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New method to calibrate binding energy using Au nanocolloids in X-ray photoelectron analysis of diamondlike carbon films with different electrical resistivities

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Abstract

A new method to calibrate the binding energy (E_B) using Au nanocolloids as a calibrant in XPS analysis of diamondlike carbon (DLC) is proposed by considering the DLC films with different electrical resistivities. A few microliters of a dilute aqueous solution containing Au nanocolloids were dropped onto a small local surface area of the DLC film, which became a stain before XPS measurements by gradually drying *in vacuo*. The observed peak E_B of the C 1s spectrum at another native surface (an area without Au nanocolloids) of the DLC film was calibrated by setting that of the Au 4f$_{7/2}$ spectrum of the Au nanocolloids to 84.0 (83.98 ± 0.02) eV. The adequacy of this method was investigated by considering the correlation among the full width at half maximums (FWHMs) of the Au 4f$_{7/2}$ spectra of the Au nanocolloids on the DLC surfaces and that of a Au plate as a reference. Consequently, the FWHM of the Au 4f$_{7/2}$ spectrum of the Au nanocolloids on the DLC surface is a candidate to investigate the differential charging effect of the DLC surface, and the calibration method is reliable if the FWHM agrees with that of the Au plate.

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1. Introduction

Diamondlike carbon (DLC) is an amorphous material, which is composed of sp^2 carbon, sp^3 carbon, and hydrogen [1]. Its surface characteristics are interesting for applications of lubricative surface coating and surface modification. A lot of surface analyses using X-ray photoelectron spectroscopy (XPS), which is one of the most suitable tools for surface analysis, have been reported [2–19]. However, they are different by authors thus the reliable analysis is required.

The shape and location of the XPS C 1s spectrum for DLC are very meaningful because they imply not only information on the C 1s core level state, but also that on the valence band, which is secondarily influenced by the remaining photoholes [19,20]. Thus, calibrating the binding energy (E_B) in XPS analysis of DLC is especially important. In the XPS analysis of a carbonaceous material or a material containing carbon, E_B is usually calibrated by setting the peak E_B of the C 1s spectrum to 284.6 eV [21–24]. However, the value is varied because of the variety of carbonaceous materials, and moreover the method is inconsistent when analyzing the C 1s spectrum itself. Another calibration method uses the Au 4f$_{7/2}$ spectrum (83.98 ± 0.02 eV for Al Kα line) of a Au film [23,25] at a local surface area of a material prepared by vacuum evaporation. Au is stable and may not influence the properties of the carbon components. However, the area where the Au film is prepared is difficult to control by vacuum evaporation and the peak E_B shifts depends on the film preparation [26–30]. Furthermore, the film is contaminated with carbon due to the heated filament, which inevitably affects carbonaceous materials in a negative manner. Thus, this method

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is not suitable for surface analysis of carbonaceous materials. Moreover, DLC is a semiconductor, and the electrical resistivity depends on the preparation. Thus, DLC usually causes ‘‘differential charging’’, which does not supply the surface with electrons sufficiently and uniformly, and complicates the XPS analysis [23,31–36]. In this paper, we propose a new method to calibrate E_B using Au nanocolloids [37] as a calibrant in XPS analysis of DLC by considering the DLC films with different electrical resistivities. We think that this method will overcome the drawbacks listed above.

2. Experimental

DLC films with different electrical resistivities were purchased from Machinery & Engineering Company, Kobe Steel, Ltd. The unbalanced magnetron sputtering (UBMS) method [38–43], which is an improved magnetron sputtering method, was used to prepare 200 nm thick DLC films on 625 μm thick single-crystal Si(1 0 0) wafers (10 mm × 10 mm) with a low electrical resistivity (0.1 Ω cm). The target was graphite fixed in the chamber. To control the electrical resistivity of the DLC films, the ratio of CH_4/Ar gas in the atmosphere was varied [44]. Table 1 lists the correlation between the ratio of CH_4/Ar gas during preparation and the electrical resistivity of the DLC films.

