3-D Electrode Configuration for Electrochemical Impedance Spectroscopy of Bulk Solution

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ABSTRACT

In this paper, a 3-D electrode configuration for electrochemical impedance spectroscopy (EIS) of a bulk solution was studied. Top- and bottom- electrode configuration, where two electrodes sandwich the sensing channel, was fabricated using the tearing the patterns from the PDMS (Polydimethylsiloxane) stamp to glass substrate approach [1] and implementation of glass via. Impedance of fabricated glass via was evaluated from 40 Hz to 110 MHz using the impedance analyzer. Measured impedance ranges from 0.3 Ω at 40 Hz to 79.0 Ω at 110 MHz, which was feasible in electrochemical impedance spectroscopy. The tearing of the patterns from the PDMS (Polydimethylsiloxane) stamp is also shown to be an effective fabrication method for microfluidic channels for top- and bottom- electrodes. The device with a 100 μm height sensing channel was studied with DI water and KCL (concentration of 10^{-3}, 10^{-2}, 10^{-1} M) for verifying the sensing performance.

Keywords: microfluidics, electrochemical impedance spectroscopy, electrode configuration

1 INTRODUCTION

One of the most widely used evaluation methods of the biomolecular and cellular analysis is electrochemical impedance spectroscopy (EIS) because of its label free, non-invasive and high throughput features. The setup of electrode configuration is one of the keys for determining the sensitivity of a device . A previous study [2] showed that top- and bottom- electrodes have a high detection sensitivity ($9.18\text{-}10^{-7}$ Ω^{-1} (cells/L)) compared to co-planar electrode designs. One of the possible reasons is that top-bottom- electrodes have a uniform electric field across the sensing [3]. However, few papers were reported because of the difficulty in the fabrication process including the creation of the microfluidic channel membrane and establishing contact to the embedded electrode. In order to overcome these challenges, tearing the patterns from the PDMS stamp to glass substrate approach [1] and glass via were implemented (Fig. 1).

2 THEORETICAL MODEL AND SIMULATION

There are several equivalent electrical circuits that have been proposed [4-6]. One of the simplified models [4, 5] is shown in Fig.1. Using complex permittivity of the medium,

$$\tilde{\varepsilon} = \varepsilon - j\frac{\sigma}{\omega} \quad (1)$$

the impedance of the medium can be written as [4, 5]

$$\widetilde{Z_m} = \frac{1}{j\omega\widetilde{C_m}} \quad (2)$$

where $\tilde{\varepsilon}$ is the complex permittivity, ε is the permittivity, j is the imaginary unit, σ is the conductivity, ω is the angular frequency, $\widetilde{Z_m}$ is the impedance of the medium and $\widetilde{C_m}$ is the capacitance of the medium.

At low frequencies, current flow is blocked by the double layer capacitor, which dominates the impedance amplitude. As the frequency increases, in the frequency range from 1 kHz to 100 kHz, the capacitor turns to be shor-ciruited and medium resistance become dominant. At high frequencies, medium capacitance and parastic capacitances are dominant in the electric circuit. A numerical simulation was performed using MATLAB (Mathworks Inc., Natick, USA) to theoretically study the impedance amplitude and phase response in the top- and bottom- electrode configuration proposed.

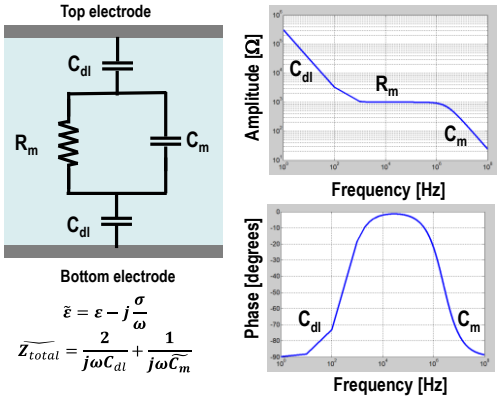

Fig. 1. (a) Simplified equivalent circuit for top bottom electrode in aqueous solution. C_{dl}; double layer capacitance, R_m; medium resistance, C_m; medium capacitance, (b) numerical simulation for impedance amplitude and phase using model (a).

