

Metal adsorption on functionalized silicon detectors for the future study of meitnerium chemistry

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One of the first attempts to coat silicon detectors with gold was reported during the chemical characterization of element 112, Cn. Better chemical sorption of this element was observed on gold-modified surfaces rather than on non-modified ones [1]. However, element 113, Nh, showed an enhanced reactivity towards gold, which prevented the proper chemical characterization of this element [2, 3]. Therefore, a need for new chemically modified silicon detectors has emerged. Such detectors will selectively bind the atoms of interest but with weaker interactions. Element 109, meitnerium, which is expected to be a member of Group 9 of the periodic table, has never been chemically characterized before. Therefore, this project aimed to study the adsorption of meitnerium's two closest homologs, namely iridium (Ir) and rhodium (Rh), on functionalized surfaces. Preliminary results are reported here.

We successfully characterized 1-(11-mercaptoundecyl)imidazole (Im-C₁₁-SH) self-assembled monolayers (SAMs) on gold-coated substrates using several surface science techniques last year [4]. In our studies, we used silicon chips (10 mm x 10 mm x 0.5 mm) coated with 100 nm of gold and glass chips (10 mm x 10 mm x 0.7 mm) coated with 50 nm of gold. Both substrates are primed with a titanium adhesion layer with a thickness of 5 nm and 2.5 nm, respectively.

Over the past year, nanoprojectile secondary ion mass spectrometry (NP-SIMS) was employed to determine whether Ir(IV) and Rh(III) bind to Im-C₁₁-SH SAMs on gold-coated glass chips. The SAMs deposition was performed by submerging two chips into 5 mM ethanolic Im-C₁₁-SH solutions for 21 hours. The coverage of gold with Im-C₁₁-SH SAMs was measured to be (90±5)% and (80±5)%, respectively. After the SAMs formation, the functionalized chips were submerged into 5.2×10^{-6} M Ir(IV), or 9.7×10^{-6} M Rh(III) solutions in 0.55 M hydrochloric acid for approximately 21 hours. During the NP-SIMS analysis, a primary beam of 520 keV Au₄₀₀⁴⁺ clusters hits the surface of the functionalized chips, and the energy transfer from the beam to the surface causes the emission of cluster ions [5, 6]. In the NP-SIMS spectra of the functionalized chips, Ir₂Cl₆⁻ and RhCl₃⁻ cluster ions were observed with high intensities which leads to the conclusion that both Ir(IV) and Rh(III) bind to Im-C₁₁-SH SAMs. The coverage was measured to be (66.0±3.4)% and (81.3±3.8)%, respectively.

Subsequently, the SAMs deposition procedure was applied to the functionalization of gold-coated silicon detectors used during online cyclotron-based experiments. Three silicon detectors were coated with 50 nm of gold after being primed with 5 nm of titanium by Platypus Technologies, LLC (Madison, Wisconsin, USA). After this, Im-C₁₁-SH, or mercaptododecanoic acid (MDDA) SAMs were deposited on the gold-coated silicon detectors from 5 mM ethanolic solutions of the corresponding thiols. The SAMs deposition was performed on each detector twice to obtain the highest surface coverage. To remove the SAMs before the second deposition, the detectors were exposed to UV light.

Two experiments utilizing the following nuclear reactions were performed: $^{141}\text{Pr}(^{40}\text{Ar}, 5\text{n})^{176}\text{Ir}$, $^{118}\text{Sn}(^{40}\text{Ar}, 5\text{n})^{153}\text{Er}$, and $^{165}\text{Ho}(^{40}\text{Ar}, 5\text{n})^{200}\text{At}$ on the AGGIE (Al Ghiorso's Gas-filled Ion Equipment) separator at the Cyclotron Institute, Texas A&M University. A simple Recoil Transfer Chamber (sRTC), composed of a funnel and a detector chamber, has been designed and used for the first time. Fig. 1 illustrates the AGGIE separator and the sRTC used in this study.

