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Micromachined Electrochemical cell platform for biosensors

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ABSTRACT

Miniaturized Electrochemical cell platforms are developed using two different approaches, namely surface and bulk micromachining technologies. Gold is used as the working electrode layer in both cases. In bulk micromachined device, electrodes are formed in the cavity created on silicon using KOH etching process while the cavity is formed using SU -8 epoxy photoresist on top of the electrodes in the micromachined device. Cyclic voltammetry is carried out on both the devices using potassium ferrocyanide $K_4(Fe(CN)_6)$ and potassium ferricyanide $K_3(Fe(CN)_6)$ redox couple as the analyte. It is observed that the surface micromachined device yields reversible electrochemical response and is easily amenable for fabrication. Further, it is compatible for functionalization of the electrode surface for electrochemical biosensor applications.

Keywords: Electrochemical cell, microelectrode, Surface micromachining, Bulk micromachining, Cyclic Voltammetry, ferrocyanide / ferricyanide redox couple

1. INTRODUCTION

Electrochemical sensing has become the ubiquitous choice when it comes to the detection of analytes of very low concentrations. Miniaturizing electrochemical sensors offers advantages in terms of sensitivity, selectivity, cost effectiveness and compatibility with the CMOS process. A CMOS controlled miniaturized electrochemical sensor array is ideal for bio-assay applications.

An electrochemical sensor or an electrochemical cell has two (working and counter) or three (working, counter and reference) electrodes immersed in an electrolyte containing an electroactive analyte. A measurement technique called 'Cyclic Voltammetry (CV)' is carried out to quantify the analyte present in the bulk of the electrolyte. In this technique, voltage is swept linearly from an initial value to a final value and then swept back to the initial value. The corresponding currents flowing in the cell, due to the oxidation or reduction of the analyte are plotted as a function of applied voltage. The i-v plot is called a cyclic voltammogram. As the concentration of analyte increases, there is an increase in current observed, provided all other parameters are constant[1].

Having the electrode dimensions in the micrometer regime offers unique advantages such as high diffusional flux of the analyte, low ohmic drop between the electrodes, high current density and small time to reach the steady state. All these result in high sensitivity towards the analysis of the species[2].

Miniaturized electrochemical sensor platforms have been fabricated with glass as the substrate in previous studies[3,4,5]. Silicon offers unique advantage of integration with the CMOS technology. This paper presents the fabrication of electrochemical sensor platforms using both bulk and surface micromachining technologies on silicon surface. The devices are compared using a preliminary screening of a redox analyte.

2. EXPERIMENTAL

2.1 Bulk Micromachined EC Cell

The fabrication process-flow is depicted in Fig.1. The substrate material is p-type (100) silicon wafer(a). A 1μm SiO_2 is thermally grown on the silicon wafer. This serves as masking layer(b). Windows are opened in SiO_2 layer by doing photolithography and subsequent etching of SiO_2 in Buffered HF(c). To create a cavity for the electrolyte,

silicon is etched in 30 % KOH at 75°C for 2 hrs and in 75% KOH at 75°C for 30 min(d). The depth of the cavity is 101 μm as measured using Veeco optical profilometer. Then the oxide is stripped off(e). After standard cleaning procedure, another 1μm SiO_2 is thermally grown on the silicon wafer(f). This serves as an isolation layer. The electrode material consisting of Cr and Au is sputter deposited sequentially. The 20nm Cr serves as an adhesive layer and the 300nm Au serves as the electrode layer (g). Photolithography is done to define electrodes (h). Au and Cr are etched in the undesired areas using gold and chrome etchants respectively. The dimensions of working and counter electrodes are 500 μm × 500 μm and 5000 μm × 5000 μm respectively. Contacts are given using silver paste. Fig 2. shows one such fabricated device.

