FABRICATION AND TESTING OF A NOVEL ALL-DIAMOND NEURAL PROBE FOR CHEMICAL DETECTION AND ELECTRICAL SENSING APPLICATIONS

H.-Y. Chan¹, D. M. Aslam¹, S. H. Wang¹, G. M. Swain¹ and K. D. Wise²

¹Michigan State University, East Lansing, Michigan, USA
²University of Michigan, Ann Arbor, Michigan, USA

ABSTRACT

Fabrication and testing of all-diamond probes for neural applications is reported for the first time. Instead of commonly used silicon, undoped polycrystalline diamond (poly-C) with resistivity of ~10⁷ Ωcm was chosen as the structural material of the probe. In addition, highly boron-doped (resistivity of ~10³ Ωcm) poly-C film was used as the electrode material due to its excellent electrochemical properties and resistance to chemical attack. The diamond probe consists of 8 electrode sites with diameters ranging from 20 to 150 µm. The measured electrochemical potential window of the poly-C electrode was approximately -0.8 to 1.4 V in 1M KCl. Initial measurements of electrochemical detection of a neurotransmitter called norepinephrine (NE) are very encouraging.

1. INTRODUCTION

One of the key components in neural prosthetic systems is the microelectrode, which interfaces with neural cells for both signal recording and simulation. Microelectrodes can be as simple as thin metal wires coated with insulating materials [1]. With the development of Micro-Electro-Mechanical Systems (MEMS) technology, multiple microelectrodes can be fabricated on microprobes. In recent decades, silicon based microprobes, with microelectrodes made of materials including black platinum, gold, iridium or glassy carbon, have been used in neural activity studies [2][3][4][5], cochlear implants [6][7] and electroanalysis [8]. However, silicon probes are easily broken due to their low flexibility. In addition, they require passivation before any in vivo implantation and thus, are often coated with flexible and biocompatible materials for better performance [9].

An alternative material is diamond. The presence of unique sp³ C-C bonds in the diamond lattice leads to its unique mechanical (large Young’s modulus, ~10¹¹ Pa), chemical (chemical inertness), electrochemical (wide chemical potential window, ~3 V), optical (band gap of 5.5 eV) and thermal (highest thermal conductivity at 300 K ~10³ W/mK) properties not matched by any other known materials. Consequently, diamond becomes a unique material for a number of applications including MEMS and wireless microsystems, especially at high temperatures and in harsh environments. However, the difficulty in forming the sp³ C-C bonds, which results in low growth rate (0.1 to 0.15 µm) of chemical vapor deposition (CVD) of diamond, is causing a delay in the development of a reliable and economical diamond micro-fabrication technology that is compatible with conventional microsystems/MEMS technologies.

Due to a unique combination of diamond’s properties, diamond electrodes are expected to be superior for chemical detection and electrical sensing in biological environments. In particular, boron-doped diamond is found to have a comparatively wide electrochemical potential window in aqueous media, resistance to fouling, low background current and good biocompatibility [10][11]. Recently, boron-doped diamond electrodes, reported for in vitro neural studies [12][13], were fabricated through diamond growth on the tip areas of thin metal wires, which have limited spatial resolution.

In this paper, by combining Si micromachining and diamond thin film technologies, all-diamond probes have been designed, fabricated and tested for the first time. The focus of current work is to develop the all-diamond probes for chemical detection (where conductive diamond has a wide potential window) and electrical sensing in biological environments (where diamond chemical inertness is advantageous). For such measurements, neural probes having precisely positioned arrays of electrodes with micrometer and nanometer dimensions are needed. Such probes may also make it possible to detect multiple chemical and electrical signals with a single probe.