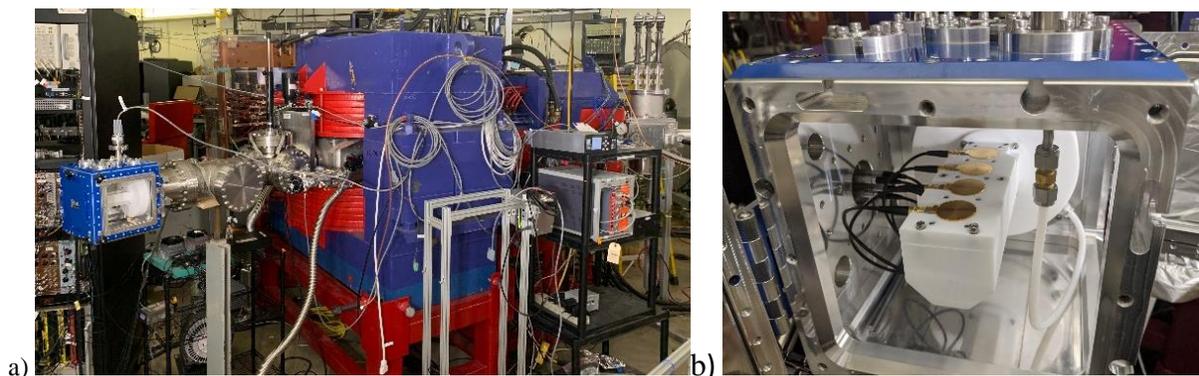


Fig. 1. The sRTC (blue box at far left) installed on the AGGIE separator (a). The (circular, gold colored) detectors installed inside the sRTC (b).

The goal of the sRTC is to stop the ions of interest in the funnel by their collision with atoms of helium gas (350 Torr) which goes through the sRTC with the flow of 500-1600 standard cubic centimeters per minute. In turn, this enables more efficient sorption and detection of the named nuclides on the non-modified and modified silicon detectors located in the detector chamber. In addition, a rotating degrader made of Mylar was installed upstream of the sRTC. Changing the angle of the rotating degrader results in the increase or decrease of the effective thickness of the material the ions are going through. As a result, we can select the rotating degrader angle at which the ions will be stopped mostly in the funnel due to their energy loss while traveling through the rotating degrader material of the corresponding thickness, and an aluminized Mylar window located in the entrance of the sRTC. Consequently, this increases the count rate of a produced nuclide.

The effect of the detector position in the detector chamber, and the detector material on the $^{173-176}\text{Ir}$, $^{152,153}\text{Er}$, and $^{199-201}\text{At}$ rates was investigated. The corresponding plots with rate as a function of detector position and material are shown in Fig. 2a-c. The materials tested were bare silicon (Bare Si), gold-coated silicon (Si+Au), gold-coated silicon functionalized with Im-C₁₁-SH SAMs (C11-Im), and gold-coated silicon functionalized with MDDA SAMs (MDAA). Four configurations were tested by cycling detectors through each position inside the detector chamber.

Results demonstrated that changing the detector position and material changes the nuclide adsorption. For $^{152,153}\text{Er}$, the highest rate was observed on the gold-coated silicon and the bare silicon detectors at a 55° rotating degrader angle. For $^{199-201}\text{At}$, the highest rate was observed on the gold-coated silicon detector at a 45° rotating degrader angle. Other materials were equally effective. For $^{173-176}\text{Ir}$, all materials were equally effective at all rotating degrader angles summed up, which was done to enable fitting of the data with low statistics. In the case of MDDA, the count rate could not be determined. Regardless of the material, the highest rate was observed at position 1.

