論文

グロー放電発光分析法による炭素堆積層の分析

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Measurements of Carbon Deposition Layers using Glow-Discharge Optical Emission Spectroscopy (GDOES)

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Abstract

In fusion devices with plasma-facing components manufactured from carbon-based materials, co-deposition of hydrogen isotopes and carbon takes place in regions where sputtering rate is relatively small. Fuel retention and recycling depend on properties of those deposits. Glow-discharge optical emission spectroscopy (GDOES) is one of attractive techniques to analyze chemical composition and thickness of these deposition layers. However, influence of hydrogen content on sputtering of these layers by glow-discharge plasma is not fully understood. In this study, two different types of carbon layer with quite different hydrogen content were deposited on stainless steel

substrate, and sputtering rate during the GDOES measurement was examined for better interpretation of results obtained.

1. Introduction

Carbon materials such as isotropic graphite and carbon fiber composite have been used as plasma-facing materials in fusion device because of various preferable properties of carbon that includes high thermal conductivity, high thermal shock resistance and low efficiency of radiation cooling of plasma due to small atomic number of carbon. However, interaction of hydrogen isotope plasma with carbon-based plasma-facing materials results in sputtering erosion. Eroded particles emitted from the plasma facing materials will form re-deposited carbon layers in areas where deposition rate is larger than erosion rate. These deposition layers in general contain a large amount of hydrogen isotopes and consequently have strong influences on tritium inventory and fuel recycling. In addition, the deposition layers degrade reflectivity of mirrors for plasma diagnostics. It is therefore important to reveal properties of the carbon deposition layers such as thickness, density, contents of hydrogen isotopes, etc.

Glow discharge optical emission spectroscopy (GDOES) is a technique to measure depth profiles of constituent elements in a solid specimen by detecting emissions from atoms accommodated in plasma by sputtering of a specimen surface [1,2]. This technique allows very quick measurements with relatively high depth resolution (a few nanometers) because ultra-high vacuum is not necessary. Besides, large-sized specimens are acceptable in the GDOES measurements. In addition, isotopic analysis of hydrogen and He detection are also possible [3]. These features of the GDOES technique are in general suitable for analysis of carbon deposition layers

formed in fusion devices. Indeed, Akiyama et al. [4] analysed the corner cube mirrors used in the Large Helical Device (LHD) and found that a thick carbon deposition layer was formed during the hydrogen glow discharge cleaning before the main plasma discharge.

There are, however, still several issues to be solved for detailed analysis of carbon deposition layers. One of those is influence of hydrogen content on sputtering rate. Sputtering rate is an essential parameter in depth profile measurements to convert sputtering time to the depth. In addition, signal intensity in GDOES measurements is proportional to sputtering rate. Carbon deposition layers formed in fusion devices contains hydrogen isotopes in various concentration levels, but the correlation between sputtering rate of the carbon deposition layers and hydrogen isotope content has not been examined. Another issue is change in sputtering rate at interface between the deposition layer and substrate material. In the depth profile reported by Akiyama et al. [4], intensity of carbon signal increases at the interface between the deposition layer and substrate stainless steel and then decreases with increase in depth in the substrate. One of the possible explanations for the observed increase in carbon intensity at the interface is the increase in sputtering rate at the interface. However, this idea has not been confirmed.

In this study, two types of diamond-like carbon films with different hydrogen contents were deposited on the stainless steel substrate and analyzed using the GDOES technique. Additionally, sputtering rates of these films and substrates were examined using a surface profiler. The influence of hydrogen content on the sputtering rate was discussed as well as the mechanisms underlying the increase in carbon intensity at the interface.

2. Experimental

Plates of type-304 stainless steel (SS304) (50×20×1 mm) were used as substrates. These SS304 plates were mirror-finished and then heated in vacuum (10^{-5} Pa) at 1073 K for 4 hours to remove hydrogen being present in the plates as an impurity. Two different types of diamond-like carbon films were deposited on the steel plates in Hokunetsu Co., Ltd., Toyama, Japan. The first type was a conventional diamond-like carbon film fabricated using a technique of unbalanced magnetron sputtering. The source of carbon was a solid target and CH_4 gas. In what follows, this film will be denoted as the DLC film. The second type was a tetrahedral amorphous carbon film prepared using an arc ion plating technique with a solid carbon target, denoted hereafter as the DLC-i film. According to the manufacturer, the mass densities of the DLC and DLC-i films are 2.2 and 3.2 g cm^{-3}, respectively.