2. THIN FILM DIAMOND GROWTH AND MICROMACHINING TECHNOLOGIES

Diamond stack growth

The Microwave Plasma Chemical Vapor Deposition (MPCVD) growth of poly-C films requires a pretreatment step to generate seeds (or nuclei) on a silicon substrate. The seeding is done by spinning diamond powder loaded water (DW, 0.5%) from Advanced Abrasives Corporation, which can achieve a uniform and nondestructive seeding [7]. DW was applied to the substrate with a 500 rpm pre-spin for 10 sec and followed by 2000 rpm for 30 sec which can provide a uniform seeding density over the entire sample. Then, two layers of diamond films (undoped/doped diamond stack) were grown on the substrate in a single run using the parameters listed in Table 1. The substrate was heated by the hydrogen/methane plasma, which was generated by a 2.45 GHz, 5 kW Sairem™ microwave power supply, and its temperature was monitored by an OMEGA pyrometer. Hydrogen diluted trimethylboron (B(OCH₃)₃, TMB) gas was introduced in-situ for boron doping to achieve different resistivities. The Scanning Electron Microscope (SEM) pictures of a poly-C electrode and its Raman spectrum are shown in Figure 1.
### Table 1: Conditions for diamond growth using MPCVD.

<table>
<thead>
<tr>
<th>Parameter(s)</th>
<th>Value(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Growth Temperature</td>
<td>750°C</td>
</tr>
<tr>
<td>Pressure</td>
<td>40Torr</td>
</tr>
<tr>
<td>Gases</td>
<td>Methane (CH₄): 1.5sccm; Hydrogen (H₂): 100sccm</td>
</tr>
<tr>
<td>In situ doping (highly doped poly-C films)</td>
<td>Hydrogen diluted trimethylboron (TMB): 10sccm</td>
</tr>
<tr>
<td>Microwave power</td>
<td>2.3kW</td>
</tr>
<tr>
<td>Growth rate</td>
<td>0.1 to 0.15 µm/hr</td>
</tr>
</tbody>
</table>

Diamond dry etching

The patterning of poly-C films was achieved using a dry etching method which results in very small feature sizes, sharp edges and clean structures. A Plasmatherm 790 reactive ion etching (RIE) system was used with 300W RF power, SF₆/O₂ (1/30 sccm) gases and an 80 mTorr chamber pressure. Aluminum was used as the masking material for etching. The etch rate of the poly-C films was ~1.2 µm/hr. The presence of fluoride attacks the surfaces of Si and SiO₂ once the diamond thin film was etched, which results in a very rough etched surface and affects the remainder of the process. However, if there were no fluoride present, micro columns would be formed [14]. Therefore, the etching of diamond thin films involves 2 steps. First, diamond is etched in the presence of SF₆ until a very thin diamond film is left on the surface. Then, SF₆ is removed at the final stage of etching and the rest of the etching is done in pure oxygen. This process leads smooth Si and SiO₂ surfaces.

The etching of the undoped/highly doped poly-C stack was monitored by measuring the resistivity of the etched surface and the step height of the patterns. Typically, the resistivity of the undoped surface is around 10⁵ Ωcm. As the resistivity reaches this high value, the doped diamond has been etched.

3. DESIGN AND FABRICATION

The all-diamond probes, with eight highly doped poly-C electrodes (with diameters ranging from 20 to 150 µm), were fabricated using a six-mask process shown in Figure 2.

![Fabrication process of all-diamond probes](image)

Figure 2: Fabrication process of all-diamond probes: (a) creation of highly boron-doped silicon region (10µm thick) followed by growth of 2µm thermal oxide, (b) growth of 3µm undoped and 1µm doped poly-C film, (c) poly-C film patterning using RIE, (d) PECVD oxide deposition (1µm) and patterning for top insulation, (e) patterning of Ti/Au (30nm/300nm) contact pads, (f) probe released by ethylenediamine pyrocatecol etching.

The fabrication process started with a bare n-type silicon wafer. A layer of 1.2 µm thermal oxide was grown on top of the wafer as an intermediate step for patterning the highly boron doped Si areas, which are the back ends of the diamond probes. As undoped poly-C growth directly on boron-doped Si makes the film conductive due to boron out diffusion (during diamond growth) from Si and incorporation in poly-C, a layer of silicon dioxide (SiO₂) was used to seal the boron out diffusion. It is found that the difference in the resistivities of poly-C films on Si substrate with and without SiO₂ protection can be 2 orders in magnitude. Therefore, SiO₂ is an essential layer for diamond growth on a boron-doped silicon substrate (Figure 2a). Next, undoped (3 µm) and doped (1 µm) poly-C films were grown using the method mentioned in the previous section with resistivities of ~10⁵ Ωcm and ~10³ Ωcm, respectively (Figure 2b). Aluminum (700 nm) was used as the mask for etching as mentioned above (Figure 2c). It was etched by Aluminum Etch Type A solution. The undoped poly-C film served as the substrate for the probe, while the doped poly-C film was used as electrodes and interconnects.

