Published in final edited form as:

Lab Chip. 2017 September 12; 17(18): 3159–3167. doi:10.1039/c7lc00229g.

Large-scale, all polycrystalline diamond structures transferred on flexible Parylene-C films for neurotransmitter sensing

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Abstract

Boron-doped diamond (BDD) has superior electrochemical properties for bioelectronic systems. However, due to its high synthesis temperature, traditional microfabrication methods have limits to integrating BDD with emerging classes of flexible, polymer-based bioelectronic systems. This paper introduces a novel fabrication solution to this challenge, which features (i) a wafer-scale substrate transfer process with all diamond structures transferred onto a flexible Parylene-C substrate and (ii) Parylene anchors introduced to strengthen the bonding between BDD and Parylene substrates, as demonstrated by peeling test. The electrochemical properties of the transferred BDD-polymer electrodes are evaluated using (i) an outer sphere redox couple $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ to study the electron transfer process and (ii) quantitative and qualitative studies of a neurotransmitter redox dopamine/dopamine-o-quinone. A linear response of the BDD sensor to dopamine concentrations of 0.5 μM to 100 μM is observed ($R^2 = 0.999$) with a sensitivity of 0.21 $\mu\text{A}/\text{cm}^2 \cdot \mu\text{M}$. Examples of fabricated diamond-polymer devices suggest a broad application in advanced bioelectronics and optoelectronics.

Introduction

Carbon materials have been the most popular material for electrochemical sensing[1],[2],[3],[4],[5],[6]. Among different carbon materials, boron-doped polycrystalline diamond (BDD) shows great promises in sensing neurotransmitters (NTs) because of its combination of unique properties. For example, BDD has a wide potential window of 2.27–3.3 V in aqueous solutions [7],[8], allowing detection of a wide variety of chemicals. Polished BDD thin films with hydrogen terminated surface demonstrate low double layer capacitance of 2.9–11 $\mu\text{F}/\text{cm}^2$ [9], which leads to lower background current and higher signal-to-noise ratio. The low absorption surface of BDD is extremely resistant to bio-fouling and deactivation, enabling long-term reliability and stability of sensors for chronic applications[7],[10]. Furthermore, the biocompatibility and high thermal conductivity of BDD can prevent cytotoxicity and potential thermal damage[11] to the target tissues surrounding the implants. Our prior study suggests that the diamond heat spreader was able to keep the maximum temperature

variation on a micro-light-emitting diode (μ LED) neural probe within 1.3 °C in the air when the μ LED was driven by 3.4 V, 100mS pulses [11],.

To date, BDD has been widely used for detecting various NTs. In particular, dopamine (DA) contracted from 3,4-dihydroxyphenethylamine is one of the most important NTs associated with many aspects of the neurophysiological processing, such as stress[12], memory[13], and addiction[14]. Abnormal activities of DA storage, release and reuptake are the main cause of several neural disorders in the central nervous system, such as Parkinson's diseases and schizophrenia[14], [15]. Besides, dysregulated DA is found to be an important factor affecting cardiovascular and renal systems [16],[17]. Hence, real-time monitoring of dynamic changes in DA concentration is very important to understand the functionality of the brain and other organs. Unlike other NTs which can be found in most of the neurons in the brain, DA is detected mostly in the striatum with few in number[18]. The concentration of DA upon external electrical stimulation is in the range of 250–500 nM in rat's brain for a single stimulation and up to 4000 nM for multiple stimulations[19], which is several orders of magnitude lower than that of biological interferences, such as ascorbic acid (AA) [20], [5]. This makes *in vivo* DA detection very challenging with commonly used electrodes, such as noble metal electrodes that usually require specific surface treatments[21], [22], [23]. In contrast, untreated BDD enables higher sensitivity DA measurements with fast-scan cyclic voltammetry *in vivo* in the presence of AA[24]. Therefore, BDD has been widely used for DA sensing. For example, BDD coated tungsten rods have been used for *in vivo* DA detection in the corpus striatum of the mouse brain [4] and thalamic targets of the human brain[25].