The hydrogen contents in the DLC and DLC-i films were measured using thermal desorption spectroscopy (TDS). The samples were heated up to 1273 K at a ramp rate of 0.5 K s^{-1}. The films were analyzed using GDOES apparatus (Horiba GD-Profiler2) operated with Ar plasma at 650 Pa and 35 W. The depth of craters formed by Ar sputtering was measured using a surface profiler (Tokyo Seimitsu SURFCOM 1500DX). All these measurements were performed at the Center for Research and Development in Natural Sciences, University of Toyama.

3. Results

Thermal desorption spectra of H_2 released from the DLC and DLC-i films are shown in Fig. 1. For the DLC film, the H_2 desorption started at about 530 K, whereas for the DLC-i film this temperature was shifted to about 830 K. The amount of H_2

desorbed from the DLC film was 1.5×10^{22} m^{-2}, whereas for the DLC-i film this value was 2.3×10^{20} m^{-2}. Note that the H content in the DLC film was higher by a factor of 65 than that in the DLC-i film because of use of CH4 gas in the fabrication process.

Depth profiles of C and Fe, the main constituent elements in the DLC specimen (i.e., in the DLC film deposited on the SS304 steel substrate), as measured by the GDOES technique, are shown in Fig. 2a. The interface between the deposited carbon layer and the steel substrate appears after sputtering for about 100 s. To determine sputtering rates of the diamond-like carbon deposition layer and the steel substrate, several different areas on the DLC specimen surface were subjected to sputtering for 30, 60, 98 (the interface) and 210 s, and depths of sputtering-formed craters were measured using the surface profiler.
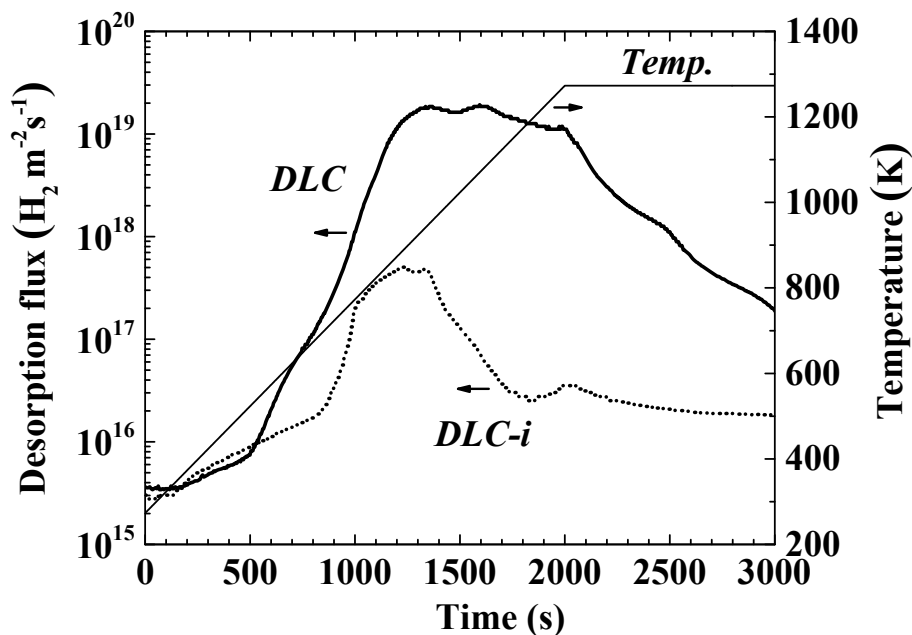

Fig. 1 Thermal desorption spectra of H2 released from a conventional diamond-like carbon film fabricated using a technique of unbalanced magnetron sputtering (DLC) and a tetrahedral amorphous carbon film prepared using an arc ion plating technique (DLC-i).

