

## Electrochemical Performances of ECR Sputter Deposited Carbon Films with Different $sp^3$ Binding Content

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Various kinds of new carbon materials have been studied for electroanalytical and sensor applications. Thin carbon film is particularly important since it can be used for microchip based electroanalytical devices. A wide potential window and low background current are required for carbon film based electrode. Boron-doped carbon film has a wide potential window and stable background current and is now used to measure the analyte with relatively high oxidation potential [1, 2]. In contrast, a simple film formation process, such as low temperature film deposition, is required for various applications, such as the formation of a film electrode on a plastic substrate. We prepared a new carbon film by the electron-cyclotron-resonance plasma (ECR) sputtering method [3]. The substrate temperature during deposition is low. The ECR film contains both  $sp^2$  and  $sp^3$  binding structure different from glassy carbon electrode which is commonly used for electrochemical measurement. The surface roughness variation of ECR carbon film is only about  $\pm 0.2$  nm, which is almost atomic level. In our previous report, we applied the film for measuring alkylphenols including nonylphenol which is well known as endocrine disruptor. We observed stable current response of alkylphenols by CV and FIA measurements. In contrast, we observed a clear reduction in the CV and FIA peaks when we used commercially available carbon and graphite-like carbon film electrodes. Although, the potential window of the film is wider than that of glassy carbon electrode, it is still insufficient to measure the analyte which oxidation potential is above 1 V. In this paper, we report the electrochemical response of ECR sputter deposited carbon film electrode containing more  $sp^3$  bindings than that of previously reported film and electroanalysis of some biomolecules.

Before sputtering, we cleaned the silicon substrate (2 inches, n-type 10-50  $\Omega$ ) with an argon ion beam. The carbon film was formed by using the ECR sputtering equipment (NTT Afty). To control the ion irradiation current density and ion acceleration voltage independently, we introduced a radio frequency bias setup for the substrate holder. The sputtering targets were sintered carbon. We performed the sputtering with the substrate at the temperature below 200  $^{\circ}\text{C}$ , which is much lower than the typical deposition temperature for boron-doped diamond (BDD) and the glassy carbon preparation. We controlled the Ar gas pressure at 0.05 Pa, controlled the ion acceleration voltage. The dc voltage is kept at 500 V during deposition (approximately 15 min). The content of the  $sp^3$  bindings in the ECR carbon film is varied by changing the sputtering conditions. The obtained film thickness is about 40 nm.

We then cut the wafer into a rectangle and fixed a

plastic tape with a 3 mm (or 6 mm) diameter hole in it to the carbon film to form disk electrode. Cyclic voltammetry and chronoamperometry were performed with a ALS/CHI 750 electrochemical analyzer with the ECR carbon films as a working electrode, an Ag/AgCl (3M KCl) reference electrode and a platinum auxiliary electrode. We also performed FIA experiments with ALS system and a thin layer radial flow cell (BAS, West Lafayette, IN, USA). The electrodechemical properties of the ECR carbon film electrode were compared with those of GC electrode.

The resistance of the ECR carbon film is increased by increasing the  $sp^3$  content. Therefore, the peak separation increases with increasing potential sweep rate at the ECR film with higher  $sp^3$  content. For example, the peak separation of water soluble ferrocene derivatives (aq-Fc, conc.=100  $\mu\text{M}$ ) is about 78 mV at GC electrode when the potential sweep rate is 100 mV/s. In contrast, the peak separation increases from 113 mV to 330 mV when increasing  $sp^3$  content in the ECR films. In contrast, the capacitive current of ECR film electrode is about 1 order of magnitude lower than that of GC electrode. This low capacitive current might be due to small surface area of the ECR film and lower density of the functional groups such as carboxyl and hydroxyl groups on the electrode surface. In fact, we observed that the surface oxygen peak of the ECR film is lower than that of GC electrode. Due to the low capacitive current, the background current of ECR film is only 0.7 nA 60 min after applying the potential of 0.7 V (vs Ag/AgCl), whereas, it is about 12 nA at the GC electrode with same measurement condition. This low background current is important to apply the electrode for detecting trace level analyte. We also compared the oxidation current of histamine at the ECR film and GC electrodes. When we swept the potential from 0 to 1.4 V, the histamine peak is clearer at GC electrode than that at ECR film, since histamine peak appeared at more positive region. This is because the peak shifts more positive due to higher resistance of the film. In contrast, the histamine peak is much clearer at the ECR film than that at GC electrode with much lower background current. This suggests that the ECR carbon film should be applied for obtaining improved detection limit of the analyte with high oxidation potential. A further study for detecting other biomolecules such as oligonucleotide will be shown in the separate report.

### References

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