Despite its many advantages, BDD is a rigid material with Young's module of ~1000 GPa[26], which is several orders of magnitude higher than that of the brain tissues ($\sim 10^3$ to 10^5 Pa[27]). The micromotion-induced strain between rigid implants and surrounding soft tissues has been hypothesized to be the main cause of harmful immune responses and even irreversible tissue damage[28]. Recently, flexible neural implants have been developed [29], [30],[31],[32], in which electrodes and interconnecting traces made of noble metal were constructed on soft polymeric substrates with low Young's moduli, such as polydimethylsiloxane (PDMS) (360–870 KPa[33]), polyimide (2.5 GPa[34]), SU-8 (SU-8 2000, 2.0 GPa[35]) and Parylene (2.8 GPa[36]). Consequently, the overall effective Young's modulus can be significantly reduced to minimize the mechanical mismatches between rigid metal and soft tissues. Unfortunately, unlike noble metal, BDD cannot be deposited directly on a polymer substrate due to its high synthesis temperature (500 – 900 °C[37]) exceeding the glass transition temperatures of polymers. To address this issue, a wafer transfer process is required to transfer BDD patterns from rigid BDD growth substrates, such as silicon, onto flexible polymer substrates. Previously, Hess et al[38] and Bergonzo et al[39] reported a method for making diamond-on-polymer electrodes. In their approaches, diamond was selectively grown and patterned on a silicon dioxide (SiO_2) substrate, and then, transferred onto spin-casted polynorbornene or polyimide by removing the SiO_2 sacrificial layer in 49% Hydrofluoric acid (HF). Whereas such processes allow transferring microscale BDD patterns such as electrodes, macroscale interconnects and contact pads must be fabricated

from metal separately. Additionally, a multi-step HF releasing process is required since polymers and large metal patterns are released faster than the small BDD electrodes[38].

In this paper, we developed an innovative method for wafer-scale transfer of all diamond macro/micro patterns from a diamond growth silicon substrate onto a flexible Parylene-C substrate[40],[41]. Parylene-C is a micromachinable, transparent, flexible, and biocompatible polymer, and has been widely used in making neural implants [42],[43]. As illustrated in Fig. 1, our approach involves three key steps: pre-transfer patterning, substrate transfer, and post-transfer fabrication. During the pre-transfer patterning (Fig 1-I), SiO₂ was deposited onto a silicon wafer as a sacrificial layer followed by BDD synthesis and patterning. After slight over-etching of SiO₂ to create undercuts around the BDD patterns, Parylene-C was conformally coated to form mechanical anchors that can improve the bonding strength between BDD and Parylene. A mesh structure was employed on large patterns to introduce more anchors for further enhancement of the bonding force. For substrate transfer (Fig 1-II), two methods for substrate removal were explored and compared: potassium hydroxide (KOH) etching and deep reactive-ion etching (DRIE). For KOH etching, a special wafer holder including a Teflon jig, KOH resistant O-ring, and chromium-coated C-clamps was designed to expose only the backside of the silicon wafer through the opening of the upper lid, while protecting the frontside to prevent the delamination between BDD and Parylene during the etching. After BDD transfer, a post-transfer fabrication process (Fig. 1-III) was employed where the free-standing BDD-polymer film was attached on a wafer, followed by subsequent micromachining processes to selectively expose the diamond nucleation side for sensing electrodes, electrical interconnect wires, and contacts.

Methodology

Fig. 1 shows a detailed process flow. In the pre-transfer patterning step, (I-a) 1- μ m-thick SiO₂ was deposited on a 3-inch Si wafer using plasma enhanced chemical vapor deposition (PECVD) (PlasmaLab 80plus[®], Oxford Instruments). (I-b) Microcrystalline BDD film was synthesized using a custom-designed 2.45 GHz microwave plasma assisted chemical vapor deposition reactor (MWPACVD) with a gas mixture of hydrogen-diborane and methane (1%) in a hydrogen atmosphere at a temperature of 700 °C, which results in a B-to-C ratio of 20,000 ppm and B-to-H ratio of 200ppm. The as-deposited BDD films initially are hydrogen-terminated. After long-time exposure to air, the surface is gradually converted to a partially oxygen-terminated surface, which is more desired for DA sensing [4],[44]. (I-c) A 1.3- μ m-thick aluminum layer was sputtered as a hard mask for diamond etching (Denton Desk Top Pro Sputtering System, Denton Vacuum, Inc.). (I-d) Aluminum is patterned via ultraviolet (UV) photolithography (ABM, Inc.) and etched using an aluminum etchant (Type A, TRANSENE, Inc.). Then BDD was plasma etched in an electron cyclotron resonance reactive ion etcher (Lambda Technologies, Inc.) using SF₆/Ar/O₂ with a microwave power of 400 W and a radio-frequency (RF) bias of 100 W (150 V). Afterward, the aluminum mask was stripped using the aluminum etchant. (I-e) SiO₂ was over-etched in buffered oxide etchant (BOE) to create undercuts for forming Parylene anchors. (I-f) The wafer was treated with the Silane A174 adhesion promoter (Sigma Aldrich, Inc.), followed by a conformal coating of ~15 μ m Parylene-C (PDS 2010, Specialty Coating System, Inc.).

