Neurochemical sensing with implantable microelectrodes has created multiple research opportunities in the field of neuroscience. The ability to record extracellular biopotentials and detect neurotransmitters with high sensitivity has enabled deeper understanding of brain and nervous system function. Diamond has many advantages over other electrode materials such as good biocompatibility, wide potential window, low double-layer capacitance, long-term stability, resistance to corrosion/fouling, and fabrication flexibility. In this work, we present a micromachined, implantable, all-diamond microfiber capable of reliable, precise neurochemical sensing. The all-diamond fiber consists of a conductive boron-doped polycrystalline diamond (BDD) core encapsulated in layers of insulating polycrystalline diamond (PCD) cladding. The PCD serves as a biocompatible and hermetic package while also acting as a dielectric barrier to prevent signal cross-talking. The all-diamond microelectrodes were thoroughly characterized using topographical and electrochemical methods. The capability for neurotransmitter sensing was completed using dopamine (DA) as the model analyte. Fast-scan cyclic voltammetry (FSCV) of DA was also completed to demonstrate the practicality of in vivo sensing at rapid rates. The fabrication is described in great detail and the capability for batch-scale process is demonstrated. These novel all-diamond microelectrodes have commercial-scale potential, generating a powerful tool for neurochemical analysis.

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Manuscript submitted April 30, 2018; revised manuscript received July 6, 2018. Published July 31, 2018. This paper is part of the JES Focus Issue on the Brain and Electrochemistry Honoring R. Mark Wightman and Christian Amatore.
cross-sectional area that matches the size of neurons, allowing for single-unit recording and NT measurements with high spatiotemporal resolution. The PCD cladding serves as a biocompatible, pinhole-free layer as well as a dielectric barrier to prevent signal cross-talking. The contact pad, which is made out of BDD, can be bonded onto a custom-designed, printed circuit board (PCB) using conductive silver paste for proper electrical connection and mechanical stability. These freestanding, all- diamond µ-fibers differ from the conventional diamond electrodes discussed above as there is no additional support structure/substrate. A wafer-level microfabrication approach is developed for batch production of microfibers with various geometries (single fibers and 2D fiber arrays) and dimensions. The fabrication of these diamond µ-fiber electrodes is described with a detailed electrochemical characterization as well. Dopamine (DA) was used as the target NT analyte; an initial feasibility study using fast scan cyclic voltammetry (FSCV) was completed.

Experimental

Chemicals and materials.—Phosphate buffered saline (PBS) was purchased from Gibco and diluted with deionized (DI) water from 10X (10.6 mM monobasic potassium phosphate, 1551 mM sodium chloride, 29.7 mM dibasic sodium phosphate) to 1X (1.1 mM monobasic potassium phosphate, 155 mM sodium chloride, 3.0 mM dibasic sodium phosphate) for a final pH of 7.4. Potassium ferrocyanide (K₃Fe(CN)₆) and potassium ferricyanide (K₃Fe(CN)₆) were purchased from J.T Baker; Hexaamine-ruthenium(III) chloride (Ru(NH₃)₆Cl₃•H₂O) was purchased from Sigma Aldrich. 50 mM stock solutions were prepared by dissolving the anodic and cathodic reactions (single fibers and 2D fiber arrays) and dimensions. The fabrication of these diamond µ-fiber electrodes is described with a detailed electrochemical characterization as well. Dopamine (DA) was used as the target NT analyte; an initial feasibility study using fast scan cyclic voltammetry (FSCV) was completed.

In the first step, a dual layer of electrically insulating and electrically conductive diamond layers was grown on a 1 mm thick 3-inch-diameter (100) µ-si wafers. Each layer was grown in a dedicated in-house built 2.45 GHz microwave plasma assisted chemical vapor deposition (MPACVD) reactor. Both diamond growth processes had similar growth parameters of 25 Torr pressure, 1.6 kW absorbed microwave power resulting in a deposition temperature of 700°C. Gas flows were set to 1% methane (CH₄) in hydrogen (H₂) balance for high quality MCD growth. Diborane (B₂H₆) was added to the conductive diamond (BDD) growth process in a B/C ratio of 20,000 ppm to achieve sufficient conductivity. The resulting electrically insulating PCD diamond layer was 1.9 μm thick. The electrically conducting BDD layer was 3.7 μm thick and had a resistivity of 1 × 10⁻⁸ Ω·cm.