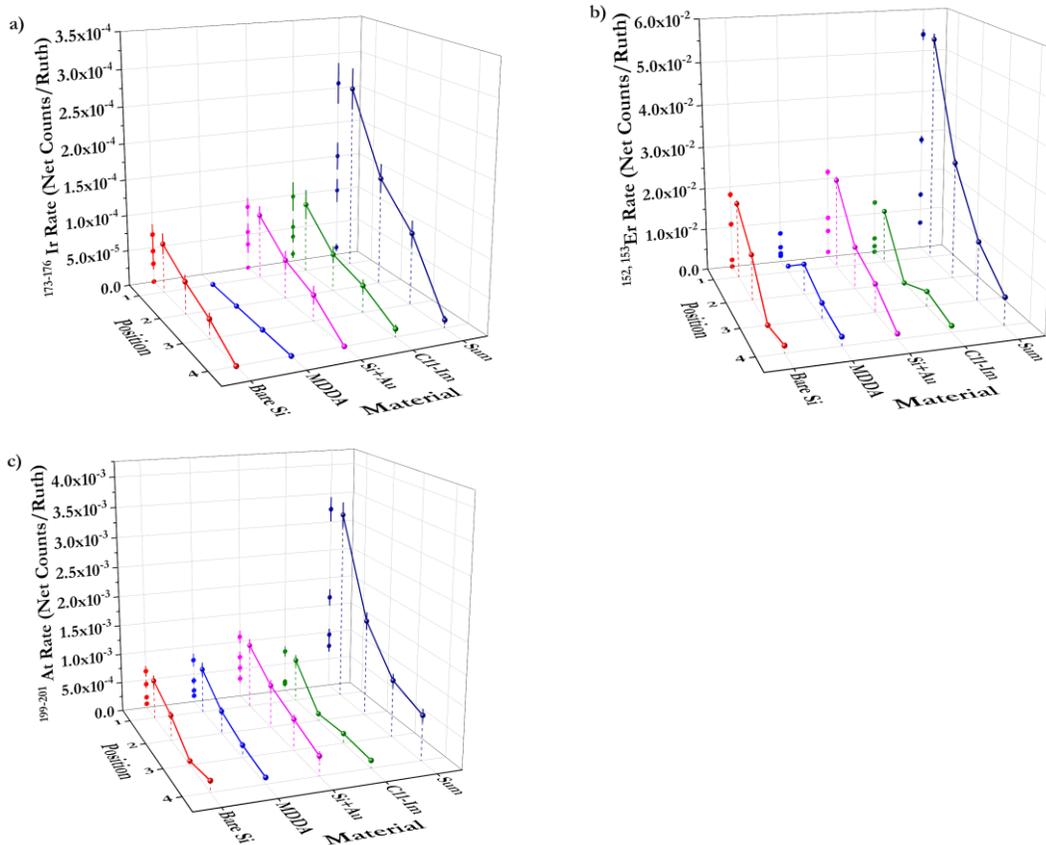


Fig. 2. (a) 3D plots of the $^{173-176}\text{Ir}$, (b) $^{152,153}\text{Er}$, and (c) $^{199-201}\text{At}$. Rates as functions of the detector position and material. All data are preliminary.

In addition, the chemical behavior study of online-produced nuclides was performed. R_0 is the slope of curves obtained after fitting the sum of the event rates as a function of position as illustrated in Fig. 3a using an exponential function. R_0 is characteristic of the chemical behavior of elements in the sRTC; the comparison of the R_0 values confirmed that Er and Ir are non-volatile elements, whereas At is a volatile element. The R_0 values for $^{173-176}\text{Ir}$, $^{152,153}\text{Er}$ and $^{199-201}\text{At}$ are 0.84 ± 0.22 , 0.72 ± 0.05 , 0.55 ± 0.07 , respectively.

The results suggest there are two possible processes: ions of interest can be adsorbed on the surface of the detector, or they can decay in flight. At the moment, we are still working to interpret the relative influence of these two effects. Fig. 3b shows that the total activity was constant regardless of the configuration. Therefore, if one detector has a higher rate than another detector within one configuration, it indicates that the variations are due to the interactions with the detector surface.

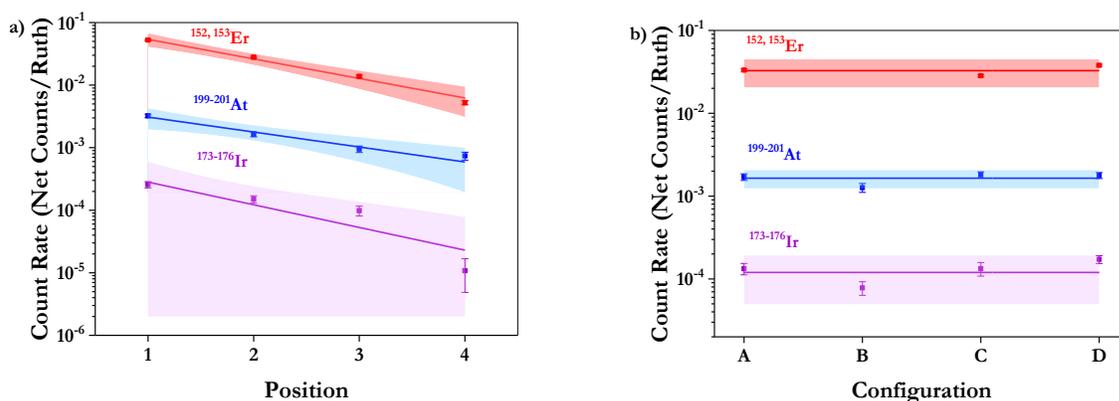


Fig. 3. (a) The count rate of $^{173-176}\text{Ir}$, $^{152,153}\text{Er}$, and $^{199-201}\text{At}$ as a function of the detector position, and (b) detector configuration.

A paper based on the offline experiments of this project is in the late stages of preparation. The results of the online experiments will be discussed in an additional paper and a dissertation is currently being written.

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