During the substrate transfer step, Parylene coating on the backside of the Si wafer was first removed in O₂ plasma (PX-250 plasma system, Nordson March, Inc.). For wet etching of silicon (II-a1), the wafer was attached to the jig and etched in the 35% KOH at 70 °C for ~9 hrs. For plasma dry etching of silicon (II-a2), the frontside of the wafer was bonded onto a 4-inch carrier wafer using polyphenyl ether and the backside was completely etched with repetitive SF₆ and C₄F₈ cycles in a DRIE system (SPTS Pegasus 4, SPTS Technologies, Ltd). (II-b) The BDD-Parylene layer was released from the carrier wafer by soaking the wafer in acetone, followed by isopropanol alcohol (IPA) and deionized (DI) water rinses. Afterward, (II-c) the sacrificial SiO₂ was etched completely in BOE.

During the post-transfer fabrication step, (III-a) the wafer-size BDD-Parylene film was attached to a carrier wafer using photoresist. (III-b) Ti/Cu was evaporated (Auto 306, Edward, Inc.) and patterned to form contact pads onto the BDD film. (III-c) and (III-d) Low melting point (LMP) solder (62 °C, 144 ALLOY Field's Metal) was applied onto the contact pads in a hydrochloride (HCl) solution (pH=1) to prevent the oxidation of the solder. (III-e) Discrete active electronics, such as μ LEDs, were self-assembled on the pads. (III-f) After releasing the device from the carrier wafer, flexible wires were soldered onto the pads using LMP as interconnects to testing instruments. Epoxy was applied to strengthen the bonding between the wires and pads. Finally, another 5 μ m Parylene-C was deposited to encapsulate the device with the electrodes being exposed for sensing.

As a proof-of-concept, two different BDD-polymer devices were designed as illustrated in Fig. 2. In particular, a μ LED probe was constructed in order to demonstrate the post-transfer fabrication step and to test the mechanical robustness of flexible BDD patterns during folding and bending. The μ LED probe consisted of two electrodes of 60 μ m in radius for both the anode and cathode. The wires were 2.4 mm long with various widths of 200 μ m and 50 μ m, resulting in different wire resistances (Fig. 2(a)). Fig. 2(b) shows a BDD electrochemical sensor designed in a three-electrode configuration with: a reference electrode (RE), a working electrode (WE), and a counter electrode (CE). The overall dimensions of the sensor were 4×4.7 mm². The effectively exposed BDD areas of WE, CE and RE were around 0.8 mm², 0.48 mm², and 0.48 mm², respectively, calculated by subtracting the areas covered with Parylene anchors (the cross-section view in Fig. 2). To create more Parylene anchors, microholes with dimensions of 30×50 μ m² and center-to-center separation of 50 μ m were uniformly distributed on large BDD patterns, such as contact pads and electrodes.

