SEIRAS-optimized ATR Wafers for Interfacial Spectroelectrochemistry

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Abstract

We show that a microgrooved Si ATR wafer designed to allow high angles of incidence at the electrode-solution interface provides improved signal-to-noise in electrochemical ATR-SEIRAS.

Introduction

Microgrooved Si ATR wafers (Figures 1 and 2) have been shown to be excellent internal reflection elements for electrochemical ATR-SEIRAS owing to their low cost and high spectral throughput.[1] A microgrooved substrate is formed by selective etching of a standard Si wafer to form an array of individual prisms which map the incoming beam by refraction to a narrow range of angles determined by the groove face angle. As SEIRAS enhancement increases with angle of incidence[2] (AOI), the face angle, Φ, of the microgroove plays a critical role in SEIRAS performance.

Figure 1. Si ATR wafer (right).

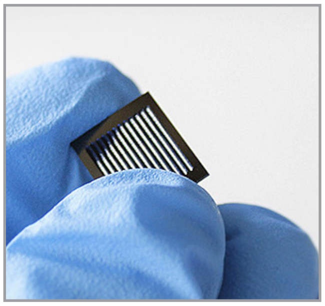

Figure 2. Schematic cross-section of microgrooved Si ATR wafer with the face angle, Φ, labelled. Only a few grooves are shown for clarity (below).

A 2nd generation SEIRAS-optimized wafer was designed with a greater groove face angle (55° compared to 35°) compared to a previously reported 1st generation Single Reflection ATR wafer. For both wafer generations, Table 1 lists the face angles and range of AOI at the electrode-solution interface, AOI_{ESI}, which results from incoming light at AOI_{inc}.

Table 1.

Groove face angle, Φ	AOI_{inc}	AOI_{ESI}
35° (Gen 1)	30° to 65°	33° to 43°
55° (Gen 2)		42° to 57°

Experimental Conditions

The performance of Gen 2 crystals (Φ = 55°, IRUBIS GmbH) was compared to that of Gen 1 crystals (Φ = 35°, IRUBIS GmbH) by preparing identical Au films. Wafers were polished for 5 minutes in 0.5 µm diamond slurry (Pace Technologies), rinsed with ultrapure water, and dried with flowing Ar. 30 nm Au films were simultaneously sputtered on the two types of wafers to ensure identical film morphology.

The wafer was loaded into a Jackfish SEC J1W spectro-electrochemical cell mounted on a PIKE VeeMAX III variable angle ATR accessory. A Au coil counter electrode and a Ag/AgCl (saturated KCl) reference electrode were used. The cell was filled with 0.1 M pH 6 acetate buffer and the Au thin film working electrode underwent voltammetric cycling as per a previous application note (*Jackfish Spectroelectrochemistry Cells*. PIKE Technologies, 2018, www.piketech.com/Jackfish-SEC-Spectroelectrochemical-Cell). Both films were cycled for the same amount of time.

The acetate electrolyte is advantageous because acetate adsorbs on the Au surface at +0.6 V but is replaced by water at -0.1 V. Thus, the intensity of the acetate symmetric v_{COO^-} stretch at 1400 cm^{-1} is an excellent diagnostic for SEIRAS enhancement. FTIR sample and reference spectra were collected by coadding 128 scans resolution at 4 cm^{-1} at the given potentials and potential difference absorbance spectra were calculated.