During the second step the dual layer was etched to what will later on become the individual µ-fibers including fiber shank, contact pad and anchor. Prior to etching, a 1.2 μm thick copper (Cu) hard mask was thermally evaporated. (Edward Auto306 thermal evaporator, Edwards, Inc.). In order to enhance the adhesion between Cu and BDD, a 50 nm thick titanium (Ti) interlayer was thermally evaporated using the same equipment. Diluted Cu etchant (ferric chloride (FeCl₃) solution: DI water = 1:2 (vol/vol)) was used to smoothly pattern the Cu mask, and the Ti layer was later patterned by dry etching. A reactive ion plasma dry etcher (Lambda Technologies) was utilized to etch the masked diamond layers with a gas mixture of 0.8:6.20 sccm SF₆/Ar/O₂. 750 W microwave power and 160 V bias at 15 mTorr. Care was taken not to over etch the Si substrate since a smooth, properly etched Si surface is essential for the third processing step. After plasma etching, the remaining Cu mask was wet etched with the same diluted ferric chloride solution and the Ti layer was removed by buffered oxide etchant (Transene Company, Inc.).

In the third processing step, the final MCD cladding was performed enclosing the µ-fiber. A Ti/Cu mask was applied via a lift-off procedure to selectively mask the top of the contact pads, thereby inhibiting diamond growth during the final growth process. A 50 nm Ti/1.2 μm Cu layer was applied with the same system as listed above. For the final insulating diamond growth, the same MWPA-CVD reactor and process parameters were used as described above. A smooth and relatively undamaged Si surface is critical to allow diamond growth only on the exposed diamond on the wafer. The third and final MCD layer was 1.3 μm thick and electrically insulating as well.

In the fourth and final processing step, the µ-fibers were released from the Si substrate by back etching the µ-fiber. A Ti/Cu mask was applied via a lift-off procedure to mask the top of the contact pads, thereby inhibiting diamond growth during the final growth process. A 50 nm Ti/1.2 μm Cu layer was applied with the same system as listed above. For the final insulating diamond growth, the same MWPA-CVD reactor and process parameters were used as described above. A smooth and relatively undamaged Si surface is critical to allow diamond growth only on the exposed diamond on the wafer. The third and final MCD layer was 1.3 μm thick and electrically insulating as well.

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cleaned using cyclic voltammetry (CV) in 1.0 M H₂SO₄ by cycling the potential from 0.0 V to +2.8 V to −2.4 V before stopping back at 0.0 V. This potential range was swept 30 times at a scan rate of 0.5 V/s. We have found that this provides a clean, reproducible BDD surface before measurements are started.

Results and Discussion

Surface and material characterization.—With the deposition flexibility exhibited by BDD as a material, it is necessary to investigate the electrode surface on a case-by-case basis. Additionally, due to the complex nature of the fabrication process, characterization of both the un-doped PCD cladding and the doped PCD core (BDD) is needed. As such, the BDD μ-fibers were investigated using SEM (described above) and Raman spectroscopy.

Boron-doping effects the film surface morphology as well as the structure and electrochemical properties. Raman spectroscopy is an excellent tool to evaluate diamond films and the spectra of the un-doped polycrystalline diamond (PCD) and boron-doped polycrystalline diamond (BDD) layers on the all-diamond μ-fiber electrodes. Inset shows a released single μ-fiber. (C) Cross-sectional image of the doped-diamond core surrounded by un-doped PCD cladding.

Figure 2. (A) Microfabrication process flow for making the all diamond μ-fibers. 1. Deposition of PCD and BDD thin film layers onto Si substrate; 2. Pattern Cu mask and plasma etching of PCD/BDD layers; 3. Pattern Cu mask and deposition of final PCD layer; 4. Cu removal, device release and fiber cleavage. (B) Scanning electron micrographs of the all-diamond μ-fiber electrodes. Inset shows a released single μ-fiber. (C) Cross-sectional image of the doped-diamond core surrounded by un-doped PCD cladding.

Electrochemical characterization.—Due to the novelty of the all-diamond μ-fiber electrodes, a thorough electrochemical characterization was completed using electrochemical impedance spectroscopy (EIS) and CV. The impedance at 1.0 kHz was found to be 1.3 MΩ (data not shown). This is comparable to CFMEs in literature. Background CV i-E curves were completed in 1.0 M H₂SO₄ and pH 7.4 PBS buffer to determine both the potential window and the double layer capacitance (Cdl); the curves are shown in Figs. 4A and 4B. The potential window was found to be ∼5.0 V in pH 7.4 PBS and ∼4.0 V in 1.0 M H₂SO₄. The wider window in PBS is due to the larger hydrogen overpotential stemming from the increased pH and subsequent lower number of H⁺ available to be reduced to H₂ at the electrode surface. In both media, the BDD μ-fiber indicated featureless background current throughout the potential region of most redox active NTs. The peak ca. +2.25 V in the PBS CV is likely due to oxidation of the PBS itself as this peak is not apparent in the 1.0 M H₂SO₄ scan. The BDD μ-fiber potential window surpasses that of many other electrode materials, both carbon and metal-based. For the measurement of Cdl, the current (A) was measured at 0.0 V in the forward segment of the final CV scan (3 scans total) and plotted against scan rate (V/s); the slope was used to calculate Cdl. Measurements were completed in triplicate. Using this methodology, Cdl was calculated to be ∼11 μF cm⁻², a typical value for diamond electrodes exhibiting low capacitance. Though the BDD μ-fibers are exposed to many different environments throughout the fabrication processes, it is important to note that the tip of the electrode is severed before analysis. This leaves behind a clean, non-contaminated BDD tip.