Results and discussion

Characteristics of the BDD films

The diamond nucleation side, which was originally in contact with the SiO₂/Si substrate, was exposed after the transfer process and served as the sensing surface of electrochemical sensors. A scanning electron microscope (SEM) image (6610V, JEOL Inc.) in Fig. 3(a) shows the smooth surface morphology of the diamond nucleation side, mainly due to the small crystal sizes of BDD. Fig. 3(b) shows the Raman spectrum (532 nm Laser, HORIBA Scientific Inc.) taken from the nucleation side of BDD, where two new bands at ~473 cm⁻¹ and ~1209 cm⁻¹ are related to boron dopants and a small peak at 1305 cm⁻¹ corresponds to

the characteristic diamond band for sp^3 carbon[45]. Compared to the standard diamond band at 1332 cm^{-1} , a 27 cm^{-1} blueshift is observed which may be caused by doping-induced stress in the film. There is a broadband around 1470 cm^{-1} originated from sp^2 bonds or amorphous defects on the diamond nucleation surface. These Raman features are similar to heavily doped BDD thin films with boron doping concentration estimated in the order of 10^{20} cm^{-3} [45]. Table 1 summarizes the film properties including the average surface roughness (Ra) of diamond nucleation side was 10.8 nm measured by an atomic force microscope (AFM) (D3100, VEECO Inc.). The thickness of the BDD thin film was around $2.7\text{ }\mu\text{m}$ for μLED probes and $3.7\text{ }\mu\text{m}$ for chemical sensors estimated based on the deposition rate of the BDD synthesis system.

Comparing the two etching approaches, KOH etching results in slightly weaker BDD-to-Parylene bond than DRIE etching, mainly due to interface damage and delamination during 9 hours soaking in corrosive KOH. While DRIE etching is relatively faster than KOH etching and eliminates chemical attack on the BDD-Parylene interface, the heat generated by aggressive plasma etching causes deterioration in mechanical flexibility and clarity of Parylene on some devices.

Mechanical properties of the transferred BDD-Parylene structure

Fig. 4(a) and 4(b) show a custom-designed KOH etching kit before and after assembly, which includes a custom-made Teflon etching jig, a KOH resistant O-ring (Mykin, Inc) and chromium-coated C-clamps (Graham field, Inc). Fig. 4(c) shows patterned BDD structures transferred on a 3-inch Parylene-C substrate, with a close-up view of contact pads and μLED electrodes. The SEM image in Fig. 4(d) shows Parylene anchors formed around the openings of the BDD mesh over large BDD patterns. The enhanced adhesion between BDD and Parylene was demonstrated using Scotch tape[®] peeling test as shown in Fig. 4(g) and 4(h). During the testing, a BDD-Parylene sensor was pressed onto a piece of Scotch tape[®] with the BDD side facing down and then peeled off slowly by fingers. Afterward, the sensor and tape were inspected under a microscope. We did not observe any BDD delamination or damage after five peelings, suggesting a strong mechanical adhesion between the BDD patterns and the Parylene-C substrate. The flexibility of the BDD-Parylene structure was tested by wrapping the device on the tip of a 2.5-mm-diameter micro punch with the μLED turned off (Fig. 4(e)) and on (Fig. 4(f)). No significant change in the LED brightness was observed after bending, indicating the integrity of the conductive BDD wires.

Characteristics of the BDD-Parylene electrochemical sensors

Potential window—Fig. 5(a) shows a fabricated BDD-Parylene chemical sensor. The electrochemical properties of the sensors were characterized using cyclic voltammetry (CV) (CHI604, CH Instruments, Inc.). First, the potential window of an as-fabricated BDD chemical sensor was quantified in 1.0 M potassium chloride (KCl) solutions, and compared with a commercial standard gold (Au) electrode (CHI101, CH Instruments, Inc.), as shown in Fig. 5(b). During measurements, a BDD or Au electrode was used as WE, commercially available platinum (Pt) (CHI 102, CH Instruments, Inc.) and Ag/AgCl electrodes (CHI 111, CH Instruments, Inc.) were used as CE and RE, respectively, with a scan rate of 0.1 V/s . Based on the CV scan, a potential window is determined as the applied potential range

between which no oxidation or reduction occurs in the redox system. The result shows that the BDD electrode exhibited featureless background current (no oxidation current or reduction current) from -2.0 V to 1.5 V, which corresponds to a potential window of 3.5 V. This value is higher than the value of 2.2 V reported in [46] under the same test conditions. The Au electrode shows reduction current at 0.5 V and oxidation current at a potential higher than 1.5 V, which defines a potential window of 1.0 V. The BDD electrode shows a much wider potential window than the Au electrode, therefore providing a bigger degree of characterizing analytes.