Fig. 2b shows the depth profiles of C and Fe in the DLC-i specimen, in which the interface is observed at the sputtering time of 13 s. For this DLC-i specimen, the crater depth was measured after the sputtering for 8, 13 (the interface) and 100 s. The
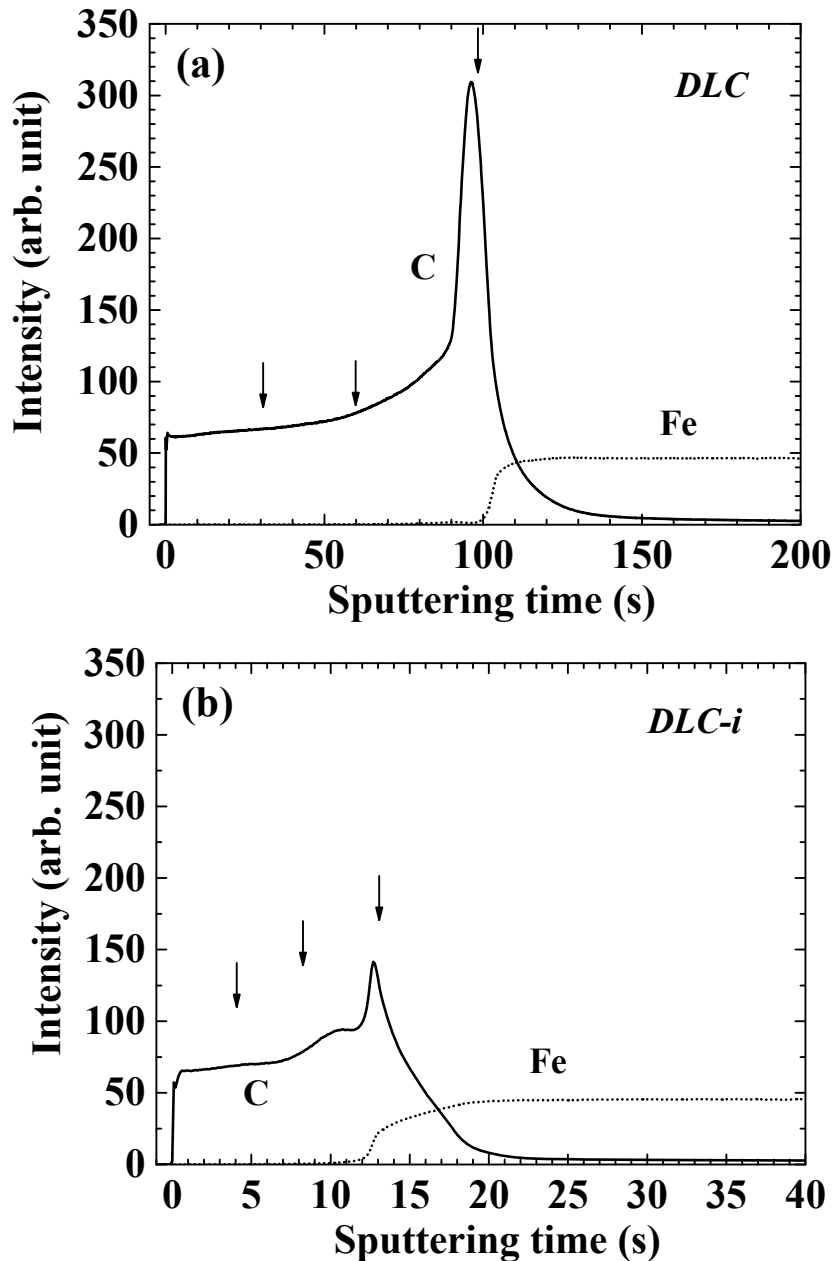

Fig. 2. Depth profiles of C and Fe in the DLC (a) and DLC-i (b) films, as measured by the GDOES technique. The crater depth was measured after sputtering for time period indicated by arrows. Results of the measurements are summarized in Table 1.

sputtering for 4 s was also performed, but accurate measurement of the crater depth was impossible due to too small depth.

Average sputtering rates and C signal intensities for the DLC and DLC-i specimens are summarized in Table 1. According to data summarized in Table 1, a thickness of the DLC and DLC-i films was 1600±60 and 240±40 nm, respectively. From these values of the layer thickness and the above-mentioned mass density and hydrogen retention, the average hydrogen concentration in the DLC film was evaluated to be $[H]/[C] \approx 0.17$, whereas in the DLC-i film the value $[H]/[C] \approx 0.01$; i.e., the average hydrogen concentration in the DLC-i film was lower by a factor of 17 than that in the DLC film. In this evaluation, the hydrogen concentration in the substrate was assumed to be negligibly small.

After beginning of sputtering, the C signal intensity (expressed in arbitrary units, a.u.) for the DLC film (~62 a.u.) was comparable with that for the DLC-i film (~65 a.u.).

Table 1 Results of depth profiling of the DLC (Fig. 2a) and DLC-i (Fig. 2b) films.

