

Electrochemical Performance of Angstrom Level Flat Sputtered Carbon Film Consisting of sp^2 and sp^3 Mixed Bonds

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Carbon materials are widely used for the electrochemical measurement of biomolecules. Glassy carbon (GC) electrodes have been used for such measurements since they have a wider potential window and a higher overpotential for oxygen reduction than metal electrodes, such as Au and Pt. A boron-doped diamond (BDD) electrode prepared by the plasma CVD (chemical vapor deposition) method has been reported that has a much wider potential window than GC and a low background noise level.^{1–3} However, the surface of the film is not flat since BDD consists of crystallites with micron-scale dimensions. Nanocrystalline diamond film has been fabricated with a root-mean-square surface roughness of 34 nm,^{4,5} and the film has a much smaller crystalline structure (~ 20 nm) than that of BDD. Flat films have various applications with regard to the fabrication of nano order devices and the observation of adsorbed molecules using STM and AFM. McCreery and McDermott et al. have formed carbon films with subnanometer flatness formed by the pyrolysis of a photoresist or electron beam evaporation.^{6,7} The film is basically graphite-like carbon with an extremely flat surface of 0.07–0.5 nm. Therefore, much a smaller capacitive current ($\sim 20 \mu\text{F}/\text{cm}^2$) than that of GC ($34 \mu\text{F}/\text{cm}^2$) can be obtained for the film formed by electron beam evaporation.

Recently, one of the present authors reported a new carbon film prepared by the electron cyclotron resonance (ECR) sputtering method.⁸ ECR sputtering equipment is now becoming very widely used to fabricate electronic and optical devices. The carbon film obtained by ECR sputtering has a very flat surface, and its mean scratch hardness is the same as that of diamond. Here, we report the electrochemical performance of ECR carbon film particularly when detecting biomolecules. We observed a potential window nearly equivalent to that of BDD and a very low capacitive current. Biomolecules with higher oxidation potential, such as each base of oligonucleotides, can be measured not only by the oxidation of guanine (G) base but also by that of adenine (A) and thymine (T) without any pretreatment. The ultra-flat surface and low oxygen-containing group of the film suppress the adsorption of oligonucleotides without any pretreatment, and so we can obtain reproducible voltammograms (5 scans), even though the same electrode was used without pretreatment.

The carbon film was deposited on undoped and highly doped silicon substrates by ECR sputtering. For the sputtering, the argon gas pressure was 5.0×10^{-2} Pa, and the substrate was kept at room temperature. The deposition temperature (RT) was much lower than the typical deposition temperature of BDD (600–900 °C) and the fabrication temperature of GC (~ 1000 – 3000 °C). Therefore, a wide

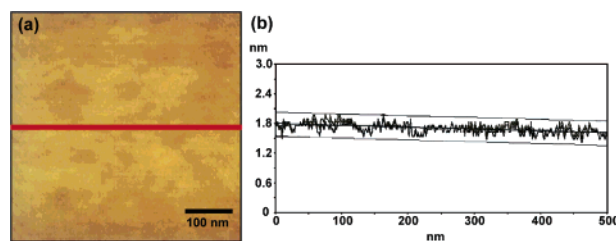


Figure 1. AFM image of ECR sputtered carbon surface (a) and line profile (b).

