The Basic Electrochemical Properties and Structure of Direct Current Magnetron Sputtered Carbon Films

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ABSTRACT

In recent years, carbon films have attracted interest as electrode materials for electrochemical sensors due to their wide potential window and acceptable electrochemical activity. The films can be fabricated into electrodes of any shape and size. The electrochemical performance of the films depends on their structural features such as the ratio of the sp2 and sp3 bonds, and the surface functional groups. Here, we report the control of both structure and electrochemical properties based on carbon films fabricated by easily available direct current (DC) magnetron sputtering equipment. The sp3 concentration (sp3/sp3 + sp2) can be controlled from 0.22 to 0.29 by changing the substrate bias power, which can be characterized with X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The potential window became wider as the sp3 concentration increased, similar to the results we previously obtained with unbalanced magnetron (UBM) sputtering. The electrochemical properties of DC magnetron sputtered carbon films were examined with four species, namely Ru(NH3)63+/4+, Fe(CN)63−/4−, Fe3+/2+, and dopamine. The peak separation of these species depended on the content of the edge plane of the film for Fe(CN)63−/4− and surface functional groups containing oxygen for Fe3+/2+, and both edge plane and surface oxygen-containing groups for dopamine. These results indicate that our carbon films perform sufficiently well for use in electroanalysis and are not inferior to previously reported carbon film electrodes.

1. Introduction

Carbon films are widely employed in electrochemical analysis because they are mass-producible and can be fabricated with any shape and size.4 Carbon films fabricated by the pyrolysis of organic (or polymeric) films can have a similar structure to that of glassy carbon,7–5 which exhibits good electrochemical activity. However, the films are often porous and require the substrates to be used at very high temperature. In contrast, carbon films deposited by vacuum processes including direct current (DC) magnetron sputtering,8–3 radio frequency (RF) magnetron sputtering,9,10 electron cyclotron resonance (ECR) sputtering,11,12 electron beam evaporation,13 and a filtered cathodic vacuum arc (FCV A) system,14 produce flat but more amorphous structures similar to diamond-like carbon (DLC), which reduces electrochemical activity.

Ferrari et al. published a ternary phase diagram of amorphous carbons, which clearly shows the relationships between DLC structures and hydrogen, sp2 and sp3 carbons.15 However, the diagram does not include high-order structural features such as degree of crystallinity, which is strongly related to electrochemical activity. Hirono et al. reported nanocarbon films formed by electron cyclotron resonance (ECR) sputtering.11 The films contain a nanographene structure, which decreases with increasing sp3 concentration. In contrast, ECR nanocarbon films with higher sp3 concentrations have excellent electrochemical properties such as sufficient electrochemical activity, lower noise, and a wider potential window, as our group reported previously.16,17

Kamata et al. subsequently reported similar carbon films prepared with unbalanced magnetron (UBM) sputtering.18 The sp2 and sp3 ratios could be well controlled by the different subtracted bias voltage between the target and substrate. More recently, Diao et al. reported carbon films fabricated by ECR sputtering containing a larger graphene structure that was realized by using low-energy electron irradiating carbon atoms instead of ion irradiation.12,19 The films have rougher surfaces than previously reported ECR nanocarbon films but exhibit better electrochemical activity. However, such equipment is not widely used and the cost is very high. In contrast, DC magnetron sputtering equipment has been commonly used to fabricate conducting films including carbon. Freire et al., Broitman et al., and Zeng et al. reported DLC carbon film prepared with a DC magnetron sputtering method, and the amorphous carbon structure realized electrochemical stability, a lower capacitive current and a smaller surface area.5–8 Here, we report the structure and basic electrochemical properties of DC magnetron-sputtered carbon films prepared with different substrate biases. We expect the application of bias to allow us to control such aspects of the film structure as sp3 concentration and improve the ordering of the film thus realizing better electrochemical activity. We characterized the surface structure of DC-sputtered carbon films using X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM). The basic electrochemical properties were studied and compared with those of UBM-sputtered carbon films by measuring the cyclic voltammetry of several redox species with different electron-transfer properties. The effect of surface functional groups on the electrochemical properties was also studied by employing DC sputtered carbon films deposited under different conditions. This is because the content of surface functional groups can affect the electron transfer kinetics of organic biochemicals.20

Keywords: Direct Current Magnetron Sputtering, Electrochemistry, Carbon Film Electrode
2. Experimental

2.1 Materials

All of the chemicals employed in this study were of analytical grade and used as received without further purification. Hexamine-ruthenium (III) chloride (Ru(NH3)6)Cl3 and dopamine hydrochloride were purchased from Sigma-Aldrich (Tokyo, Japan). Potassium chloride (KCl), iron (II) chloride tetrahydrate (FeCl2·4H2O), and potassium hexacyanoferrate (III) (K3[Fe(CN)6]) were purchased from Wako Pure Chemical Industries (Tokyo, Japan). The glassy carbon electrode (GC) was purchased from BAS (Tokyo, Japan).

