Microfabrication of a Polymer Based Bi-Conductive Membrane for a Polymer Electrolyte Membrane Fuel Cell

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Abstract. This paper reports a novel fabrication process of a high active area ratio bi-conductive membrane for PEMFCs. The fabricated device is a 50µm thick flexible polyimide based membrane that integrates for the first time lateral electrical conductive layers on both sides with a through ionic conductive path. With the use of thermo-conductive rubber as a bonding agent allowing a quick-flip process, five configurations of double-sided multilayer metal sputtering on polyimide were tested. An approach for filling through pores in the membrane with the ionic conductor (Nafion) with a temporary reservoir was also developed. The development of these new processes allowed to fabricate a membrane with 50µm wide holes filled with ionic conductor with double-sided electrical conductive layers.

1. Introduction
Polymer electrolyte fuel cells (PEMFCs) benefit of potential advantages compared to lithium batteries to power small portable devices. In addition to their ability to deliver simultaneously high energy and power densities, PEMFCs provide power as long as they are supplied by reactants. At small scales however, packaging and peripheral components tend to dominate the size, being significantly larger than the fuel cell stack itself.

Recently, some efforts have been made to replace the bulky bipolar plates of the fuel cell system using microfabrication approaches to pattern silicon or polymer substrates [1-5]. While this approach reduces substantially the volume of the system, swelling of the membrane induces stresses on surrounding materials or generate delamination of the catalyst membrane. To bypass these issues, Esquivel et al. integrated directly ionic conductive material in the microfabrication process [6], but hot pressing assembly steps were required. To remove assembly steps, current collectors can be integrated directly to the ionic conductive membrane with a support material. Photosensitive glass and polymer [7-9] have been successfully used as a substrate but the active area in these designs covered only very small portion of total surface of the device. Large patterns etched in SOI wafers filled with Nafion and with peripheral sputtered gold used as current collectors were used by Zhu et al. [10] to obtained reasonable power density. In this case, reducing the pattern size could reduce electrical and ionic losses significantly.

To contribute to the effort of minimizing low power PEMFCs, a novel fabrication process of a flexible polyimide based bi-conductive membrane that integrates for the first time a lateral electrical conductive layers on both sides with a through ionic conductive path is presented (Figure 1). The device aims to integrate, on the same polymer sheet; mechanical support, ionic conduction and current collection while keeping low ionic and electrical resistance and high active area ratio. The
The proposed membrane consists of a square 1 cm$^2$ and 50 µm thick patterned polyimide sheet (Kapton 200HN, Dupont®) between two electrically conductive 300nm thick gold layers. Holes in the polymer layer are plasma etched and filled with an ionic conductive polymer, Nafion (Dupont®). Dimensions have been selected in order to reduce ionic and electrical resistivity while easing fabrication. This design brings down the total thickness of the cell from millimetres to tens of microns. On the other hand, this important gain in volume brings up important fabrication challenges concerning metallic deposition on polyimide and Nafion filling of the holes.

![Figure 1 - Isometric cut view of the polymer-based bi-conductive membrane](image)

In this work, we report the fabrication techniques that have been used to achieve the desired configuration. Double-sided multilayer metal sputtering on polyimide and Nafion filling are discussed in more depth.

2. Fabrication process & challenges

The fabrication process of the bi-conductive membrane is shown in figure 2. It consists of three critical steps; metal sputtering, metal and polyimide etching, and Nafion filling.

2.1. Metal double-sided multilayer sputtering on polyimide

The process starts with a 400µm thick silicon wafer that is used as a mechanical support for the subsequent steps. A thermo-conductive adhesive rubber (λgel COH-4000 by Taica®) is laid on the silicon substrate (Figure 2a) and a Kapton 200HN 50µm thick sheet is fixed on top of the gel with a bearing roller to eliminate trapped air bubbles (Figure 2b). Gold (300 nm) and then titanium (100 nm) are sputtered on the Kapton top surface (Figure 2c). The gold layer acts as a current collector in the final device while the Ti layer is used as an etching mask for the plasma etching process. After the first sputtering step, the metalized Kapton sheet is peeled off of the λgel with tweezers (Figure 2d). The sheet is turned and bonded again on the same λgel layer (Figure 2e). The sputtering process is then repeated on the second side with the same conditions as before (Figure 2f).

A variety of techniques has been developed for a single side metallic layers deposition on polyimide [11, 12], however due to the low thermal conductivity and flexibility of the polyimide film, thermal management and fixing issues appear during the double-sided deposition process. Also, Au/Ti combination has been chosen in the final device, but other configurations have been tested as conductive/protective layers.