variety of substrate materials, such as plastic, could be used. During deposition, the irradiation ion current density was $5.8 \text{ mA}/\text{cm}^2$, and the ion acceleration voltage was 75 V. The obtained film was 40 nm thick, and the conductivity (4 terminal method) was $20 \text{ S}/\text{cm}$ when measured for film formed on undoped silicon. The obtained conductivity is 19 orders of magnitude larger than that of undoped diamond but with a comparable scratch hardness. The conductivity of the film is sufficient for electrochemical measurements even when it is deposited on an insulating substrate without any doping. Figure 1 shows an AFM image and line profile. No apparent structure can be observed at the surface. By scanning along the red line seen in Figure 1a, we obtained a film average roughness (R_a) of 0.7 \AA (Figure 1b), which is much flatter than that of nanocrystalline diamond (typically around 34 nm)⁴ and equivalent to that of carbon films fabricated by the pyrolysis of a photoresist or by electron beam evaporation.^{6,7} Although, the ultra-flat carbon films reported by McCreery et al. are graphite-like, ECR carbon film consists of sp^3 and sp^2 mixed bonds. The sp^3/sp^2 ratio of ECR sputtered carbon film obtained with XPS spectra (Kratos Axis-Ultra equipment, 0.65 eV resolution) by comparing the magnitudes of the peaks observed at 284.3 eV (sp^2) and 285.3 eV (sp^3)⁹ was 0.702. This suggests that the sp^3 bonds accounted for 35.1% of the total bonds in the film. Therefore, we can expect improved electrochemical properties, such as a wide potential window and a low background current.

Figure 2 compares background voltammograms for ECR sputtered carbon, GC, and BDD¹⁰ electrodes. The potential limit for ECR sputtered carbon (current limit $< \pm 500 \mu\text{A}/\text{cm}^2$) in the positive direction is 2.0 V vs Ag/AgCl and that for a GC electrode is 1.7 V. The potential window of the BDD electrode for the positive direction is still about 0.1 V higher (2.1 V vs Ag/AgCl) than that of ECR carbon. However, the potential window is greatly improved compared to that of GC despite the large sp^2 bonds' content. In contrast, the ECR sputtered carbon film shows an excellent potential limit for the negative direction compared with GC and BDD electrodes since few catalytic sites for oxygen reduction exist without doping. Duo et al. reported the effect of sp^2 carbon on the BDD surface.¹¹ The pseudo-capacitance of BDD after mild anodic

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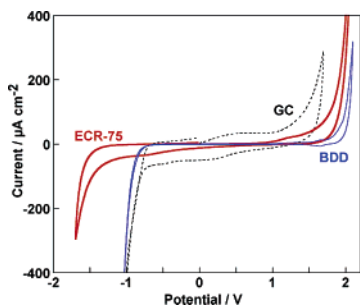


Figure 2. Voltammograms of ECR sputtered carbon films (acceleration voltage = 75 V) compared with those of GC and BDD in 0.05 M H₂SO₄ deoxygenated with Ar. Scan rate = 100 mV/s. The reference electrode is Ag/AgCl. BDD (boron > 1000 ppm) electrode was purchased from Sumitomo Electric Hardmetal Corporation.

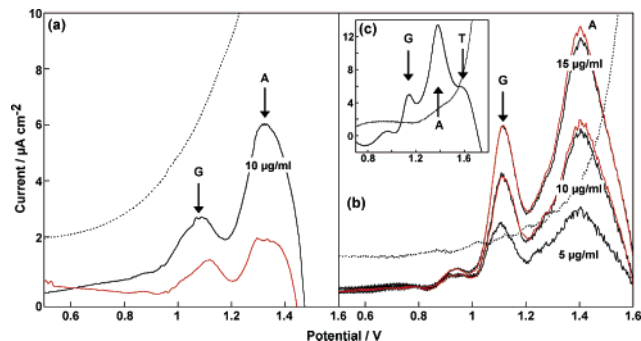


Figure 3. Background-subtracted DPVs of various concentrations of 5'-GAGA-3' at GC (a) and ECR sputtered carbon (b) electrode in 1.0 M pH 5.0 acetate buffer. Inset (c), background-subtracted DPV of 30 μg/mL 5'-TTGAGA-3' at ECR sputtered carbon electrode. $\Delta E = 4$ mV, pulse amplitude = 50 mV, pulse width = 50 ms. Black and red lines represent first and second scans, respectively. Dotted lines are background scans.

polarization (48 $\mu\text{F}/\text{cm}^2$) increases to 136 and 306 $\mu\text{F}/\text{cm}^2$ when the sp^2 coverage is 2.8 and 6.4%, respectively.