2.2 Carbon film preparation

The carbon films were deposited on highly doped silicon (100) substrates with DC magnetron sputtering equipment. The Ar gas pressure was 2.5 × 10−1 Pa. The substrate temperature was 200°C, and the voltage and current of the target were 640 V and 0.68 A, respectively. In the film fabrication, DC is applied to the target and RF bias is applied to the substrate. The powers of substrate bias were 0, 12, 20, 30, and 35 W (namely, the substrate biases were 0, −130, −230, −300, and −350 V). The DC carbon film formation time was less than 5 mins.

2.3 Carbon film characterization

The surface properties of the DC carbon films were characterized by X-ray photoelectron spectroscopy (XPS, ESCA Quantum 200, Ulvac-phi Co., Japan) using Al Kα monochromatic X-rays (1486.6 eV) to determine the elemental composition and the quantity of chemical bonds in the carbon film electrode surfaces. The surface structure of the DC carbon films and UBM nano carbon film were characterized by a high-resolution transmission electron microscopy (TEM, Tecnai Osiris, FEI Co., Japan) with a point-to-point resolution of 0.25 nm, and the acceleration voltage is 200 kV.

2.4 Electrochemical measurements

Cyclic voltammograms (CVs) were obtained with an electrochemical analyzer (ALS model 720E BAS Co. Ltd., Tokyo, Japan) using a three-electrode system. DC carbon films, Ag/AgCl (RE-3 V BAS Co. Ltd., Tokyo Japan) and Pt wire were used as working, reference and counter electrodes, respectively. All of the chemicals employed in this study were of analytical grade. Hexaammineruthenium (III) chloride [Ru(NH3)6]Cl3 and dopamine hydrochloride were purchased from Sigma-Aldrich (Tokyo, Japan). The glassy carbon electrode (GC) was purchased from BAS (Tokyo, Japan).

3. Results and Discussion

3.1 Surface characterizations of DC sputter deposited carbon films

We prepared DC magnetron sputtered carbon films under different conditions by changing the power of the substrate bias (0, 12, 20, 30, and 35 W). The carbon films were characterized by XPS and TEM measurements. Figure 1 compares the C 1s TEM spectra of DC carbon films formed with different substrate powers (to generate the substrate bias) (0, 12, and 30 W) and UBM carbon film formed at −20 V.

As shown in Fig. S1(B), the C 1s XPS spectra were fitted into two peaks by using Shirley's method as we reported previously.16,18 The peaks that appeared at 284.5 and 285.5 eV were assigned to sp2 and sp3 hybrids, respectively. And GC consists of sp2 bonds, and approximately without sp3 bonds, thus the sp2/total sp and sp3 ratio of GC is 0%.21 The sp2/sp3 + sp2 ratio obtained from the C 1s XPS spectrum and the content of oxygen-containing functional groups obtained from the O 1s XPS spectrum are summarized in Table 1. The sp2 ratio increased as the substrate bias increased from 0 to 12 W, and then the ratio gradually decreased as the bias was further increased from 12 to 35 W. The sp2 content of DC carbon film is insufficient compared with that of UBM carbon film, suggesting that high-energy ion irradiation is beneficial as regards the formation of sp3 structures on the carbon surface during UBM sputtering. These results indicate that the sp2 content could be successfully controlled by employing DC sputtering equipment, which is simpler and less expensive than ECR and UBM sputtering equipment.

We also obtained the TEM images of the carbon films as shown in Fig. 1. The film prepared with a 0 W bias has an amorphous structure without any observable layered nanocrystalline graphite structures. With the bias increased to 12 W, layered structures can be observed. A further increase in bias up to 30 W increases the layered graphene structure as shown in Fig. 1(C). In our previous report using UBM sputtering, the increase in the bias voltage from 0 to −75 V increased the size of the nanocrystalline structure and improved the electron transfer rate of Fe(CN)64−/3−,18 which agrees well with the result we obtained when we increased the bias power to 30 W. Therefore, we must further optimize the sputtering condition and study the mechanism if we are to control the sp2 ratio with DC magnetron sputtering.

Table 1 also shows the ratio of oxygen-containing functional groups and O/O + C ratios of DC carbon films prepared by different power of bias. The O/O + C ratio is varied from 0.21 to 0.67 at% and it tends to decrease as the current power increases, which might affect the electrochemical properties of redox species.

