Electrochemical properties of sputter deposited diamond-like carbon film and graphite-like carbon film electrodes containing metal nano-particles

Osamu Niwa[1], Tianyan You[1], Katsuyoshi Hayashi[1], Masato Tomita[1] and Shigeru Hirono[2]

NTT Microsystem Integration Laboratories, NTT Corporation[1], 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, NTT Afty Corporation, Midori-cho, Musashino, Tokyo, 181-8585, Japan[2].

INTRODUCTION

Various kinds of new carbon materials have been developed for electroanalysis and electrochemical sensor applications. Boron-doped carbon film has a wide potential window and a stable baseline current and is now used to measure various analytes [1, 2].

A simple film formation process such as low temperature film deposition is required for a number of applications including film electrodes on plastic substrates. We prepared diamond-like carbon film by the electron-cyclotron-resonance plasma (ECR) sputtering method [3, 4]. This film is amorphous-like and has an extremely flat surface. Here, we report the structure and electrochemical properties of ECR sputter deposited film. In addition, we describe the electrochemical properties of carbon film electrodes containing metal nano-particles designed to detect various analytes such as neurotransmitters.

EXPERIMENTAL

We formed carbon film using ECR sputtering equipment (NTT Afty). To control the ion irradiation current density and ion acceleration voltage independently, we introduced an RF-bias setup for the substrate holder in conventional ECR apparatus. We deposited non-hydrogenated amorphous carbon films on the surfaces of silicon substrates using the ECR sputtering method at low temperature (around 100 ℃). We characterized the film using AFM, TEM, Raman spectroscopy and XPS. We then used the film to detect alkyl-phenols that are known to be endocrine disruptors and which easily foul the electrode surface after electrochemical oxidation. We also fabricated a Pt-nanoparticle dispersed carbon film electrode. We characterized the electrode using TEM and XPS and evaluated the electrochemical properties with cyclic voltammetry and flow injection analysis. The film was used as a detector in liquid chromatography to detect trace amounts of acetylcholine (ACh), which is a well-known neurotransmitter.

RESULTS AND DISCUSSION

The XPS spectra of ECR sputter deposited carbon film proved that the film was composed of sp^2 and sp^3 bond hybrids. The results obtained by means of TEM, conductivity measurements, Raman and XPS spectra showed that the structure of ECR sputter deposited carbon film is different from that of diamond, HOPG and GC film. Variations in the oxidation peaks of various alkylphenols obtained by CV at ECR carbon film and GC are shown in Figure 1. The CV was measured with a 5 minute interval. The peak current decreased more rapidly for the phenols with longer alkyl chains at the conventional GC electrode. In contrast, the oxidation current was much more stable at the ECR carbon film electrode. This suggests that the passivation of the oxidized phenols on the electrode surface is suppressed at the ECR carbon film. We also studied the variation in electrochemical properties under different sputtering conditions.

When we co-sputter deposit Pt and carbon by the RF-deposition method, the obtained film is graphite-like containing 2-3 nm diameter Pt nano-particles [5]. The film shows excellent electrochemical performance for hydrogen and oxygen reduction and hydrogen peroxide oxidation. We used the film as a liquid chromatography detector to determine ACh and choline (Ch). Figure 2 shows the chromatogram we obtained when we injected 100 fmoles of ACh and Ch using a separation column and an enzymatic reactor inmobilized with ACh esterase and Ch oxidase. The baseline shift was more stable and had a lower background noise level than obtained with the Pt bulk electrode. The baseline was stable because Pt nano-particles are stable against oxidation. Other metal dispersed carbon film electrodes such as Pd and Ni dispersed films will be introduced.

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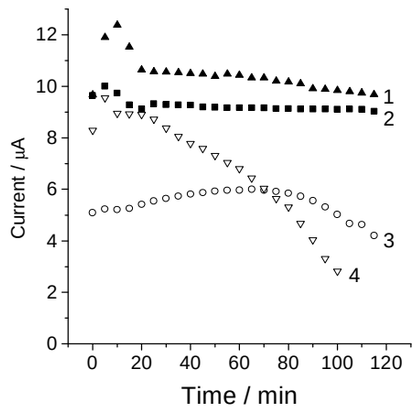

Figure 1 Variation in anodic peak current of CVs for 100 μ M of ρ–nonylphenol (1,4) and ρ-hexylphenol (2,3) obtained at ECR carbon (1,2) and GC (3,4) electrodes.

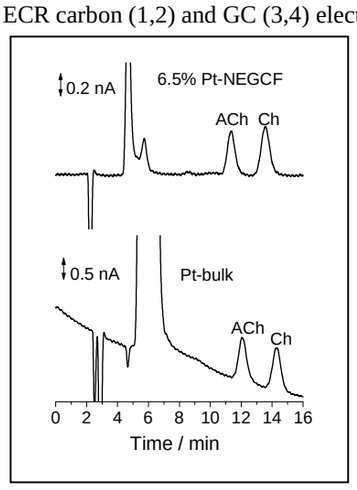

Figure 2 Chromatograms of ACh and Ch (100 f moles) at carbon and Pt bulk electrodes containing dispersed Pt nano-particles .