Double-layer capacitance—The double-layer capacitance (C_{dl}) resulted from an electrical double layer effect determines the background current of a redox system using either a potential control or potential sweep method. A lower double-layer capacitance can reduce the charging current and background noise, which contributes to a higher signal-to-noise ratio of chemical sensing. Experimentally, C_{dl} (in F/cm^2) can be determined by Eq (1), where i_{av} (in C/s) is the average current of the forward and reverse sweep of the CV, v (in V/s) is the scan rate of the CV, and A (in cm^2) is the electrode area[47]

$$C_{dl} = i_{av} / vA \quad (1)$$

To quantify the C_{dl} of the BDD electrode, CV measurements were performed in 1.0 M KCl solution with various scan rates. All the three electrodes on the same BDD sensor were used as RE, CE, and WE in the measurement. Fig. 5(c) shows the voltammograms with scan rates of 0.1 , 0.5 , 1.0 , 2.0 and 3.0 V/s. The average current of forward and reverse sweeps at -0.9 V vs. BDD with different scan rates was used to derive a linear regression equation ($y=24x+23$) with an R^2 number of 0.979 , in which the slope defines the C_{dl} of $24 \mu F/cm^2$. The relatively high double-layer capacitance is mainly caused by the sp^2 impurity on the diamond nucleation side. Besides, the unpolished and partially oxygen-terminated BDD surface can result in an increase in double layer capacitance[9].

Chemical redox characteristics—For a full evaluation of the electrochemical characteristics of the as-fabricated BDD sensor, the sensors were tested with both outer and inner-sphere electron transfer processes by CV. For an outer-sphere electron, the one electron transfer, $Ru(NH_3)_6^{2+/3+}$ redox couple was studied. During experiments, BDD was used as the WE, CE, and RE. Fig. 6(a) shows the CV curves of the sensor with various concentrations of $Ru(NH_3)_6^{2+/3+}$ (262005 – 250 MG, Sigma-Aldrich) in 1.0 M KCl solution at a constant scan rate of 0.1 V/s. The peak potentials (E_p), half peak potentials ($E_{p/2}$) and peak currents (I_p) of oxidation process for different concentrations were extracted and summarized in Table 2. The peak current of oxidation process vs. different $Ru(NH_3)_6^{2+/3+}$ concentrations was fitted to a linear regression response ($y=228.8x-14.6$) with an R^2 value of 0.991 , indicating that this oxidation peak is assigned to $Ru(NH_3)_6^{2+/3+}$. In addition, the resistance of the electrochemical cell caused by solution resistance, contact resistance, BDD thin film resistance, *etc.* was measured to be around 1 k Ω using a CH Electrochemical Analyzer. The corresponding iR drop were calculated using the following equation: $iR = I_p \times A \times R$ [48], where I_p is the peak oxidation current density (in $\mu A/cm^2$), A is the surface area

of the WE ($A = 0.008 \text{ cm}^2$) and R is the resistance of the electrode ($R = 1011.7 \Omega$). The iR was calculated to be 0.940, 1.46, 1.69, and 2.65 mV at the peak oxidation potentials (E_p) and 0.47, 0.73, 0.85 and 1.33 mV at the half peak oxidation potentials ($E_{p/2}$) for the $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ concentration of 0.6, 0.8, 1, and 1.5 mM, respectively. The values of $|E_p - E_{p/2}|$ were calculated to be 87.0, 86.0, 89.0, and 89.0 mV before iR compensation and 86.5, 85.3, 88.2, 87.7 mV after iR compensation, at the $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ concentration of 0.6, 0.8, 1, and 1.5 mM, respectively. The experimental values were larger than the theoretical value of 58.5 mV calculated from $58.5/n$ at room temperature, where n is the number of electrons transferred in reaction [47]. This implies a quasi-irreversible/irreversible electron transfer process with a small standard rate constant (k^0), during which an activation overpotential η beyond the Nernstian equilibrium potential (E_{eq}) is required to drive the system to achieve the same exchange current level determined by a reversible redox system, which leads to a relative larger E_p . The voltammograms with different scan rates in 2.0 mM $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ solution with 1.0 M KCl supporting electrolyte were collected as shown in Fig. 6(b). The peak current of oxidation process versus the square root of the scan rates was quantified, resulting in a linear regression ($y=0.42x+0.52$) with an R^2 value of 0.985. This suggests that, although mesh structures were introduced at the electrodes, the mass transfer process of such a system is still controlled by semi-infinite linear diffusion of macroelectrodes rather than spherical diffusion of microelectrodes. It is of note that the peak-to-peak separation in Fig. 6(b) increased and the peak potential shifted as the scan rate increased. This is mainly caused by the slow kinetic of the electrode since the iR drop effect is relatively small.

