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"Clicking" Thiophene on Diamond Interfaces. Preparation of a Conducting Polythiophene/Diamond Hybrid Material

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This paper reports on the preparation of a conducting polythiophene polymer covalently bonded to a thiophene-terminated boron-doped diamond (BDD) electrode. The thiophene-terminated BDD surface was prepared using "click" chemistry in a stepwise process. Azide termination on BDD was obtained via esterification reaction of photochemically oxidized diamond surfaces with 4-azidobenzoic acid in the presence of *N,N*-dicyclohexylcarbodiimide at room temperature. The applicability of azide−alkyne [3 + 2] cycloaddition reaction was successfully demonstrated using ethynyl thiophene. Electropolymerization was conducted on the thiophene-terminated BDD surface in the presence of thiophene monomer to form a polythiophene film covalently grafted on the BDD interface. The resulting surfaces were characterized using cyclic voltammetry, X-ray photoelectron spectroscopy, scanning electron microscopy, and contact angle measurements.

1. Introduction

Surface functionalization via self-assembled monolayers (SAMs) has been intensively investigated in various areas from both fundamental aspects and for the expected potential technological applications.[1] The covalent attachment of organic monolayers to semiconductor interfaces is of growing interest for applications in molecular electronics, photovoltaic devices, and chemical/biological sensing.

Surface functionalization of diamond surfaces has generated big interest from fundamental and applied research view points.[2−5] Boron-doped diamond (BDD) has emerged as an alternative electrode material due to its good electrical conductivity, low background current density, and wide electrochemical potential window.[6,7] Its high chemical and morphological stabilities under extreme conditions have made BDD an attractive interface for electrochemical studies.

The successful electrodeposition of heterocyclic conjugated polymers (e.g., polypyrrole or polythiophene) on diamond electrodes rather than conventional metal deposition (e.g., platinum, gold, etc.) should result in highly stable interfaces with potential applications for sensing. The covalent attachment of conducting polymers increases considerably the stability of the polymer/diamond interface.[8] Electrochemical polymerization of pyrrole and thiophene monomers is a fast and reliable method for the generation of functional polymers onto a conducting surface with a desired thickness.[9] The use of thiophene polymers is in particular driven by the potential applications in nonlinear optical and electroluminescent devices.[10] Recently, the sensitivity of polythiophene composite films to a series of gas vapors was

reported.[11,12] It is known that thiophene monomers undergo electropolymerization via radical cation intermediates rather than radical anions as in the case of pyrrole monomers. As radical cations are generated at higher oxidation potentials, the electrochemical polymerization of thiophene is a more challenging task due to overoxidation.[13]

Furthermore, for device-driven applications good adherence characteristics are sought after. Better film adherence can be obtained on interfaces, where the monomer unit was covalently linked before polymerization in the presence of the monomer in solution was carried out. Photoelectrochemical oxidation of a thiophene-terminated silicon surface in the presence of thiophene in solution yielded conducting organic films covalently linked to silicon, which exhibited adherence characteristics better than those of the same polymer electrodeposited on unmodified silicon.[14,15] Comparable results were reported on polished diamond interfaces when polypyrrole films were locally deposited.[8]

"Click" chemistry is a class of robust and selective chemical reactions with high yields, tolerant to a variety of solvents (including water), and can be performed in the presence of many other functional groups.[16] The copper-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and alkynes to form stable 1,2,3-triazoles is one of the best example of "click" chemistry. This cycloaddition reaction is irreversible and proceeds in quantitative yields without any side product and has been successfully applied for the modification of different SAMs on gold,[17] carbon nanotubes,[18] glass,[19] and silicon.[20]

In search for new strategies for diamond functionalization, we have recently used "click" chemistry to incorporate electroactive ferrocene groups onto an azide-terminated BDD surface.[21] In continuation of our work on diamond functionalization, we report here on the introduction of thiophene functional group on oxidized BDD electrodes using "click" chemistry. First, covalent linking of commercially available 4-azidobenzoic acid in the presence of carbodiimide reagent to