3.2 Potential windows of DC-sputtered carbon films

As we previously reported with ECR and UBM sputtered carbon
film electrodes, we varied the sp³ concentration and potential window by changing the substrate bias. It is significant that we are able to control such structures and properties using less expensive and commonly used DC sputtering equipment. Figure 2 shows voltammograms of GC and carbon films with different biases (12 and 30 W) in 0.05 M H₂SO₄ solution with a scan rate of 100 mV/s. The potential window is defined as the potential range between current limits that do not exceed 500 µA/cm², as Swain et al. previously reported.22 As shown in Fig. 2, the potential window of the film prepared with a bias is significantly extended compared with GC and 12 W film. Figure 3 shows the relationship between the sp³/ sp³ + sp² ratio of the GC and carbon films and their potential window. The potential window of a GC electrode is 2.70 V as shown in Fig. 2. The potential windows of carbon films increase from 2.90 to 3.44 V as the sp³/sp³ + sp² ratio increases from 0.22 to 0.29, which agrees well with the results obtained with ECR and UBM sputtered carbon films, although the controllable range of the sp³/ sp³ + sp² ratio and the widths of the potential windows are limited.16,18

3.3 Basic electrochemical properties of DC carbon films
Since the redox behavior of electroactive species are varied by reflecting the carbon film structure, we compared the responses of Ru(NH₃)₆³⁺/²⁺, Fe(CN)₆⁴⁻/³⁻, Fe²⁺/³⁺, and dopamine at DC-magnetron sputtered carbon film, UBM sputtered carbon film and commercially available GC electrodes as shown in Fig. 4. Figures 5(A) and 5(B) show the relationships between the peak separations (ΔE) calculated from voltammograms and the sp³/ sp³ + sp² ratio. Ru(NH₃)₆³⁺/²⁺ is known to be an outer-sphere redox system that is insensitive to surface functional groups. Therefore, the ΔE values of Ru(NH₃)₆³⁺/²⁺ are similar at DC-magnetron sputtered carbon films with different sp³ concentrations,
UBM-sputtered carbon films and GC electrodes as shown in Figs. 4(A) and 5(A).

The voltammograms of 1 mM Fe(CN)₆⁴⁻/³⁻ at three carbon electrodes are shown in Fig. 4(B). It has been reported that Fe(CN)₆⁴⁻/³⁻ is an inner-sphere redox system and sensitive to the edge-plane structure.¹⁸ Therefore, GC shows the narrowest peak separation when compared with DC and UBM carbon films because GC has a much more ordered edge-plane graphene structure than DC magnetron and UBM carbon film electrodes. Kamata et al. reported that the nanocrystalline graphene structures observed in a TEM image of UBM sputter deposited carbon film decreases with increasing sp³ concentration.¹⁸ With DC magnetron sputtered carbon film, the ΔE value of Fe(CN)₆⁴⁻/³⁻ also increases with increasing sp³ concentration as shown in Fig. 5(B), which is similar but little inferior to the result for UBM carbon film. Unlike Fe(CN)₆⁴⁻/³⁻, an Fe²⁺/³⁺ redox system is sensitive to a group containing surface oxygen. In fact, a voltammogram of Fe²⁺/³⁺ at a GC electrode reveals a smaller ΔE than those at UBM and DC magnetron sputtered carbon film electrodes. This is because the GC was well polished just before the measurement, and so surface oxidation could be minimized. The relationship between ΔE and OPh-OH/(C + O) is shown in Fig. 5(C), which clearly indicates that ΔE decreases with increasing surface OPh-OH concentration similar to the previous results obtained with UBM sputtered carbon film electrodes.¹⁸ Figure 4(D) compares voltammograms of DA at three carbon electrodes and Fig. 5(D) shows the relationship between ΔE and OPh-OH/(C + O) of DA. ΔE decreases with increasing OPh-OH/(C + O). This result agrees well with previous work by McCreery et al. who reported that surface anionic sites improved the DA reaction rate by employing a GC electrode.¹⁸ However, the correlation between ΔE and OPh-OH/(C + O) is not as good as that observed with an Fe²⁺/³⁺ redox system. Therefore, we also plotted the relationship between ΔE and sp³/sp² for DA as shown in Fig. S2. ΔE increases as the sp³ ratio decreases, suggesting that the amount of edge plane also contributes to the redox reaction of DA. Since the redox properties of the above four redox systems agreed well with the results for UBM carbon films, carbon films formed by DC magnetron sputtering can be used for electrochemical measurement whose performance is not inferior to that of previously reported carbon films prepared with more expensive equipment.

4. Conclusion

We studied the structure and electrochemical properties of DC-magnetron sputtered carbon film electrodes prepared with different substrate bias powers and compared the results with those obtained for previously studied UBM sputtered carbon film and GC electrodes. With inexpensive DC magnetron sputtering equipment, the sp³ concentration can be controlled by changing the bias power, and the potential window increases with increasing sp³ concentration. The redox reaction of four redox species agreed well with our previous results obtained with UBM sputtered carbon films. Although the controllable sp³ concentration region is not still wide (about 10%) compared with that of UBM sputtered carbon films, further optimization of the sputtering conditions such as substrate bias power and pressure might realize a more controllable carbon film structure and electrochemical properties.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.20-00142.

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