An Infrared Thin-Layer Spectroelectrochemical Cell with Silicon Micromachining Technique

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A novel, silicon based thin-layer spectroelectrochemical cell was constructed with micromachining techniques. The cell consists of an etched cover wafer and a base silicon wafer which contains a whole set of a gold working electrode, a gold counter electrode and an Ag/AgCl reference electrode. The thickness of a cell can be controlled easily by changing the etching time of a cover wafer and some drawbacks (e.g. complexity and high cost) of previous IR thin-layer cells, which have been made by manual combination of electrodes and IR transparent plates, were solved. The performance of the cell was examined by in situ monitoring of FT-IR (Fourier Transform Infrared) spectra and electrochemical characteristics of Fe(CN)₆³⁻/²⁻ and ferrocene/ferrocinium ion redox couples, respectively. The cell showed capacity for a rapid and exhaustive electrolysis of chemicals in a cell, the typical characteristic of a thin-layer cell, in both aqueous and organic media.

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Introduction

Transmission IR spectroelectrochemistry technique plays a very important role in identification of products or intermediates of chemical redox reactions. Furthermore, with a thin-layer configuration, the rapid and exhaustive electrolysis of reagents is possible. Using in situ monitoring of FTIR (Fourier Transform Infrared) spectra and its electrochemical characteristics, we can detect the products or intermediates which have a lifetime of more than several seconds.¹

Since the appearance of in situ IR spectroelectrochemical methods, several optically transparent IR spectroelectrochemical thin-layer cells have been designed.²⁻⁵ The cells have been made of carved IR transparent salt plates such as NaCl and CaF₂, a manually combined gold mesh electrode and a separate reference electrode. These cells have some drawbacks: their cost is high; they are easily strained and even damaged during experiments, and the cell has a fixed depth. Moreover, many of these IR cells are difficult to clean because of their complicated structures. In this paper we propose a new infrared thin-layer cell fabricated on silicon wafers, monolithically integrating both working and reference electrodes by using micromachining techniques.

Experimental

Reagents

FeCl₃, K₃[Fe(CN)₆]₃, KCl, dicypentadienyliron (ferrocene), and a 5% Nafion solution were purchased from Aldrich Chemical Co. and used as received. Tetrahydroammonium perchlorate (TBAP) (Fluka chemical Co.), the supporting electrolyte used in organic solvent, was dried in vacuum. Analytical grade CH₃Cl, was freshly distilled from P₂O₅ before use.

Aqueous solutions were prepared with triply distilled water from Modulab water system (U.S. filter corp.). All the experiments were carried out at room temperature.

Instrumentation

The BAS 100B PC-controlled electrochemical analyzer (BioAnalytical Systems, Inc.) with a three-electrode system was used for all measurements. A Perkin-Elmer Paragon 500 FTIR spectrometer was used to record in situ FTIR spectra. All reported potentials are referenced to a solid-state Ag/AgCl reference electrode unless mentioned.

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Fig. 1. Structure of IR thin-layer cell
Fabrication of the thin layer IR cell

Figure 1 shows the schematic structure of the IR thin-layer cell. There are three electrodes in the cell. Two gold electrodes (a working electrode mesh and a counter electrode) and an Ag/AgCl reference electrode are integrated in the micromachined silicon cavity. The in situ FTIR spectrum is externally monitored during the electrochemical reactions of the sample solution in the silicon cavity.

Figure 2 shows the process flow of thin-layer cell. We used a double polished silicon wafer as a starting material to minimize IR interference at the surface. Using the oxide as a mask, the cover wafer is anisotropically etched in 25% TMAH (tetramethyl-ammonium hydroxide) to make an etched cavity (Fig. 2(a)) and finally the oxide film is removed. By changing the etching time, the thickness of a thin layer can be controlled with ease. To fabricate the bottom wafer containing working, counter and reference electrodes, thermal oxide is grown and a Cr/Au (200/3000 Å) layer is patterned by lift-off method (Fig. 2(b)). The reference electrode of Cr/Au/Ag (200/200/4000 Å) is defined and the top silver layer is oxidized to make a solid-state reference electrode (Ag/AgCl) as reported before (Fig. 2(c)). The fabricated bottom electrode is shown in Fig. 3.