For further electrochemical characterization of the BDD μ-fibers, the behavior toward several traditional analytes was assessed. This included the ferri/ferrocyanide (Fe(CN)₆³⁻/⁴⁻), hexamine ruthenium (Ru(NH₃)₆³⁺/²⁺), and hexouquinone (HQ) redox couples and the CV i-E curves are shown in Fig. 4C. Excellent steady state response was achieved with each redox couple, indicating that the diffusion layer thickness is larger than the radius of electroactive BDD μ-fiber core (rD < r₀). Contrarily, when the diffusion layer is smaller than the electrode area (r₀ < rD), semi-infinite linear diffusion is observed and voltammetric peaks are seen. As such, the smaller the electrode, the quicker steady-state conditions are achieved. This behavior is described at length by Kissinger, Heineman, Wightman, and Michael.
The electron transfer kinetics toward the Fe(CN)$_{6}^{3-/4-}$ couple (inner sphere electron transfer) is sensitive to the BDD surface morphology. On the other hand, the Ru(NH$_3$)$_6^{2+/3+}$ redox couple is an outer sphere electron transfer reaction and thus, is not as sensitive to the BDD surface. However, as evident in Fig. 4C, excellent steady state current response was achieved for each redox couple. The HQ voltammogram exhibited larger current response but it is important to consider that this is a 2-electron transfer reaction, compared to the 1-electron transfer Fe(CN)$_{6}^{3-/4-}$, Ru(NH$_3$)$_6^{2+/3+}$, and 2.5 mM hydroquinone in pH 7.4 PBS. Reference electrode: Ag/AgCl, counter electrode: BDD disk. Scan rate for (C): 0.1 V/s.

Dopamine fast scan cyclic voltammetry.—To effectively measure DA transients in vivo, measurements must be executed on the milli-second (ms) time scale. This is due to a combination of the neuron firing rate as well as diffusivity of DA into the extracellular space. It is important to note that for any electroanalytical in vivo application, the microelectrode sits in the extracellular space around the target neuron. In FSCV, the background charging current stabilizes after repeated cycling of the electrochemical potential and thus, can be subtracted from the measured faradaic current. This enables the sensing of rapid changes in analyte concentration (NT transients) at the ms scale.

The color plot shown in Fig. 6A shows a time plot of a constant dopamine concentration and the inset shows a time plot of the background prior to addition of DA to the stagnant electrochemical cell. Future work will utilize a flow cell to calibrate the dopamine response of the BDD μ-fiber electrodes. Nonetheless, the color plot shows a solid current response from both the oxidation and reduction peaks for DA, signifying that the BDD μ-fibers exhibit the conductivity needed for neurochemical sensing. The electrode consists of a conductive BDD core with an insulating PCD cladding. During fabrication, the PCD/BDD/PCD layers were patterned and subsequently released from the substrate.

Conclusions

In this paper, we report a novel, all-diamond μ-fiber electrode for neurochemical sensing. The electrode consists of a conductive BDD core with an insulating PCD cladding. During fabrication, the PCD/BDD/PCD layers were patterned and subsequently released from the substrate.
the Si substrate, leaving behind the freestanding μ-fibers. Raman and SEM were completed and a clear distinction between the BDD and PCD layers was observed. The calculated surface area of the conductive BDD core was ~70 μm²; the overall dimensions of the fiber were found to be 6 μm × 25 μm. Prior to analysis, the tip of each fiber was either soldered or pre-conditioned in 1.0 M H₂SO₄ by scanning a wide voltage range with CV (−2.4 V to +3.0 V). The diamond μ-fibers were then evaluated via an electrochemical characterization. In pH 7.4 PBS buffer, the potential window was ~5.0 V and the Cₒₒ was calculated to be 11 μF cm⁻² (using the electrode surface area calculated with SEM). Three redox couples were also studied (Fe(CN)₆³⁻/⁴⁻, Ru(NH₃)₆³⁺/²⁺, and HQ); excellent steady-state conditions were achieved for each suggesting a hemispherical diffusion case, typical for microelectrodes of this size. The μ-fibers were also studied for their ability to execute FSCV of DA. Using a concentration of 20 μM, a "fiber electrode was severed and pre-conditioned in 1.0 M H₂SO₄ −/+ 0.6 nA

The authors gratefully acknowledge Madeline Mackinder for her help testing the BDD μ-fiber electrodes. The authors also acknowledge Dr. Bin Fan and Dr. Lindsay Walton for helpful discussions. The project was internally funded through a collaboration of the Michigan State University-Fraunhofer USA, Inc. Center for Coatings and Diamond Technologies.