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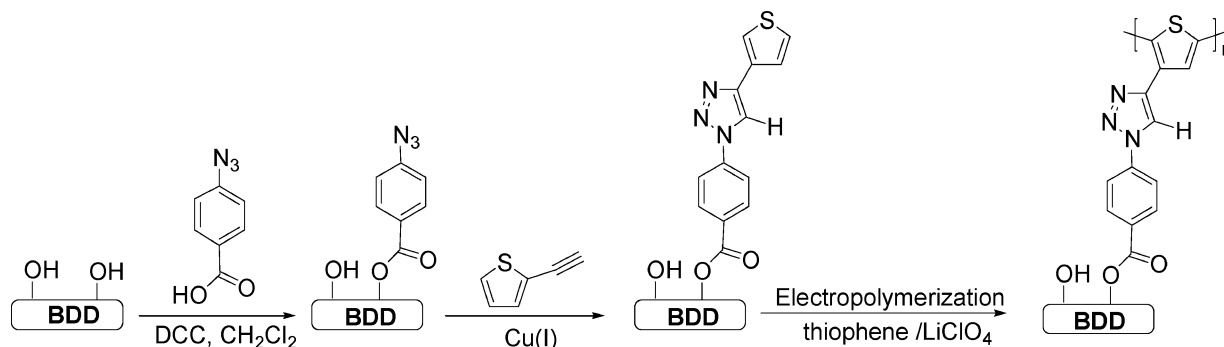[‡] Shandong University.

"Clicking" Thiophene on Diamond Interfaces

J. Phys. Chem. C, Vol. 113, No. 39, 2009 **17083**

Figure 1. Schematic illustration of the preparation of a conducting polythiophene polymer covalently bonded onto thiophene-terminated boron-doped diamond surface.

the oxidized BDD surface produced an azide termination.[21] Coupling of the azide-terminated surface with thiophene bearing an acetylene terminal group was successfully achieved using "click" chemistry. The thiophene-terminated BDD surface was electrochemically polymerized in the presence of thiophene monomer in solution to yield a conducting polythiophene thin film. The resulting surfaces were characterized using, X-ray photoelectron spectroscopy (XPS), contact angle, and electrochemical measurements.

2. Experimental Section

2.1. Materials. All chemicals were reagent grade or higher and were used as received unless otherwise specified. Milli-Q water (18 MΩ) was used for all experiments. *N,N*-Dicyclohexylcarbodiimide (DCC), ethynyl thiophene, 3-sodium ascorbate, copper sulfate ($CuSO_4 \cdot 5H_2O$), dichloromethane (DCM), tetrahydrofuran (THF), thiophene, lithium perchlorate ($LiClO_4$) were purchased from Aldrich. 4-Azidobenzoic acid was obtained from TCI Europe.

Polycrystalline boron-doped diamond films of $1.5-2$ μm thickness were purchased from CSEM (Neuchatel, Switzerland). The BDD thin films were deposited on silicon substrates in a hot filament-assisted chemical vapor deposition reactor supplied with diborane and methane in hydrogen. The doping level of boron was determined to be $N_A \approx 3 \times 10^{19}$ B cm^{-3} by SIMS measurements, according to the supplier.

2.2. Sample Preparation. 2.2.1. Diamond Oxidation. A low-pressure mercury arc lamp (UVO cleaner, No. 42-220, Jelight, Irvine, CA, $P = 1.6$ mW cm^{-2}, distance from sample: 3 mm) was used to photochemically oxidize BDD samples as reported previously.[22]

2.2.2. Azide Termination. 4-Azidobenzoic acid (2 mmol), DCC (2.2 mmol), and 45 mg of 4-dimethylaminopryridine (DMAP) were dissolved in dry tetrahydrofuran (20 mL). The oxidized BDD was immersed in the solution and left at room temperature for 24 h under nitrogen atmosphere. The sample was then washed with THF (5 min, 2 times), dichloromethane (5 min, 2 times), ethanol (5 min, 2 times), and finally with water and dried under a nitrogen stream.