Fig. 2. Fabrication process flow: (a) Silicon cover wafer after TMAH etch, (b) Cr/Au electrode lift-off pattern, (c) Ag lift-off pattern and oxidize to Ag/AgCl, (d) Combined IR thin-layer cell.

Results and Discussion

IR characteristics of the cell

To examine the performance of this noble thin layer cell, IR spectra without any electric connection were obtained. Figure 4 shows a FTIR spectrum of a double-polished silicon wafer. There is no absorption peak, and this result well matches with the fact that the silicon is transparent to IR. Fig. 7 compares the FT-IR spectrum of a commercial CaF₂ cell for 2.0 mM K₃[Fe(CN)₆] solution with that of the fabricated thin-layer cell. In the case of the fabricated thin-layer cell, the total transmittance decreases, but the peak of Fe(CN)₆³⁻ at 2114 cm⁻¹ is clearly shown.

Fig. 4. FT-IR spectrum of a bare double-polished silicon wafer.

Fig. 5. Comparison of FT-IR spectra of Fe(CN)₆⁴⁻ between a commercial CaF₂ cell and the fabricated silicon thin-layer cell.

Cyclic voltammetry

The electrochemical responses of this IR cell were examined in an aqueous solution of 2.0 mM K₃[Fe(CN)₆] (0.1 M KCl). The cyclic voltammogram obtained from cells having various cavity depth at the scan rate of 2.0 mV/s are shown in Figure 6. The shapes of the current-potential curves are symmetric and are characteristic for a thin-layer cell.¹,² The cathodic and anodic peak currents, iₚ and iₚ, are almost same at each depth (57±1.5, 109±2.7, 170±4.6 μA, respectively) and are proportional to the cell thickness because the total volume in the cell increase.
Fig. 6 Cyclic voltammetry of thin-layer cell for various cavity depth.

In situ FTIR spectroelectrochemistry

An example of the application of this silicon-based thin layer cell in in situ spectroelectrochemistry for hexacyanoferrate redox couple in aqueous solution (0.1 M KCl) is shown in Figure 7. The strong peak at 2114 cm$^{-1}$ is the characteristic absorption of Fe(CN)$_6^{3-}$, this peak rapidly decrease as the potential goes negative. In contrast, a sharp peak at 2040 cm$^{-1}$ for Fe(CN)$_6^{3-}$ appears, which demonstrates that Fe(CN)$_6^{3-}$ is completely reduced to Fe(CN)$_6^{4-}$.

It should be noted that in aqueous solution, the strong absorption bands from the solvent (water) in the 1350-1740 cm$^{-1}$ and 2920-3700 cm$^{-1}$ regions occur and may interfere with the target signals in these wavenumbers. Meanwhile, organic solvents show little absorption in most of the IR regions (500-4000 cm$^{-1}$) and the solvent problem is diminished in organic system.

The possibility of this cell to the organic system is examined by the in situ FTIR measurement with the electrolysis of 10 mM ferrocene in 0.1 M TBAP/CH$_3$Cl$_2$ solution. As shown in Figure 8, the IR absorption peak from C-H parallel bending modes of ferrocene$^{10}$ at 1004 cm$^{-1}$ decreases in intensity while a new peak due to the C-H bending mode of the ferrocenium ion$^{11}$ grows at 1012 cm$^{-1}$. This sensitive spectra changes show that this cell is capable of monitoring very weak IR signals.

Fig. 7. In situ FTIR spectra of 2.0 mM K$_2$[Fe(CN)$_6$] in aqueous solution at different potentials.

Fig. 8. In situ FTIR spectra of 10 mM ferrocene in 0.1 M TBAP/CH$_3$Cl$_2$ solution at different potentials.

Conclusion

A new design of IR thin-layer cells have been fabricated by using silicon micromachining technology. The fabricated thin-layer cell includes an anisotropically-etched silicon cover plate and a bottom plate containing a gold working electrode, a counter electrode and an Ag/AgCl reference electrode. We have successfully monitored the spectroelectrochemical characteristics of the Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$ and ferrocene/ferrocenium ion redox couples by using fabricated thin-layer cell. This micromachined thin-layer cell allows a low-cost convenient detection of intermediates or products in chemical redox reactions and accurate identification of the reaction mechanisms of chemical redox couple in both aqueous and organic media.

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References