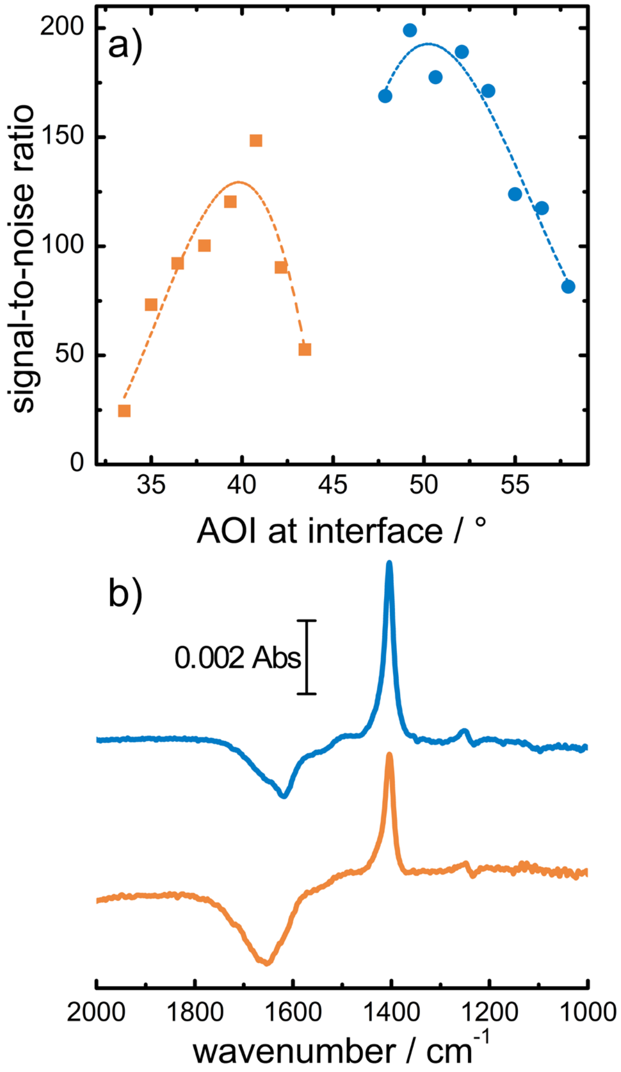

Figure 3. ATR-SEIRAS performance of Gen 1 and Gen 2 wafers. a) Signal-to-noise of the acetate ν_{COO^-} 1400 cm^{-1} band versus AOI at the electrode-solution interface for Gen 1 (orange squares) and Gen 2 (blue circles) wafers. Dotted lines were added to guide the eye. b) Potential difference absorbance spectra of adsorbed acetate at peak SNR for Gen 1 (orange, AOI_{ESI} = 49°) and Gen 2 (blue, AOI_{ESI} = 40°) wafers.

Results

Figure 3a plots the signal-to-noise ratio of the acetate ν_{COO^-} band as a function of AOI_{ESI} for the two wafers. The Gen 2 wafer (blue circles) SNR peaks near 50° and is greater than the corresponding peak for the Gen 1 wafer (orange squares), which reaches a maximum near 40°. There are two reasons for this. Both wafers were measured by varying the VeeMAX III angle of incidence in the range $30° \leq AOI_{inc} \leq 65°$. As shown in Table 1, the greater face angle in the Gen 2 wafer maps this range to a higher range at the electrode-solution interface than that of the Gen 1 wafer, allowing greater SEIRAS enhancement. At peak SNR, IR light is optimally coupled through the wafers, resulting in a low noise measurement. Second, the Gen 2 wafer throughput is greater overall than that of the Gen 1 wafer, further improving SNR. These factors are evident in Figure 3b, where potential difference absorbance spectra at peak SNR are shown for the Gen 2 (blue) and Gen 1 (orange) crystals. The upward going band at 1400 cm^{-1} is the acetate ν_{COO^-} stretch. The weak band near 1200 cm^{-1} is due to potential dependent Si phonon modes. The broad negative band near 1650 cm^{-1} is due to loss of adsorbed interfacial water upon replacement with acetate. Both the higher signal and lower noise of the ν_{COO^-} stretch at 1400 cm^{-1} are apparent in the Gen 2 spectrum.

Conclusions

The higher throughput and greater accessible AOI at the electrode-solution interface allow the 2nd generation SEIRAS-optimized crystal to achieve a 35 % greater SNR than that of the 1st generation wafer in an electrochemical ATR-SEIRAS experiment.

References

(1) Morhart, T. A.; Unni, B.; Lardner, M. J.; Burgess, I. J. *Anal. Chem.* **2017**, *89* (21), 11818–11824.

(2) Suzuki, Y.; Osawa, M.; Hatta, A.; Suëtaka, W. *Appl. Surf. Sci.* **1988**, *33–34*, 875–881.