Specimen	Sputtering time (s)	Depth (nm)	Average sputtering rate, S_{av} (nm s^{-1})	C signal intensity (arb. units)
DLC	25	180±30	7±2	66
	60	610±60	10±1	78
	98	1,600±60	16.3±0.6	288
	210	10,000±800	48±4	–
DLC-i	4	–	–	67
	8	90±20	11±3	77
	13	240±40	18±3	130
	100	5,600±560	56±6	–

This C signal intensity increased with an increase in the crater depth and reached 310 a.u. for the DLC specimen and 140 a.u. for the DLC-i specimen at the interface, as shown in Figs. 2 (a) and (b). It should be noted that the average sputtering rate, S_{av}, also increased with an increase in the depth (Table 1). In other words, the sputtering rate of the diamond-like carbon deposition layers was clearly smaller than that of the steel substrate.

4. Discussion

In GDOES measurements, the signal intensity of element i, I_i, is

$$I_i = a \cdot W_i + b, \tag{1}$$

where a is the sensitivity factor of element i, W_i is the mass of element i sputtered per unit area in unit time $(g \cdot cm^{-2} \cdot s^{-1})$, and b is the background. Here,

$$W_i = C_i \cdot \rho \cdot S, \tag{2}$$

where C_i is the mass fraction of element i in a sample, ρ is the mass density of the sample $(g \cdot cm^{-3})$ and S is the sputtering rate $(cm \cdot s^{-1})$.
Therefore,

$$I_i = a \cdot C_i \cdot \rho \cdot S + b. \tag{3}$$

As described above, the C signal intensity at the interface was significantly higher than that at the near-surface region of the DLC and DLC-i films. In addition, the sputtering rate increased with increase in the crater depth. As indicated by Eq. (3), the C signal intensity is proportional to the sputtering rate. In the case of the DLC film, the C signal intensity at the interface (after sputtering for 98 s) was 288 a.u., and larger than that in the deposition layer (66 a.u. after sputtering for 25 s) by a factor of 4.4. On the other hand, the average sputtering rate, S_{av}, during sputtering at 0–25 s was 7 ± 2 nm·s^{-1}

(Table 1), whereas for sputtering at 60–98 s the value of S_{av} was evaluated to be 26 ± 2 nm·s^{-1}; the latter value was larger than the former one by a factor of 3.7. Thus, the differences in the C signal intensity and sputtering rate were comparable with each other. Hence, it is appropriate to consider that the increase in the C signal intensity at the interface was due to increase in the sputtering rate. It was impossible to perform the similar comparison for DLC-i film since the crater depth after sputtering for 4 s could not be measured, as mentioned above. Further investigation on the interface microstructure (mixing of C and metal atoms, carbide formation, etc) is necessary to understand the mechanisms underlying the enhanced sputtering at the interface.

The C signal intensities for the DLC and DLC-i films immediately after beginning of sputtering were comparable. This observation suggests that, for the DLC and DLC-i films, the masses of C sputtered per unit area in unit time were also comparable (see Eq. (1)) despite the significantly different hydrogen concentration ($[H]/[C] \approx 0.17$ in the DLC film and $[H]/[C] \approx 0.01$ in the DLC-i film). It means that the C signal intensity in the GDOES measurement was insensitive to hydrogen content in deposited diamond-like carbon film. On the other hand, because the mass density of the DLC-i film (3.2 g·cm^{-3}) was higher than that of the DLC film (2.2 g·cm^{-3}), the sputtering rate (nm·s^{-1} or cm·s^{-1}) of the DLC-i film should be smaller than that of the DLC film (see Eq. (3)).

5. Summary

Two different types of diamond-like carbon films were deposited on type 304 stainless steel substrate and examined using the GDOES technique operated with Ar plasma. The first carbon film was characterized by the mass density of 2.2 g·cm^{-3} and

hydrogen concentration of [H]/[C]~0.17. For the second carbon film, the corresponding parameters were 3.2 g·cm^{-3} and [H]/[C]~0.01, respectively. In the GDOES measurements, the C signal intensities for these two films were comparable in a value despite the significant difference in the hydrogen concentration. This observation suggested that the amount of C sputtered per unit area and unit time was insensitive to hydrogen content. The C signal intensity markedly increased at the interface between the deposited film and stainless steel substrate. This increase in the C intensity was ascribed to an increase in the sputtering rate at the interface.

Acknowledgements

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