Then, a 1.4 µm SiO₂ layer was deposited using GSI plasma enhanced chemical vapor deposition (PECVD). This layer was patterned and etched using buffered oxide solution in order to expose the contact pads located on the back end and the poly-C electrodes (Figure 2d). A layer of titanium/gold (50 nm/300 nm) was then, deposited and patterned as the contact pads (Figure 2e). Finally, the Si substrate was thinned by HF-nitric (HNA) down to 200 µm and the probes were released by the
Electrochemical properties of diamond electrodes

For the purpose of potential applications in neural signal recording and stimulation, the impedance spectrum of the poly-C circular electrodes with diameters of 20 µm with diamond interconnects was measured. This measurement was performed in saline solution (900 mg NaCl: 1000 ml DI H2O) and a platinum wire acted as the counter electrode. The corresponding impedance and phase spectra are shown in Figure 5 and its inset. It is found that the impedance is ~1.5 MΩ at 1 kHz which is the typical frequency of the neural signals. This impedance is comparable to those of needle electrodes suitable for neural signal recording [3].

Electrochemical properties of diamond electrodes

Cyclic voltammograms (CV) were done to characterize the electrochemical properties of the poly-C electrodes. A potentiostat (CH650C from CH instrument) with a three electrode configuration and a Faraday cage were used in the experiment for minimizing the surrounding noise. The CV done on the probe, as shown in Figure 6, reveals a potential window of -0.8V to 1.4 V in 1M potassium chloride (KCl). It is comparable with data reported in [13], which indicate a high overpotential for oxygen and hydrogen evolutions. In other words, there is no oxygen and hydrogen evolution which may interfere the signals from target species undergoing redox reaction within this range. As a result, more species can be detected in this window with reasonable signal to noise ratio. As shown in the figure, the measured background current is ~10^-8 A.

Figure 4: An all-diamond probe was bent in out-of-plane (bending angle was larger than 180°) direction with tweezers.

Figure 3: Released all-diamond probe on US Penny. The highly doped Si backend was removed in this probe.

Figure 5: Impedance spectrum of a 300µm² poly-C electrode (the inset is the corresponding phase spectrum).

Figure 6: Cyclic voltammetric current-voltage curve of the fabricated diamond electrode in 1M KCl. Scan rate was 100 mV/s. The reference and counter electrodes are Ag/AgCl and platinum, respectively.

Electrochemical measurement of NE in Krebs buffer solution has been done and the result is shown in Figure 7. Norepinephrine is one of the neurotransmitters which can be found in the sympathetic nervous system and acts as a stress hormone. Norepinephrine can be detected electrochemically
according to the following $2e^-/2H^+$ redox reaction. The NE is oxidized to form NE-o-quinone.

\[
\text{NE} + 2H^+ + 2e^- \rightarrow \text{NE-o-quinone}
\]

It can be seen in Figure 7 that the oxidizing current starts at 0.2 V which is consistent with data reported in [13]. The difference in the order of magnitude of current is due to size difference of the electrodes. In the same figure, the cyclic voltammogram of the Krebs solution without NE is shown and there is no significant current recorded even as the applied voltage reaches 1 V.

![Figure 7: Cyclic voltammetric current-voltage curves for the diamond probe](image)

Next generation all-diamond probes

The results reported in this paper have focused on the Gen-1 diamond probe. The Gen-2 all-diamond probe, designed and fabricated using an 8 mask process, integrates the working, reference, and counter electrodes on the front end. It also explores the use of different interconnect (e.g., Pt) and insulator (e.g., SiO$_2$) materials. It is expected that the probe cab used for electrical stimulation applications.

5. CONCLUSIONS

For the first time, a novel all-diamond microprobe, with a potential window of -0.8 to 1.4 V, has been successfully fabricated. With the exception of probe backend, which contains Au contact pads and p$^{++}$-Si, the probe front end is all-diamond. The electrical impedance of the electrode is comparable to those of other electrodes reported in the literature. While the electrical signal sensing measurements are in progress, detection of norepinephrine in Krebs solution has been demonstrated.

REFERENCES