3 DEVICE FABRICATION

The fabrication process is summarised in Fig. 2. The device was fabricated using photolithography and soft-lithography. Additionally, tearing the patterns from the PDMS stamp to glass substrate approach and the implementation of glass via are introduced for fabricating the top- bottom- electrode.

In order to fabricate the glass via, 1 mm diameter holes were mechanically drilled into the slide glasses using diamond drill bit (Fig.2 a). After washing out the dust, a metal was patterned with photolithography using SU-8 negative photoresist (SU-8 2010, Micro-Chem Corp., Newton, MA, USA) (Fig.2 b) following sputtering onto the front and back side, which allows contact embedded electrode from backside of glass slide via following lift-off process (Fig.2 c). Then, uncured PDMS was poured to seal the glass hole (Fig.2 d). Here, PDMS materials were made using pre-polymer and curing agent (Sylgard 184, Dow Corning Co., Midland, MI, USA) with the mixing ratio of 10:1. The mixture of the pre-polymer and the curing agent was poured into the hole and cured at 100 °C for 15 min.

In order to fabricate a sensing channel, an oxygen plasma bonded PDMS slab was teared off from the glass slide. Oxygen plasma treatment allows a permanant bond between PDMS and glass. By tearing off the bonded PDMS from the glass, a pattern can form on the glass. This residue served as a sensing channel wall (Fig. 2). In detail, first off, Si mold was fabricated using traditional photolithography process. (Fig. 2 a'). The 100-µm-thick master mold was fabricated with photolithography using SU-8 2050, a negative photoresist following treating the surface with hexamethyldisilazane (Sigma Aldrich, Saint Louis, MO, USA) in a vacuum chamber for 1 h to allow for the PDMS stamp to be peeled off from the mold. Next, uncured PDMS (mixing ratio of base polymer:curing agent = 15:1) was poured on the mold and cured at 100 ºC for 15 minutes following peeling off. (Fig. 2 b'). As described in the paper [1], the stiffness of the PDMS stamp can be controlled by adjusting the mixing ratio between the base polymer and the curing agent. Lower ratios of the curing agent lead to the decreased stiffness and hardness of the PDMS, mainly caused by a decrease in cross-linking at the low cross-linking density. Therefore, the transfer rate can be increased using lower cross-linking desity since the PDMS can be easily elongated.

Then the PDMS slab was bonded irreversibly on to glass substrates by oxygen plasma treatment using plasma cleaner PDC-32G (Harrick Plasma, Ithaca, NY, USA) at power of 18 W (Fig. 2 e). Then the PDMS was lifted from the bottom glass substrate which leaves PDMS channel wall on the substrate (Fig. 2 f). Finally, the top glass electrode and bottom chip were bonded using oxygen plasma treatment (Fig. 2 g).

The final device picture is shown in Fig. 3. As shown in the Fig. 3 (d), PDMS cylindrical posts [7] were transferred on the substrate with microfluidics channel wall using PDMS stamp, which is for protecting channel wall torn out from substrate.