Acknowledgment

Emerald Publishing Limited, 2019. DOI: 10.1080/00220221.2019.1578094

Figure 6. Dopamine FSCV in a stagnant electrochemical cell. (A) Color plot from HDCV software, courtesy of the University of North Carolina at Chapel Hill. (B) Individual FSCV i-E curve of DA in pH 7.4 PBS buffer. The FSCV color plot for the PBS buffer background is inlayed in (A). Scan rate - 400 V/s; Reference electrode- Ag/AgCl; [Dopamine]: 20 μM. L. Heien, M. A. Johnson, and R. M. Wightman, ACS Chemical Neuroscience, 8, 221 (2017). M. L. Heien. A. S. Khan, J. L. Ariansen, J. F. Cheer, P. E. Phillips, and R. M. Carelli, Journal of Neural Engineering, 13, 046009 (2015). A. Fujishima, T. N. Rao, E. Popa, B. Sarada, I. Yagi, and D. Tryk, Journal of Electroanalytical Chemistry, 614, 113 (2008). W. Schultz, P. Apicella, and T. Ljungberg, Journal of Neuroscience, 13, 900 (1993). A. Fujishima, T. N. Rao, E. Popa, B. Sarada, I. Yagi, and D. Tryk, Journal of Electroanalytical Chemistry, 473, 179 (1999). A. E. Hess, D. M. Sabens, H. B. Martin, and C. A. Zornam, Journal of Microelectromechanical Systems, 20, 867 (2011). A. L. Sanford, S. W. Morton, K. L. Whitehouse, H. M. Oara, L. Z. Lugo-Morales, J. G. Roberts, and A. Sombers, Analytical Chemistry, 82, 5205 (2010). R. M. Wightman, M. L. Heien, K. M. Wissam, L. A. Sombers, B. J. Aragona, A. S. Khan, J. L. Ariensan, J. F. Cheere, P. E. Phillips, and R. M. Carelli, European Journal of Neuroscience, 26, 2046 (2007). P. R. Patel, K. Na, H. Zhang, T. D. Kozai, N. A. Kotov, E. Yoon, and C. A. Chestek, Journal of Neural Engineering, 12, 046009 (2015). P. R. Patel, 2015. P. R. Patel, H. Zhang, M. T. Robbins, J. B. Nofar, S. P. Marshall, M. J. Kobylarek, T. D. Kozai, N. A. Kotov, and C. A. Chestek, Journal of Neural Engineering, 13, 066002 (2016). H. Varai and J. E. Collazo-Castro, ACS Applied Materials & Interfaces, 7, 27015 (2015). B. D. Bath, D. J. Michael, B. J. Trafford, J. D. Joseph, P. L. Runnels, and R. M. Wightman, Analytical Chemistry, 72, 5994 (2000). M. Ates, J. Castillo, A. S. Sarac, and W. Schuhmann, Microchimica Acta, 160, 247 (2008). B. J. Venton, K. P. Troyer, and R. M. Wightman, Analytical Chemistry, 74, 539 (2002). M. L. Huffman and B. J. Venton, Analyst, 134, 18 (2009). T. H. Yoon, E. J. Hwang, D. Y. Shin, S. I. Park, S. J. Oh, S. C. Jung, H. C. Shin, and S. J. Kim, IEEE Transactions on Biomedical Engineering, 47, 1082 (2000). T. J. Cho, H. W. Baac, and E. Yoon, In Micro Electro Mechanical Systems (MEMS), 2010 IEEE 23rd International Conference on; IEEE, 2010, pp 995. C.-H. Chen, D.-J. Yao, S.-H. Tseng, S.-W. Lü, C.-C. Chiao, and S.-R. Yeh, Biosensors and Bioelectronics, 24, 1911 (2009). F. Wu, E. Stark, M. Jin, J. L. Cho, E. S. Yoon, G. Buzsaki, K. D. Wise, and E. Yoon, Journal of Neural Engineering, 10, 056012 (2013).
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