2.2.3. "Clicking" Thiophene to Azide-Terminated BDD Surface. The azide-terminated BDD surface was immersed in 15 mL of ethanol/water (1:2) solution of ethynyl thiophene (2 mM), $CuSO_4 \cdot 5H_2O$ (100 μM), and sodium ascorbate (150 μM) and kept for 24 h at room temperature. The resulting surface was washed with ethanol and water and dried under a stream of nitrogen.

2.2.4. Electropolymerization. Electrochemical polymerization was carried out in an acetonitrile/0.1 M $LiClO_4$ electrolyte solution with or without thiophene monomer (0.2 M) by

TABLE 1: Water Contact Angle of BDD Surfaces with Different Terminations

BDD	−OH	−N₃	−thiophene	−polythiophene
Θ (deg)	6 ± 2	53 ± 2	47 ± 2	51 ± 2

sweeping the potential between -0.2 and $+2.0$ V vs Ag/AgCl at a scan rate of 100 mV s^{-1}.

2.3. Surface Characterization. *X-ray Photoelectron Spectroscopy.* XPS measurements were performed with an ES-CALAB 220 XL spectrometer from vacuum Generators. A monochromatic Al Kα X-ray source (1486.6 eV) was operated in the CAE (constant analyzer energy) mode (CAE = 100 eV for survey spectra and CAE = 40 eV for high-resolution spectra), using the electromagnetic lens mode. No flood gun source was needed due to conducting character of the substrates. The angle between the incident X-rays and the analyzer is 58°. The detection angle of the photoelectrons is 90°, as referenced to the sample surface.

Scanning Electron Microscopy. Scanning electron microscopy (SEM) images were obtained using an electron microscope ULTRA 55 (Zeiss, France) equipped with a thermal field emission emitter, three different detectors (EsB detector with filter grid, high efficiency In-lens SE detector, Everhart–Thornley Secondary Electron Detector) and an energy dispersive X-ray analysis device (EDX analysis).

Contact Angle Measurements. Water contact angles were measured using deionized water. We used a remote-computer controlled goniometer system (DIGIDROP by GBX, France) for measuring the contact angles. The accuracy is ±2°. All measurements were made in ambient atmosphere at room temperature.

Electrochemical Measurements. All electrochemical experiments were performed using a three-electrode configuration. Platinum and Ag/AgCl electrodes were used as counter and reference electrode, respectively, using an Autolab potentiostat 20 (Eco Chemie, Utrecht, Netherlands). The BDD working electrode ($A = 0.20$ cm^2) was sealed against the bottom of a single-compartment electrochemical cell by means of a rubber O-ring. The electrical contact was made to a copper plate through the bottom of the silicon substrate.