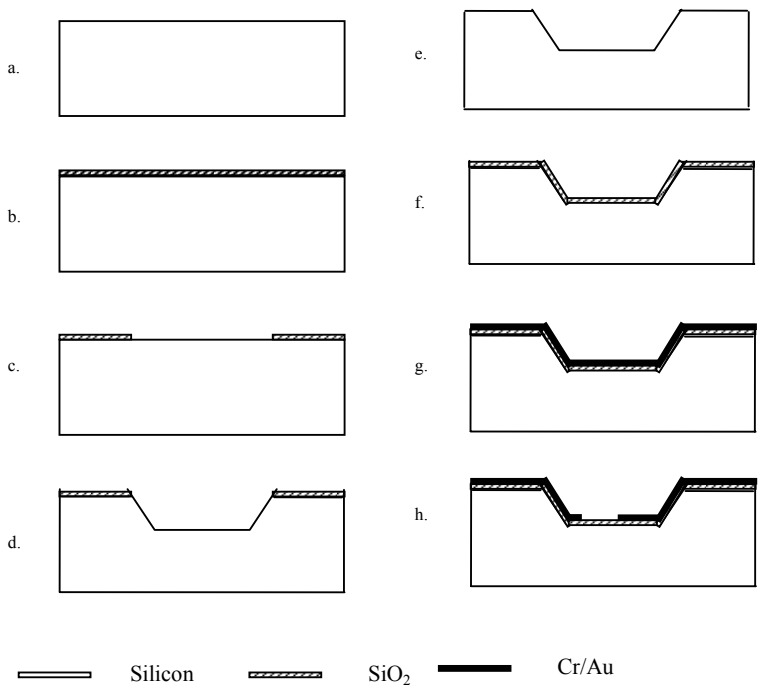


Figure 1. Fabrication steps of Bulk micromachined EC Cell.

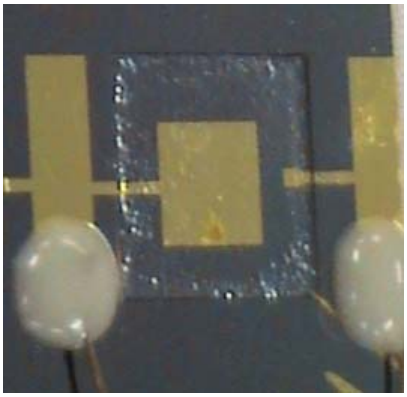


Figure 2. Bulk micromachined device with electrodes inside the KOH cavity.

2.2 Surface micromachined device

The fabrication process flow is shown in the Fig.3. Here also the substrate material is P-type (100) Si wafer(a). A 1μm SiO_2 is thermally grown on the silicon wafer (b). Cr and Au are sputtered and photolithography is

done to define electrodes. The 20nm Cr serves as an adhesive layer and the 300nm Au serves as the electrode layer(c). For the cavity a thick photoresist SU-8 is used to create a well with a height of 100 μm and width of 6000 μm. SU-8 photoresist is spun at 500 rpm for 5 sec, 5000 rpm for 55 sec. Prebake is done at 95°C for 45 min on a hotplate. Then exposure is done using Laser writer. After exposure, a bake is given at 95°C for 15 min to do the image reversal. It is then developed in SU-8 developer for 5 min and rinsed in IPA and blow dried using nitrogen gun. To harden the SU-8 photoresist, a bake is done at 200°C for 30 min on a hot plate(d). Working electrodes of different areas are incorporated in the same device. The working electrode areas range form 300 μm^2 to 2000 μm^2. The counter electrode dimensions are 1000 μm × 1000 μm. Fig. 4 shows one such fabricated device.

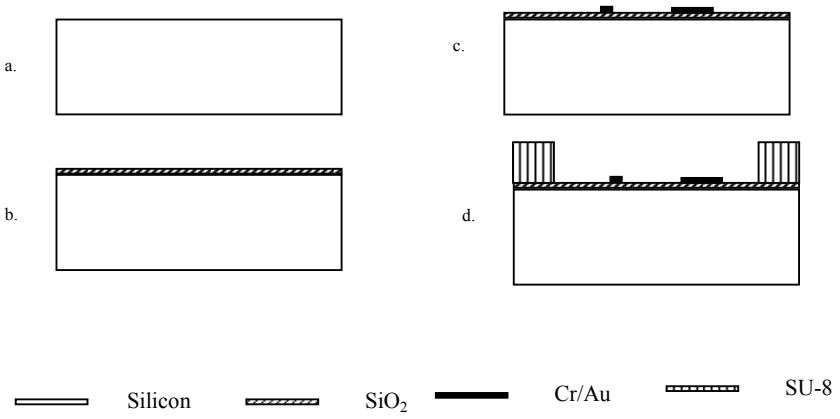


Figure 3. The fabrication process flow for surface micromachined EC cell.