The electrical resistivities of the samples (a), (b), and (c) listed in Table 1 were measured by the ‘‘four’’-point probe method [45,46] in a vacuum chamber having four probes designed by Seinan Kogyo Co., Ltd. equipped with a KEITHLEY 4200 semiconductor characterization system. All measurements were carried out at room temperature at a pressure about 1×10^{-1} torr. Four probes were contacted with the DLC surface in a line at regular intervals of 1 mm. A known current is flowed from one outside probe to another through the surface of the sample, and the voltage between the inside probes is measured. If the thickness of the film t is much thinner than the probe interval d ($t \ll d$) and the diameter of the film L is much larger than d ($d \ll L$), the (volume) electrical resistivity by the four-point probe method ρ_{v4} is calculated by Eq. (1)

$$\rho_{v4} = \left(\frac{\pi}{\ln 2}\right)\frac{V}{I}t \approx 4.53\frac{V}{I}t \quad (1)$$

where V is the observed voltage, and I is the observed current. Here the DLC film is assumed to be a homogeneous film in electrical resistivity without showing the anisotropy such as highly oriented pyrolytic graphite (HOPG) though DLC is amorphous. When comparing the XPS analysis with the electric resistivity, it is appropriate to use the concept of the sheet (surface) electric resistivity $\rho_{s4} = \rho_{v4}/t$ instead of the volume electric resistivity ρ_{v4} because the escape depth of the XPS photoelectron is only a few nm and several tens atomic layers. However, in this comparison we also observed the DLC film with a higher electric resistivity, which cannot be measured by the four-point probe method, thus we used the concept of the (volume) electric resistivity.

Table 1
List of the preparation conditions for the DLC films with different electrical resistivities by the UBMS method

Sample	Electrical resistivity (Ω cm)	Ratio of CH_4/Ar gas in the atmosphere
(a)	$(2.4 \pm 0.1) \times 10^{-1}$	0/100
(b)	$(2.7 \pm 2.0) \times 10^{2}$	6/100
(c)	$(2.0 \pm 1.4) \times 10^{5}$	12/100
(d)	$(2.4 \pm 2.8) \times 10^{10}$	36/100

The electrical resistivity of the other sample (d) listed in Table 1 was measured by the ‘‘two’’-point probe method instead of the four-point probe method because its electrical resistivity was too high. One probe was contacted with the Al pad with a diameter of 1.5 mm (1.77 mm^2) prepared on the DLC surface by vacuum evaporation through a mask. Another probe was contacted with the conductive sample stage as the earth, on which the sample was fixed through a silver paste. A known current is flowed from one probe to another through the sample perpendicularly, and the voltage between the same probes is measured. The electrical resistivity by the two-point probe method ρ_2 is calculated by Eq. (2)

$$\rho_2 = \frac{V}{I}\frac{S}{t} \quad (2)$$

where S is the area of the pad. The electrical resistance measured by the two-point probe method is a result of a series resistance between the contacts of the probes and is not equal to the true value of the DLC film. However, the electrical resistance of the DLC film (d) is much higher than the other resistances. Thus the result is almost same as the true value.

The XPS measurements were conducted on a surface area of 0.8 mm × 2.0 mm with an ULVAC-PHI PHI 1600 system with an unmonochromated Al Kα (1486.3 eV) line, which had a voltage of 15 kV and a power of 400 W. All measurements were carried out at room temperature at a pressure below 3.0×10^{-9} torr. The background line of every spectrum was subtracted by the Shirley method [23,47,48]. As estimated from the Fermi edge of the Au valence band spectrum of a Au plate, the energy resolution of the system was 0.6 eV.

Before the XPS measurements, a few microliters of a dilute aqueous solution, which contained the Au nanocolloids with a diameter of 11 nm [37], were dropped onto a small local surface area of the DLC film, which measured about 2 mm × 2 mm, using a syringe in air. The DLC surface with the Au nanocolloids was then gradually dried *in vacuo* to be a stain. It should be noted that the Au nanocolloids are larger than the Au clusters with a diameter below 3 nm which show the size-dependent XPS spectra, and thus the XPS spectrum of the Au nanocolloids can be regarded as same as that of a Au plate [49,50]. Moreover, the characteristics of the Au $4f_{7/2}$ spectrum of the Au nanocolloids do not depend on the takeoff angle of the photoelectrons because the Au nanocolloids are randomly deposited on the DLC surface [51].

3. Results and discussion

Table 2 lists the components of the DLC surfaces with and without Au nanocolloids. These components were roughly