environment

IMPACT

Logical Path:
Detector design and electrodeposition development will proceed in parallel. Detectors must be fabricated, characterized both electrically and spectroscopically, and then tested with representative samples. Electrodeposition techniques must be optimized for rate, quality, and repeatability. Once the detectors and electrodeposition components are adequately addressed, the two components must be brought together to perform integrated tests of the overall electrodeposition actinide monitoring procedure.

Outcomes:
Alpha particle detectors will be produced and will measure actinide concentration in LiCl-KCl salt by electrodeposition of actinides onto the detector surface.

RESULTS

Results:

Figure 1: 238U alpha spectrum from electrodeposited U source

Figure 2: Packaged detector with electrodeposited U source

- U sources were electrodeposited onto the surface of 5 fully packaged 4H-SiC detectors.
- An alpha spectrum was acquired from the electrodeposited source by the best surviving detector on which it was deposited to determine isotopic concentrations of different uranium isotopes.

Accomplishments:
- An actinide source from a molten salt was electrodeposited onto the surface of a 4H-SiC alpha detector Schottky contact.
- Isotopic concentration of 234U of 0.00347 weight percent was determined from alpha spectrum collected.
Publications

Journal papers:


4. Eric Moore, Josh Jarrell, Lei Cao, “Heteroepitaxial Diamond Growth on 4H-SiC using Microwave Plasma Chemical Vapor Deposition.” In: Heliyon. (Sep 2017) 3(9)


**Conference proceedings:**