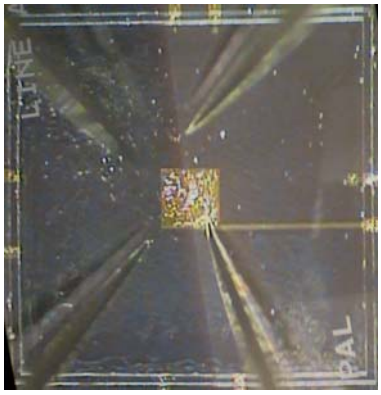


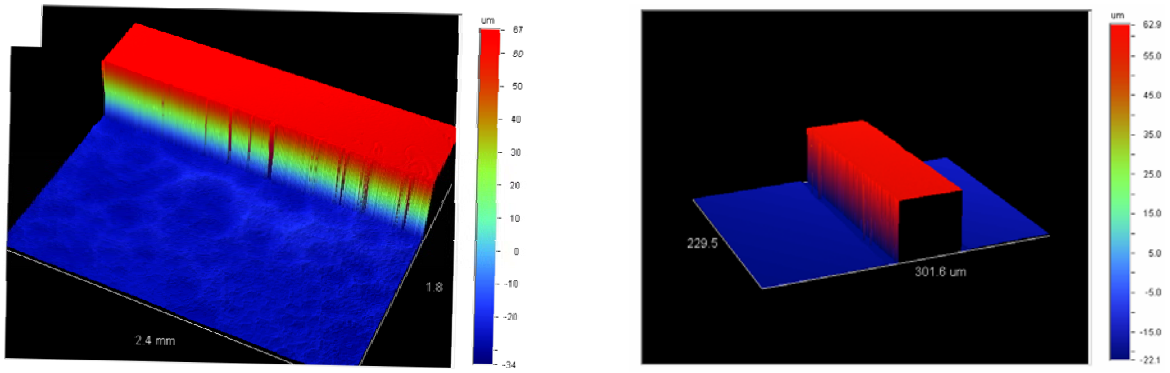
Figure 4. Surface micromachined EC cell with electrodes inside SU-8 Photoresist based cavity.

3. DISCUSSION

Surface micromachined EC cell offers many advantages as compared to the bulk micromachined device. The number of steps involved in the fabrication of the devices is less for surface micromachining than that involved in bulk micromachining. The contacts for the electrodes are taken from the bottom in the first case, whereas the contacts are taken from the top in the second case. Since Silicon is etched by 100 μm, it is difficult to cover the sidewalls and get a good contact. It is well known that evaporation is a line of sight non conformal deposition[6]. It is observed that even with sputtering technique, the sidewall coating is very thin and the contact is not good for a considerable length of time.

Electrochemical response is sensitive to the roughness of the electrodes. All the electrochemical reactions are surface reactions and the mass transport of the redox species get affected by the roughness. In addition, the surface roughness plays a role in the energetic requirement and hence affects the redox potentials. The KOH etching

technique, inherently introduces roughness on the surafce[7]. Etching is carried out using 30% KOH, wherein the etch rate is fast but the roughness is large as well. Subsequent etching is carried out using 70% KOH, wherein the etch rate is small and the roughness is small. This roughness of the surface is determined to be around 2 µm. The roughness and the step height of the bulk micromachined device are shown in figure 5(a). Miniaturization is restricted in the case of bulk micromachined device since the etching is partially anisotropic. The side wall angle is 57.4°. After (111) plane is reached, the etching process stops. As the device dimension shrinks laterally, the volume of the analyte that can be introduced reduces drastically. This is not the case with the SU-8 system since SU-8 photoresist has the unique advantage of getting vertical side walls. Additionally, the height of the photoresist can be increased by lowering the spinning speed. A 750 µm thick SU-8 cavity is possible as well. The non-uniformity of the surface is not an issue as the Si surface is very smooth (±10 A°).The roughness and the step height profile of SU-8 side wall are shown in figure 5 (b).