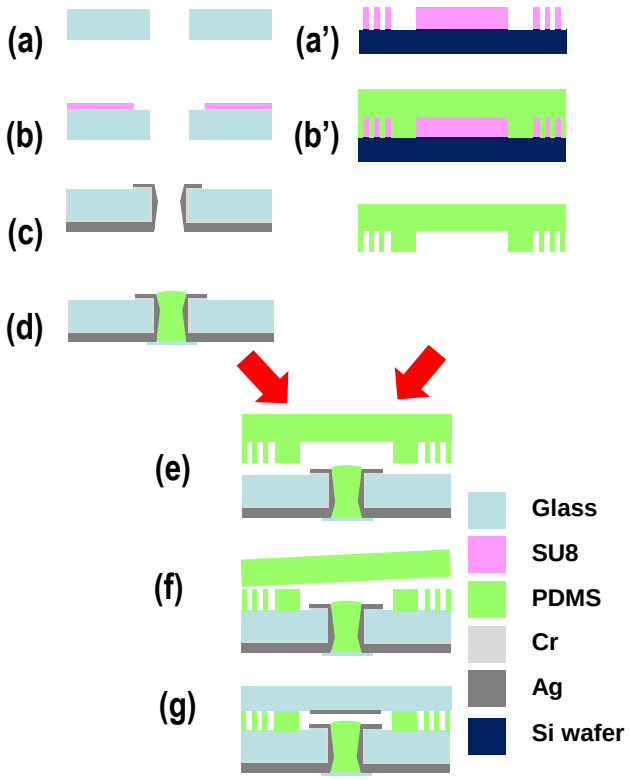

Fig. 2. Fabrication process of the device. (a) Mechanically drill 1mm hole diameter in glass slide (b) Photolithography and patterning photoresist (c) Sputter metal (Cr 10 nm/Ag 300 nm) on front side and (Ag 700nm) for back side and lift-off. (d) Pour uncured PDMS (mixing ratio 10:1) on coverslip and cured at 100 ºC for 15 minutes. (a') Photolithography and SU-8 pattering on Si wafer. (b') Injection mold using PDMS (mixing ratio 15:1) (e) Oxygen plasma bonding (f) Tear off PDMS slabs from substrate resulted in PDMS thin membrane, which serves as a microfluidics channel wall. (g) Bonding top glass electrode with PDMS using oxygen plasma treatment.

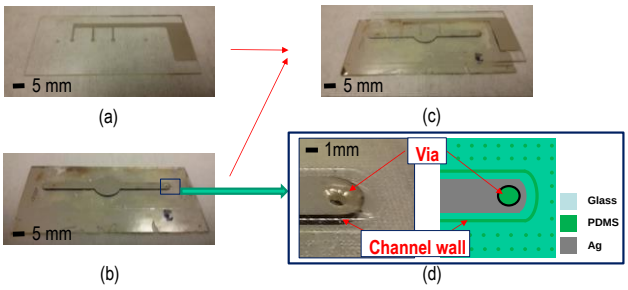

Fig. 3. Photographs of the (a) top electrode (b) bottom electrode with microfluidics channel made by PDMS membrane and glass via for accessing embedded electrode. (c) Entire device (d) magnified view of glass via and a microfluidics channel wall

4 RESULTS AND DISCUSSION

Evaluation of the glass via was conducted using an impedance analyzer (High precision impedance analyzer, 4294 A Agilent) with two terminal method, probe 42941A. The measured frequency range was from 40 Hz to 110 MHz, with a 20 mV AC signal. The fabricated glass via was evaluated by measuring the impedance from electrode on the front of the glass to the back of it, as indicated in the inset of Fig. 3. As shown in Fig. 3, measured impedance ranges from 0.3 Ω at 40 Hz to 79.0 Ω at 110 MHz, which was feasible in electrochemical impedance spectroscopy. At frequency higher than 100 kHz, impedance increased. This can be attributed to the capacitance increase as shown in the phase response data. Possible reasons are the self inductance and parasitic capacitance of the electrode and measuring environment. Next, impedance amplitude and phase for electrolyte solution were measured. The measurement results are shown in Fig. 5. For DI water in the low frequency (below 1 kHz), double layer capacitance is dominant, while in the frequency range from 1 kHz to 100 kHz, impedance amplitudes are stable which indicates solution resistance. Above 100 kHz, dielectric capacitance of the solution becomes dominant. In the very high frequency region > 100 MHz, impedance amplitude becomes the same order as metal, resulting in the same behavior with the glass via. Finally, linearity of solution resistance was studied against electrolyte concentration. As shown in Fig 6, the impedance amplitude response to the change in KCL concentration from 1 mM to 0.1 M showedlinearity, thus verifying the feasibility of fabricated electrode.