2.1.1. Fixing polyimide on a solid substrate and thermal management

The developed quick-flip approach using λgel lowers thermal resistance between the sample and the substrate compared to tape or photoresist bonding. The risk of sample overheating leading to damaged polyimide or alloy formation between the metal layers is thereby considerably reduced. Indeed, all samples that have been set with tape or photoresist were damage by heat generated by the sputtering process. Moreover, the bonding force between λgel and polyimide is strong enough to withstand a sputtering or evaporation process but the layers can be easily peeled and bond again on the other side for another deposition without cleaning since the λgel doesn’t leave any residue on the Kapton sheet. This quick-flip process reduces greatly the handling time between two depositions.
2.1.2. Multilayer metal sputtering configuration

The \( \lambda \text{gel} \) quick-flip approach was used to test five metal layer configurations (Table 1). These metal layers were sputtered on 2cm x 2cm polyimide sheets in argon plasma at 0.5 Pa with no temperature control. The resulting metalized polyimide samples were evaluated under three criteria.

| Metal Integrity | Polyimide Integrity | Adhesion between Metal and Polyimide |
|-----------------|---------------------|-------------------------------------|
| Cr/Au/Cr/Au     | Good                | Good                                |
| Cr/Au/Al        | Alloy formation     | N.D.                                |
| Au/Al           | Alloy formation     | N.D.                                |
| Cr/Au/Ti        | Good                | Good                                |
| Au/Ti           | Good                | Passable                            |

Thickness (µm): Cr: 60, Au: 300, Al: 400, Ti: 100
Deposition rate (nm/min): Cr: 20, Au: 60, Al: 30, Ti: 15

Figure 2 - Fabrication process of the membrane
First, metal layers integrity was verified by patterning each layer with its corresponding etchant. Unlike other samples, those containing Al formed an alloy, and were not possible to etch. Secondly, etching rate was measured to confirm the integrity of the polyimide, since heat damaged polyimide etches much faster than normal in O₂ plasma. All the samples were etched normally, which means the polyimide was not damaged by the sputtering process. Finally, adhesion between the metal layers and the polyimide was verified. An adhesion layer (Cr) increases the bond strength between metal and polyimide, but is not essential. In rare cases only, for Au/Ti samples, part of the metal layers peeled off during the etching and cleaning steps. Nevertheless Au/Ti combination was considered as the best choice since Cr etchant would damage Ti layer during etching.

2.2. Metal and Polyimide etching
After the sputtering steps, metal layers and polyimide must be etched (Figure 2g). The top metallic layers are patterned using a 4µm thick layer of photoresist (OFPR-800, Tokyo Ohka Kogyo Co., Ltd.) as an etching mask, giving 50µm squares holes spaced by 50µm large of metalized polyimide. Titanium is first etched with a diluted HF solution (49%) for approximately 20s and gold with Aurum-302 (Kanto Chemical Co., Inc.) for 10 minutes. The titanium layer is then used as masking layers for the 50µm deep polyimide etch by RIE (O₂ plasma, 120W RF power, 80sccm, 60min) giving etch angle near 90°. This good etch profile suggests that the walls could be reduced between holes, thus increasing the active surface of the membrane. Once the polyimide layer is etched through, the bottom gold layer is exposed and must be etched. Therefore, it is essential that the top Ti layer resists well to the RIE step to protect the top gold layer. The bottom Ti layer will remain to avoid bonding between Nafion and λgel, and will only be etched at the end of the process.

2.3. Nafion filling and etching
After etching, the 50µm wide holes are filled with Nafion. Esquivel et al. [6] reported filling of 250µm wide holes in a polymer substrate using a liquid solution of Nafion with a permanent reservoir to maintain the solution. In this work, the reservoir had to be removed after the filling process to expose the metallic conductive layer. A new technique has therefore been developed using a temporary reservoir.

A 3mm thick reservoir patterned in λgel is bonded to the sample (Figure 2h). The reservoir is then filled with Nafion in liquid solution (Liquion 10%wt, Ion Power) and dried at 60°C for 30min and 15min at 110°C (Figure 2i). The λgel reservoir is then peeled off (Figure 2j). Another step of RIE is required to etch Nafion that overflowed to expose the metallic layer underneath (Figure 2k). The RIE conditions are the same as the polyimide etch, but the time varies between 1 and 10 minutes depending on the thickness of the Nafion film to be removed. With this technique, holes are completely filled with Nafion, while the gold layers are exposed allowing electrical and ionic connection with the future carbon electrodes. The membrane is then peeled off from the λgel (Figure 2l) and is quickly dipped in a HF diluted solution (49%) to etch the remaining Ti (Figure 2m). A SEM image of the resulting membrane is shown at figure 3. An easy to handle bi-conductive membrane is then obtained and is ready to be integrated in a PEMFC.

Figure 3 - SEM picture of the resulting membrane at the end of the fabrication process.
3. Conclusion
Double-sided multilayer metal deposition was achieved on polyimide sheet to provide lateral electrical conduction directly on an ionic conductive membrane for a PEMFC. With the use of λgel as a bonding agent between polyimide and a solid substrate, thermal management and fixing issues have been bypassed and three configurations of double-sided multilayer metal sputtering were achieved successfully. A novel approach using a temporary λgel reservoir to completely fill the holes with Nafion has been developed. These processes allowed the microfabrication of high active area ratio bi-conductive membrane for PEMFCs. Techniques developed here can also enable the fabrication of a variety of polymer-MEMS with through substrate vias and composite polymer structures.

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