Dopamine sensing characteristics: For evaluation of the BDD sensors with an inner-sphere electron transfer system, DA was studied by CV and chronoamperometry based on the chemical reaction in Fig. 7(a), where DA is oxidized to dopamine-o-quinone with two electrons transferred in the reaction[49]. Fig. 7(b) shows the voltammograms of the BDD sensor vs. BDD at a scan rate of 1.0 V/s with various concentrations of DA (H8502-10G, Sigma-Aldrich) in 0.1 M, pH=7.4 phosphate-buffered saline (PBS) buffer solution. The inset of Fig. 7(b) shows the voltammogram of 100 μM DA after subtracting the background charging current in the PBS solution, where an anodic peak potential (E_p) was observed at 1.0 V vs. BDD with a peak current of 0.66 $\mu\text{A}/\text{mm}^2$. The corresponding half-peak potential ($E_{p/2}$), which defines the potential at the half peak current, is 0.816 V. The iR drops at E_p and $E_{p/2}$ were measured and calculated using the aforementioned method, which were 2.56 mV and 1.28 mV, respectively. These values are two orders of magnitude smaller than the values of E_p and $E_{p/2}$ and can be neglected. Since this redox is an inner-sphere system, the electron transfer process has a strong interaction with the redox couple and the electrode surface chemistry. In our study, the as-fabricated BDD is dominated by H-termination, which does not have strong adsorption of the reactants and causes a slower electron transfer process[44]. The calculated value of $|E_p - E_{p/2}|$ was 184 mV, much larger than the theoretical value of 29.25 mV [47], indicating an electrochemically irreversible/quasi-irreversible process.

Chronoamperometry was used to study the ability of BDD sensors to detect low DA concentrations. In this study, a single step of 1.0 V vs. BDD was applied and exponential

current decayed versus time was recorded. Fig. 7(c) shows chronoamperograms with 0.5 μM to 100 μM DA in 0.1 M, pH=7.4 PBS buffer solution. A linear response ($y=0.21x-0.07$) of background-corrected current to DA for the concentration of 0.5 μM to 100 μM was observed with $R^2 = 0.999$ and a detection sensitivity of 0.21 $\mu\text{A}/\text{cm}^2 \cdot \mu\text{M}$. Our flexible BDD sensor shows a DA sensitivity comparable to the devices reported in [50], [51] and is suitable for use in DA detection *in vivo*. All the above electrochemical experiments were conducted at room temperature in air. The BDD sensors were initially cleaned with isopropanol and then deionized (DI) water rinse before beginning experiments, and with DI water between individual trials.

Conclusions

In summary, this paper presented a novel fabrication method of transferring macro/microscale, all diamond structures from a diamond growth substrate (silicon) onto a flexible Parylene-C substrate, which enables the fabrication of all diamond-on-polymer devices without any metal patterns in a wafer-scale fabrication fashion. The unique design of Parylene anchors greatly enhanced the bonding strength between BDD and Parylene-C. The integrity of BDD thin films was demonstrated by bending a lit μLED -on-BDD device over the tip of a micropunch. Comparative study shows that the flexible BDD chemical sensor has a much wider potential window and smaller double layer capacitance than traditional gold electrodes, enabling wider freedom on detecting various chemicals and higher signal-to-noise ratio. The electron transfer process and mass transfer process were studied quantitatively using the outer-sphere redox couple $\text{Ru}(\text{NH}_3)_6^{2+/3+}$, showing low iR drops and competitive E_p under various $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ concentrations. The capability of sensing various concentrations of DA was demonstrated using chronoamperometry. A linear response to various DA concentration of 0.5 μM to 100 μM was observed with $R^2 = 0.999$ and a reasonably good sensitivity of 0.21 $\mu\text{A}/\text{cm}^2 \cdot \mu\text{M}$. The diamond growth side was found to have good resistance to fouling even at high DA concentrations. It should be pointed out that the higher sp^2 content of the diamond nucleation side may impede further improvement in sensor performance. To realize the full potential of sp^3 -bonded diamond, fabrication process will be revised and optimized in the future to expose the diamond growth side after transferring BDD films onto polymer substrates.