(a) **(b)**

Figure 5. Roughness and Stepheight profile of (a) side wall of KOH etched cavity (b) side wall of SU-8 cavity.

4. CYCLIC VOLTAMMETRY

CV measurements are carried out on both the electrochemical cells using the 1mM potassium ferricyanide $K_3Fe(CN)_6$ / potassium ferrocyanide $K_4Fe(CN)_6$ redox couple in 100 mM aqueous KNO_3 supporting electrolyte solution. The voltammogram for bulk micromachined EC cell is shown in figure 7. A quasi-reversible redox behavior with a ΔE_p (difference between two forward and reverse peak potentials) of 230 mV at a scan rate of 100mV/sec is observed. Ideally, the ΔE_p for a reversible redox system such as ferrocyanide / ferricyanide should be 59 mV and is independent of scan rate. The value being high in the case of bulk micromachined device may be attributed to the surface roughness and possible surface modification of the working electrode. The roughness also changes the mass transport characteristics of the analyte present in the bulk of the solution.

The voltammogram of $K_3Fe(CN)_6$ / $K_4Fe(CN)_6$ on a surface micromachined device with a working electrode area of 1400 μm^2 is shown in figure 8. A reversible redox behavior is observed with a ΔE_p of 60 mV. This is close to the expected value for a reversible redox couple at 25° C. The surface micromachined device thus results in working electrodes that are close to ideal surfaces for reversible redox electrochemistry. Additional experiments using other redox probes and biomolecules are being carried out.

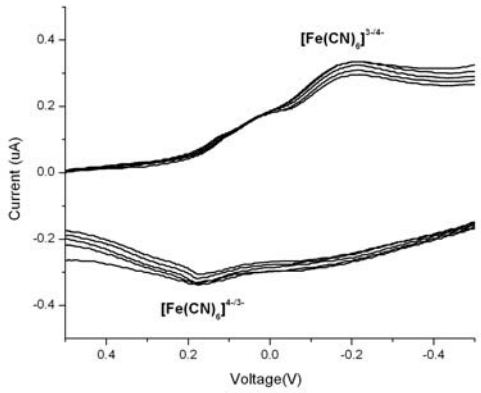


Figure 7. Voltammogram of 1 mM each of ferrocyanide ($Fe(CN)_6^{4-}$) / ferricyanide ($Fe(CN)_6^{3-}$) redox couple on the bulk micromachined Electrochemical cell.

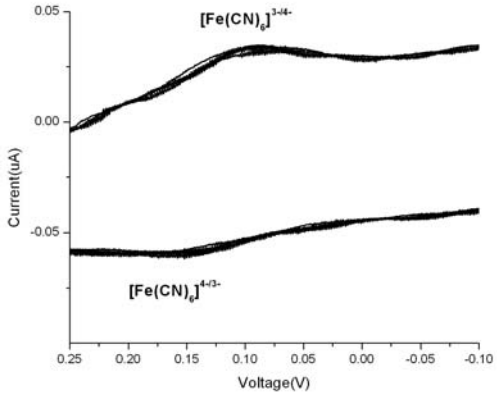


Figure 8. Voltammogram of 1mM each of ferrocyanide ($Fe(CN)_6^{4-}$) and ferricyanide ($Fe(CN)_6^{3-}$) redox couple on the surface micromachined Electrochemical cell.

6. CONCLUSIONS

Two types of Micromachined Electrochemical cell platforms are fabricated using silicon micromachining technology. These platforms are compared in terms of its fabrication complexity and electrochemical compatibility. Surface micromachined device is easy to fabricate and shows better results and reproducibility in terms of electrochemical measurements than the bulk micromachined device.

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