3. Results and Discussion

3.1. Grafting of Ethynyl Thiophene on BDD. We have recently shown that UV/ozone oxidation of hydrogen-terminated polycrystalline BDD surface at room temperature using a low-pressure mercury arc lamp yields a surface with a complex chemical composition (C−O−C, C=O, C−OH).[23] The surface displays a high concentration of surface hydroxyl groups that can be easily coupled to trichlorosilane molecules[8,22,24] or
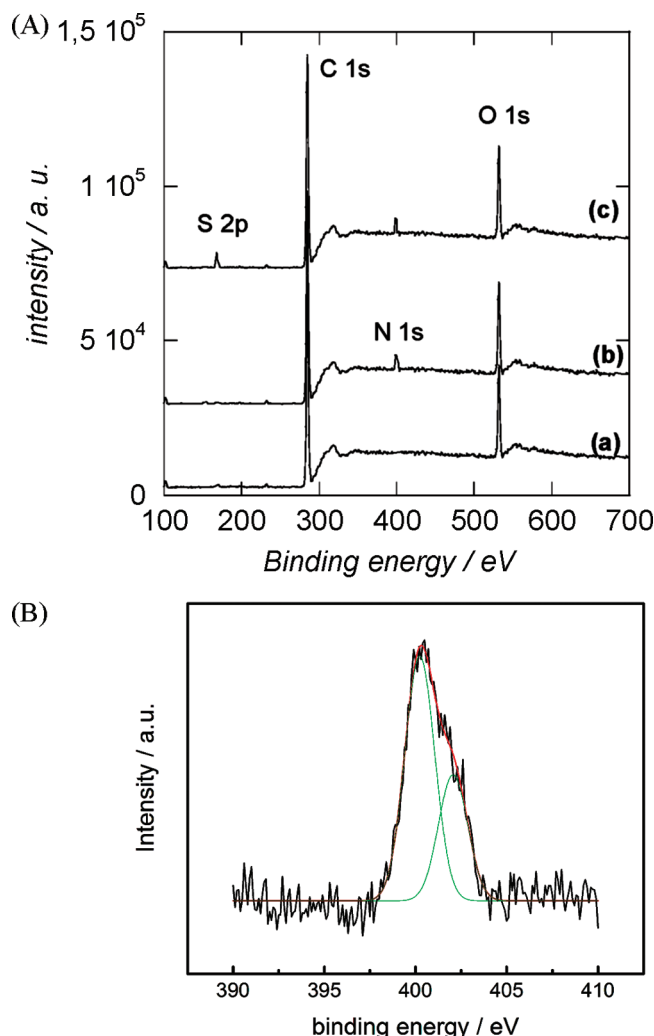
(A)

(B)

Figure 2. (A) XPS survey spectra of photochemically oxidized BDD surface (a) and azide-terminated BDD surface before (b) and after coupling of ethynyl thiophene via click chemistry (c). (B) High-resolution XPS spectra of N 1s band of the triazole moiety

3-benzoylbenzoic acid.[25] In a similar way, 4-azidobenzoic acid was successfully coupled to the BDD surface under mild conditions.[23]

Figure 1 shows the three-step procedure used to link ethynyl thiophene on an oxidized BDD surface. The "click" derivatization of the azide-terminated BDD surface with ethynyl thiophene units was carried in ethanol/water solution in the presence of copper(I) catalyst and ascorbic acid.

Water contact angle measurements were performed next to XPS to evaluate the changes in the surface chemical composition and wetting properties occurring during surface derivatization. Oxidized BDD substrate exhibits a contact angle of 6°, characteristic of a hydrophilic surface. Chemical esterification of the terminal hydroxyl groups of the photochemically oxidized BDD with 4-azidobenzoic acid led to an increase in contact angle from $\theta = 6° \pm 2°$ to $53° \pm 2°$. After clicking ethynyl thiophene groups to the azide terminal groups, the contact angle dropped to $\theta = 47° \pm 2°$. Electropolymerization of the thiophene-terminated BDD surface in the presence of thiophene monomer caused a slight increase of the contact angle to $51° \pm 2°$ (Table 1).

Figure 2 displays the XPS survey spectra of the oxidized BDD surfaces before and after functionalization. Photochemically oxidized BDD surface shows a main peak at 285 eV due to C
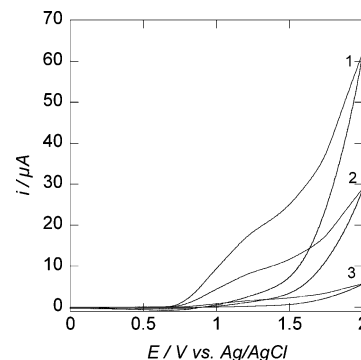