Acknowledgments

This work was supported by the National Science Foundation under the Award Numbers CBET-1264772 and ECCS-1407880. The authors would like to thank Dr. Baokang Bi for the help on microfabrication.

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Fig. 1. Illustration of the fabrication processes for I. pre-substrate transfer patterning; II. Substrate transfer; and III. Post- transfer fabrication.

Fig. 2. Device design of μ LED probes and chemical sensors used to demonstrate the BDD transfer process. The black and grey colors represent BDD and Parylene, respectively. Insets show the top and cross-section views of the mesh structure.

Fig. 3.

(a) A SEM image shows the surface morphology of the BDD nucleation side. (b) A Raman spectrum shows both boron and diamond characteristic bands from the BDD nucleation side.

Fig. 4.

The custom designed KOH etching kit (a) before and (b) after assembly. (c) BDD patterns on a wafer-scale flexible Parylene-C substrate after removing the Si substrate. Microscope images shows contact pads and μ LED electrode probes with 200 μ m and 50 μ m trace width. (d) A SEM image shows the mesh structure of the contact pads, where Parylene anchors, Parylene substrate and BDD are highlighted in white, green, and blue, respectively. (e) and (f) Flexibility of a BDD μ LED probe wrapped around the tip of a micro punch, with μ LED off and on. (g) and (h) Scotch tape[®] testing before (g) and after (h) peeling a BDD-Parylene sensor off the tape, with the BDD side facing down.

Fig. 5.

(a) A fabricated BDD-Parylene sensor with three electrodes. (b) Voltammogram of Au and BDD electrode in 1.0 M KCl solution vs. Ag/AgCl at a scan rate of 0.1 V/s (CE: Pt electrode, RE: Ag/AgCl). (c) Voltammograms of BDD electrodes vs. BDD at various scan rates (CE: BDD, RE: BDD). The voltammograms are offset for better visibility.

Fig. 6.

(a) Voltammograms of the BDD sensor with various concentrations of $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ in 1.0 M KCl solution vs. BDD at a scan rate of 0.1 V/s. (CE: BDD, RE: BDD) (b)

Voltammograms of BDD electrodes vs. BDD at various scan rates (CE: BDD, RE: BDD) in 2 mM $\text{Ru}(\text{NH}_3)_6^{2+/3+}$ with 1.0 M KCl solution.

Fig. 7.

(a) Dopamine/Dopamine-o-quinone redox. (b) Voltammograms of the BDD sensor in various concentrations of DA with 0.1 M PBS vs. BDD. The scan rates are 1.0 V/s (c) Chronoamperograms of various concentrations of DA in PBS buffer solution vs. BDD at an applied potential of 1.0 V.

Table 1

Summary of BDD film characteristics

Doping level	Surface roughness	Film thickness	
		μ LED probes	Chemical sensors
$\sim 10^{20}\text{cm}^{-3}$	10.8nm	2.7 μm	3.7 μm

Table 2

CV with different concentrations

Conc. (mM)	E_P (mV)	I_P ($\mu\text{A}/\text{cm}^2$)	$E_{P/2}$ (mV)	iR drop (mV) @ E_P	iR drop (mV) @ $E_{P/2}$	$ E_P - E_{P/2} $ before iR (mV)	$ E_P - E_{P/2} $ after iR (mV)
0.6	-51.0	116	-138	0.940	0.470	87.0	86.5
0.8	-44.0	181	-130	1.46	0.730	86.0	85.3
1.0	-51.0	209	-140	1.69	0.850	89.0	88.2
1.5	-55.0	328	-144	2.65	1.33	89.0	87.7