Bennett et al. also studied the effect of sp^2 -bonded non-diamond impurity by increasing the CH_4/H_2 (C/H) ratio during CVD deposition and reported that increasing the C/H ratio increases the sp^2 -bonded non-diamond carbon content.¹² The first-order diamond phonon line can be observed for 3% C/H film, but not when C/H is 5%. They also reported that the peak separation of $\text{Fe}^{3+/2+}$ and 4-*t*BC (4-*tert*-butylcatechol) decreases with increasing C/H. The capacitance of ECR carbon film is 3 times as large as that of BDD and 5.5 times lower than that of GC. With our ECR film, the peak separation of $\text{Fe}^{3+/2+}$ is from 587 to 752 mV, depending on the sample, indicating that the surface oxygen concentration is very low, although the sp^2 ratio is about 65% and no first-order diamond phonon line can be seen in the Raman spectrum of ECR film. These results clearly suggest that ECR carbon film is much more stable than conventional graphite-based carbon film despite its different structure from diamond.

One of the authors has previously published an image of ECR carbon film obtained with an H-9000 high-resolution transmission microscope (HRTEM).⁸ The film consists of fine graphene sheets vertically oriented to the film surface. The ECR film consists of 2–5 nm scale crystallites. With graphite, the crystalline structure consists of parallel layered planes. However, a curved and fine closed structure is dominant in the ECR film. We previously measured the electrochemical properties of ECR carbon films with a much lower sp^3 bond content (sp^3/sp^2 ratio = 0.274).¹³ In such a case, the parallel structure is dominant in the film as found with graphite, and a narrower potential window can be observed. These results suggest that a new fine closed structure, which could not

be observed in the graphite carbon, could suppress the surface oxidation despite the relatively large sp^2 (about 64.9%) content. This structure is completely different from that of nanocrystalline diamond since it is heterogeneous and consists of diamond nanocrystals with sp^2 carbon in the boundary region. ECR film can be used to measure biochemicals with higher oxidation potentials.

Figure 3 shows background-subtracted differential pulse voltammogram (DPV) of oligonucleotides at GC and ECR sputtered carbon electrode in 1.0 M pH 5.0 acetate buffer. As shown in Figure 3a, the peak currents assigned for G and A oxidation at second potential scan reduce to about 30% of those of first potential scan at GC electrode. In contrast, the peaks at ECR did not change after the same experiment. In addition, the oligonucleotides from 5 to 15 $\mu\text{g}/\text{mL}$ can be measured quantitatively without any pretreatment of the electrode surface, as shown in Figure 3b. The oxidation of T, which has higher oxidation potential, was also distinguished when we measured 5'-TTGAGA-3', as shown in Figure 3c. These results indicate that ECR sputtered carbon electrode can quantify the oxidation peak for each base in oligonucleotides without any pretreatment with performance similar to that of BDD electrodes.^{14,15} The ultra-flat surface and low oxygen surface concentration of ECR sputtered carbon film may suppress fouling with oligonucleotides after oxidation. This high surface stability against fouling was also observed when we measured other analytically important analytes, such as NADH and bisphenol A (BPA). With BPA, the oxidation current does not decrease after 20 times potential scan with ECR sputtered carbon film.

In conclusion, we have developed an ultra-flat carbon film electrode consisting of sp^2 and sp^3 mixed bonds by using the ECR sputter deposition technique. The film shows a wide potential window and a low capacitive current. The film can be applied to measure each base in the oligonucleotides reproducibly with high stability. A possible future application is as various biosensors with less surface fouling, or the nano-gap electrodes for molecular wires, such as DNA, since our flat electrode is suitable for nano-fabrication and carrier injection due to its stability against oxidation. The ultra-flat surface of the film is suitable for studying adsorbed biomolecules with STM or AFM combined with electrochemistry.

Supporting Information Available: Cyclic voltammetry of bisphenol A and differential pulse voltammetry of the oligonucleotide. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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