Figure 3. Cyclic voltammetric $i-E$ curves of a thiophene modified BDD electrode in LiClO$_4$ (0.1 M)/acetonitrile solution; $A = 0.20$ cm^2; scan rate = 0.1 V s^{-1}.
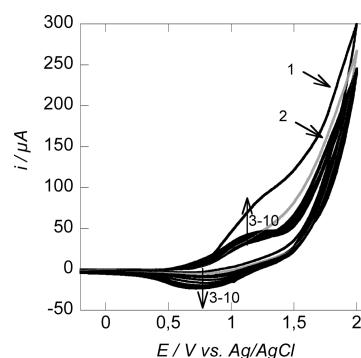

Figure 4. Cyclic voltammetric $i-E$ curves of thiophene modified BDD in LiClO$_4$ (0.1 M)/acetonitrile/thiophene (0.1 M) solution; $A = 0.20$ cm^2; scan rate = 0.1 V s^{-1}.

1s from the bulk and a peak at 532 eV due to O 1s (Figure 2Aa). The BDD surface is composed of C–O–C, C–OH, and C=O groups, in accordance with our previous results.[22,23] After esterification of the terminal hydroxyl groups with 4-azidobenzoic acid, an additional peak at ~400 eV was observed, in agreement with the chemical composition of the molecule (Figure 2Ab). Subsequent reaction of the terminal azido groups with ethynyl thiophene in the presence of Cu(I) catalyst led to the appearance of new peaks in the XPS survey spectrum at 165 eV due to sulfur S 2p and S 2s, respectively (Figure 2Ac). The covalent linkage of thiophene to the azide-terminated BDD interface was confirmed by high-resolution XPS of the N1s band (Figure 2B). The broad signal centered at 401 eV, which fits to two bands at 400.2 and 402.0 eV with an intensity ratio of 2:1, is characteristic for the formation of surface-confined triazole groups.[26,27] The S 2p high-resolution spectrum (not shown) is composed of 2p$_{3/2}$ and 2p$_{1/2}$ peaks at binding energies of 164.1 and 165.7 eV, respectively. The separation of the 2p$_{3/2}$ and 2p$_{1/2}$ peaks by 1.3 eV and their area ratio of 0.5 are in agreement with values reported in the literature.[14,28] Integration of the peak area of N 1s and S 2p gave N 1s/S 2p ratio of 1.6, smaller than the theoretical value of 3. This corresponds to a conversion of ~53% of the azide groups into triazole rings. This is in accordance with the 47% conversion yield recently reported for clicking ethynyl ferrocene groups to BDD modified with 4-azidobenzoic acid.[21] To rule out nonspecific adsorption, azide-terminated BDD was kept in a solution of ethynyl ferrocene without the addition of the catalysts, sodium ascorbate, and copper-sulfate. No XPS signal due to S 2p was detected in this case.

3.2. Electrochemical Characterization. Figure 3 shows the voltammetric behavior of thiophene-modified BDD in dry acetonitrile/0.1 M LiClO$_4$. In the first scan, an irreversible
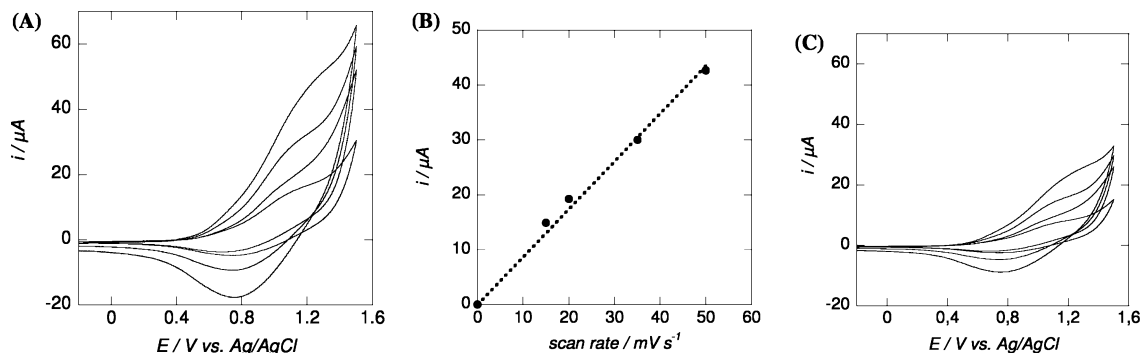
Figure 5. (A) Cyclic voltammograms of polythiophene formed on thiophene-modified BDD measured in monomer-free acetonitrile/0.1 M LiClO$_4$ solution at various scan rates (15, 20, 35, and 50 mV s^{-1}). (B) Dependence of the anodic peak current on the scan rate of the polymer film. (C) Cyclic voltammograms of polythiophene formed on oxidized BDD measured in monomer-free acetonitrile/0.1 M LiClO$_4$ solution at various scan rates (15, 20, 35, and 50 mV s^{-1})

