Iridium and rhodium adsorption on functionalized silicon chips 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. This resulted in better chemical sorption of this heavy element on the modified surfaces rather than on a non-modified surface [1]. However, element 113, Nh, showed an enhanced reactivity towards gold, which prevented the proper chemical characterization of this element [2]. Therefore, a need for new chemically modified silicon detectors has emerged. Such detectors should selectively bind the atoms of interest but with weaker interactions.

The formation of thiolate self-assembled monolayers (SAMs) on gold is a well-known approach to the functionalization of gold surfaces. SAMs are arrangements of molecules that can be spontaneously adsorbed on solid surfaces from a solution or a vapor phase [3]. In this work, the functionalization of gold-coated silicon chips with 1-(11-Mercaptoundecyl)imidazole (Im-C_{11}-SH) SAMs has been

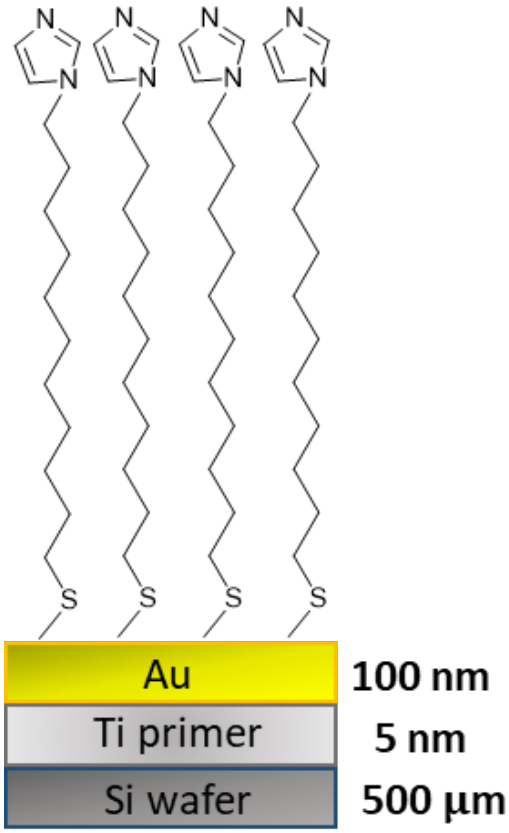

Fig. 1. Schematic diagram of the substrate investigated in this study.

investigated. This thiol is a commercially available compound and has already been used to form SAMs on gold surfaces [4]. The experiments were conducted on 1 cm^2 silicon chips covered with a 5 nm titanium adhesion layer and coated with 100 nm of gold. A schematic diagram of the corresponding substrate is shown in Fig. 1.

We are interested in studying the chemical properties of iridium and rhodium because it will help us better understand the chemistry of meitnerium which is believed to belong to Group 9 of the periodic table. Im-C_{11}-SH was chosen as the closest analogue of imidazolium-based ionic liquids that have already been used to extract metals, in particular iridium from hydrochloric acid solutions [5].

The functionalized surfaces were characterized using several techniques. Atomic force microscopy was used to evaluate the roughness of pure gold and substrates with SAMs. The average roughness of pure gold is on the order of 1-2 nm. The roughness remains in the same range after the SAMs deposition. The average surface coverage with Im-C_{11}-SH SAMs was measured using cluster secondary-ion mass spectrometry (SIMS). SAMs were found to cover up to 99.5% of the gold surface when being deposited from a 5 mM ethanolic thiol solution, which indicates quantitative adsorption. X-ray photoelectron spectroscopy was used to study the chemical state of SAMs. The sulfur 2p XPS spectrum of a fresh sample displayed in Fig. 2 contains primarily a spin-orbit split doublet with S $2p_{3/2}$