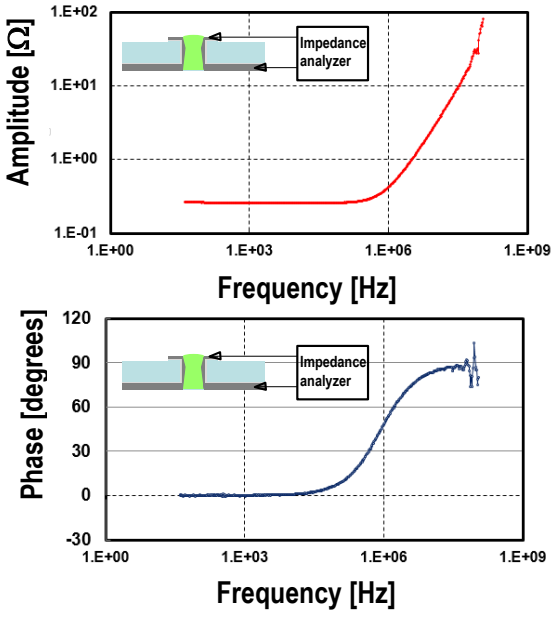

Fig. 4. Impedance amplitude and phase response of fabricated glass via. At frequencies higher than 100 kHz, impedance increased as well as the phase.

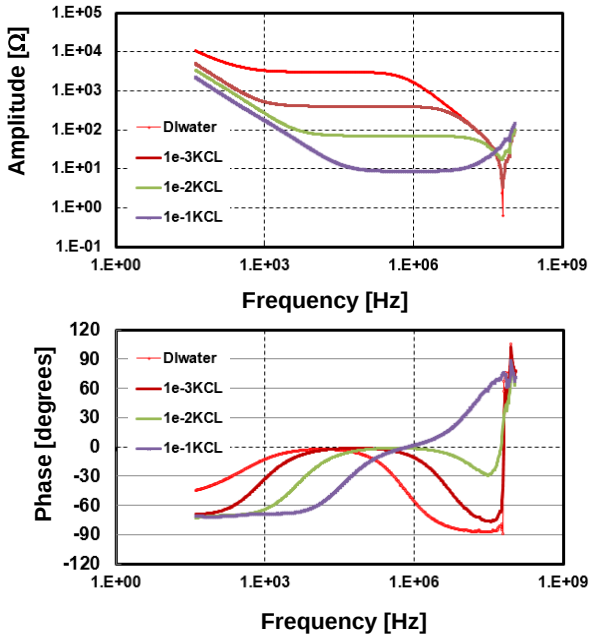

Fig. 5. Electrochemical impedance spectroscopy, in terms of amplitude and frequency response of the fabricated top-bottom electrode under KCL electrolyte varying concentrations.

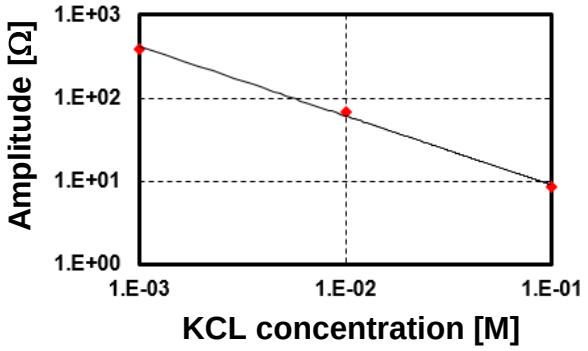

Fig. 6. Solution resistances, which are the stable resistances from 100 kHz to 1 MHz dependence on KCL electrolyte medium with 10^{-3} to 10^{-1}M concentration.

5 CONCLUSION

In this paper, a 3-D electrode configuration for electrochemical impedance spectroscopy (EIS) of a bulk solution was studied. Top- and bottom- electrode configuration, where two electrodes sandwich the sensing channel, was fabricated by PDMS stamp and implementation of glass via. Impedance amplitude of fabricated glass via ranges from 0.3 Ω at 40 Hz to 79.0 Ω at 110 MHz, which was feasible in electrochemical impedance spectroscopy, which was feasible in electrochemical

impedance spectroscopy. The tearing of the patterns from the PDMS (Polydimethylsiloxane) stamp is also shown to be an effective fabrication method for creating the microfluidic channel for the top- and bottom- electrode device. The device with 100 μm height sensing channel was studied with DI water and KCL (concentration of 10^{-3}, 10^{-2}, 10^{-1} M) for characterizing and verifying the sensing performance. Downscaling the sensing area and sensitivity study using the cells should be left as future studies.

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