shoulder is observed at ~1.27 V (vs Ag/AgCl: 0.01 M) with an intense increase in current at potentials higher than ~1.3 V. Indeed, the oxidation of thiophene group to its radical cation occurs at potentials of ~2.0 V vs SCE.[29] The shoulder at ~1.27 V could be due to the oxidation of thiophene dimer 2,2′-bithiophene.[29] In a consecutive second scan, the oxidation current is decreased and no oxidative shoulders are observed after the third scan. This indicates that most of the aromatic rings have reacted. As the formed radical cations are highly reactive species, the most likely reaction path is the coupling with neighboring radical cations to form oligomeric and polymeric structures on the BDD interface. The surface coverage of the electroactive species can be estimated from the current intensity of the anodic shoulder observed at 1.27 V presented in Figure 3. Using the voltammetric response of unmodified BDD as the background current, the surface coverage Γ can be estimated using eq 1:[30]

$$i_{pa} = \frac{(1 - \alpha)n n_a F^2 A \nu}{2.718 RT} \Gamma \tag{1}$$

where i_{pa} is the anodic peak current, α the charge transfer coefficient (assumed to be 0.5), n the total number of electrons, n_a the number of electrons involved in the rate-determining step, F the Faraday constant, and ν the scan rate. Assuming $n = n_a = 2$ electrons, a surface coverage of 3.55×10^{-10} mol cm^{-2} is obtained. This compares well to the surface coverage reported by Fabre et al. on thiophene-terminated alkyl monolayer Si(111) surface (4.7×10^{-10} mol cm^{-2}).[14]

3.3. Electrochemical Polymerization. To obtain a higher coverage of conducting polymer material, the thiophene-terminated BDD interface was furthermore electrochemically oxidized in the presence of thiophene monomer. Electrochemical polymerization of thiophene monomers can be carried out by using potentiostatic, galvanostatic, and cyclic potential sweep techniques. In the present study, a cyclic potential sweep technique was employed. Although this method requires longer reaction times to obtain a polymer film, as compared to potentiostatic and galvanostatic methods, it is advantageous as the electrochemical characteristics of the growing polymer can be monitored during the polymerization process. Figure 4 shows typical cyclic voltammograms of the electrochemical polymerization of thiophene on thiophene-modified BDD in a 0.1 M LiClO$_4$ acetonitrile solution. The anodic peak at 1.17 V and cathodic peak at 0.78 V appearing after the third scan correspond to the oxidation of polythiophene. As the polymerization process
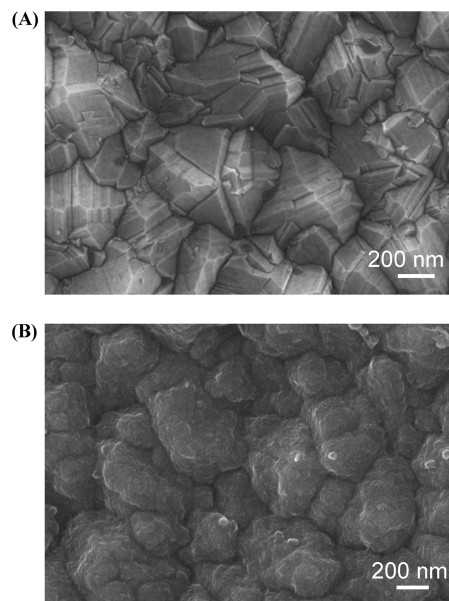

