Materials Day

Abstract

Maximizing SEIRAS response with ATR electrodes for IR spectroelectrochemical cells

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Abstract: Electrochemical energy conversion and storage technologies, such as fuel cells, electrolyzers, and batteries, offer promising solutions to the challenges posed by fossil fuels. Their performance largely depends on the behaviour of electrochemical interfaces, where understanding molecular interactions is crucial for improving device efficiency. Spectroelectrochemical (SEC) techniques, particularly Surface-Enhanced Infrared Absorption Spectroscopy (SEIRAS) combined with Attenuated Total Reflectance (ATR), provide a powerful non-invasive approach for characterizing these interfaces. However, the fabrication of SEIRAS active electrodes, particularly gold on silicon, is often limited by surface energy mismatches and native oxide layers. We found six gold deposition methods for SEIRAS applications, with electroless deposition standing out due to its reported high enhancement. Six electrodes were fabricated using this method, but the SEIRAS responses varied significantly, with a peak area variation exceeding 40%. AFM analysis revealed that this variation was linked to differences in surface roughness, with higher roughness correlating with stronger SEIRAS signals. However, this method also exhibited a significant drawback: time-dependent delamination of the gold film during testing, compromising long-term stability. To address these issues, we employed a NaOH etching method, which etches Si (100) surfaces at a faster rate, producing a rougher substrate. Gold was sputtered onto these etched surfaces, followed by electrochemical cleaning. This method resulted in electrodes with significantly improved adhesion, passing peel tests, and exhibiting SEIRAS responses 13 times stronger than those fabricated using electroless deposition. Additionally, these electrodes enabled time-dependent data acquisition, producing spectra at 1-second intervals with minimal RMS noise (5×10^{-5}). Our future work will focus on understanding the role of surface roughness in SEIRAS enhancement and developing reliable fabrication protocols. We will also explore multilayer gold deposition techniques to further improve sensitivity, particularly for detecting low-concentration species at electrochemical interfaces.