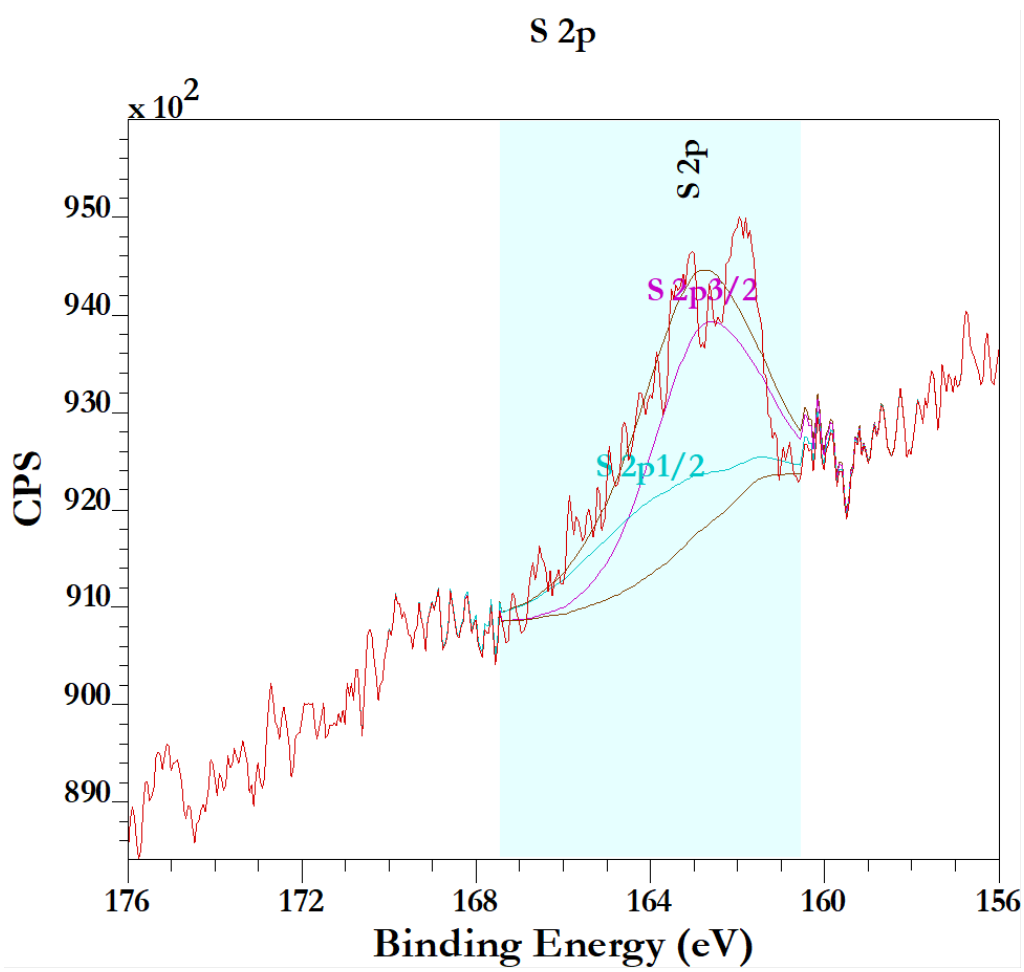

Fig. 2. XPS of S 2p region of Im-C_{11}-SH SAMs on gold.

component at 162.8 eV which corresponds to a thiol bound to gold [6]. H_2O_2-mediated liquid UV-light photooxidation treatment was employed to remove thiolate SAMs. The XPS spectra showed that peaks of S 2p and N 1s disappear after the removal of thiols. This means the gold-coated silicon chips can be reused. Also, the effect of aging was studied by recording XPS spectra over time. The results illustrated that SAM-functionalized surfaces remain stable for at least 1 week of sample storage in wafer carrier trays wrapped with aluminum foil under ambient laboratory conditions.

Ellipsometry was used to determine the thickness of SAMs, which was found to be 1.690±0.014 nm. This result indicates the presence of a single monolayer on the surface of gold and is in good agreement with the literature results obtained for similar films [7, 8]. Neutron activation analysis (NAA) showed that iridium can be adsorbed from 2% hydrochloric acid solution on functionalized gold-coated silicon chips with a sorption efficiency of approximately 77%. The results for rhodium are still being analyzed. SIMS was also employed to study which types of iridium and rhodium chloro-complexes are bound to Im-C_{11}-SH SAMs during the metal deposition. These results are still being analyzed.

A paper based on this project is under preparation and will be finalized after analyzing the NAA and SIMS data.

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