Figure 6. SEM images of thiophene-terminated BDD surface before (A) and after electropolymerization (B).

proceeds, the peak current increases in the successive cycles, indicating the growth of the polymer on the BDD surface. The anodic peak shifts gradually to higher values as the thickness of the polymer film increases and could be attributed to a decrease of the film conductivity.[31]

Cyclic voltammograms of the polythiophene film resulting from the above polymerization reaction were measured in monomer free LiClO$_4$/acetonitrile solution (Figure 5A). The redox process of the polymer is chemically reversible, as the amount of the cathodic charge is essentially the same as the anodic charge. Both anodic and cathodic peaks are quite broad, which is probably caused by the slow diffusion of the dopant anions (ClO$_4^-$ in our case) in and out of the film. The peak-to-peak separation ΔE_p is ~39 mV as expected for surface confined redox species. A linear relationship was observed between the anodic peak current and the scan rate (Figure 5B) characteristic of an electroactive polymer film grafted on an electrode where the current is not diffusion controlled.[32] In the case of physisorbed polythiophene formed electrochemically on oxidized BDD under the same conditions as on thiophene-modified BDD (Figure 5C), the electroactivity of the formed polythiophene film was reduced.

The morphology of the polythiophene was investigated using SEM. Figure 6 shows a SEM image of a thiophene-modified
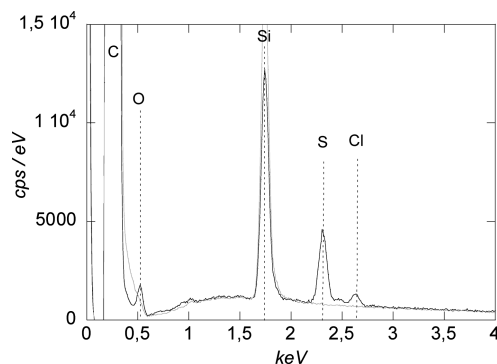
17086 *J. Phys. Chem. C, Vol. 113, No. 39, 2009*

Wang et al.

Figure 7. EDX of the BDD (gray) and polythiophene/BDD hybrid structure (black).

polycrystalline BDD before and after polythiophene deposition. The polycrystalline structure of the diamond interface can be easily seen on the thiophene-modified BDD. After electrochemical deposition of a polythiophene onto the BDD interface, the polycrystalline structure is covered with cauliflower-like structures, characteristic of polythiophene.

Finally, the chemical composition of the resulting polythiophene/BDD hybrid material was analyzed using EDX (Figure 7). The EDX spectrum displays main signals due to C, Si, and S, and small peaks due to O and Cl elements. The C and Si elements originate from the bulk BDD film and the underlying crystalline silicon substrate onto which the BDD was deposited. The presence of sulfur is in accordance with the formation of a polythiophene film on the BDD surface. Furthermore, the incorporation of small amounts of oxygen and chloride is a good indication of the doping of the BDD film with ClO_4^- anions.

4. Conclusion

The preparation of a conducting polythiophene covalently bonded onto thiophene-terminated BDD surface using a cyclic potential sweep technique was demonstrated. The strategy proposed in this work exploits the versatility of the "click" chemistry to introduce thiophene units in a controlled way onto an azide-terminated BDD surface. Electropolymerization of the thiophene-terminated BDD surface in the presence of thiophene monomer in solution leads to the formation of a conducting polythiophene film doped with ClO_4^- anions. Such hybrid interfaces can find applications in areas ranging from electronic/photovoltaic devices to chemical/biological sensing.

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