IRSTI 29.27.51

Etching characteristics of diamond-like carbon in fluorocarbon plasmas

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Diamond-like carbon (DLC) is one of the promising materials with biocompatibility. Applications for medical coating, biochip, and so on, have been widely expected in this decade. Fabrication process of biochips such as etching and removing requires patterning of the DLC to give surface of the chips functions for medical diagnostics. The present study reports etching characteristics of the DLC in fluorocarbon plasmas, comparing with those of Si and SiO_2. In the plasmas, F radical was found to be an etchant for the DLC, the same as etching of Si and SiO_2. The O radical is well known to be so reactive on the DLC. The O_2-addition to the plasmas was obviously effective in the DLC etching, and making balance of the radicals of F and O, resulting in changing etch rate of the DLC and morphology of surface. The etch rate could be controlled in changing gas flow rate of CF_4 to O_2 with Ar dilution. The morphology, which is indispensable to determine the characteristics on the surface of the biochip and so on, showed that fluorine-content plasmas suppressed roughness compared with pure-O_2 plasmas.

Key words: Diamond-like carbon, plasma etching, fluorocarbon, plasma.
PACS numbers: 52.77.-j, 52.77.Bn, 81.05.U-, 81.65.Cf

1 Introduction

Diamond-like carbon (DLC) has been focused attention on in many technological fields. The properties of electron emission, low friction, wear resistance, high hardness, chemical stability, and biocompatibility make it useful for applications of hard coating, semiconductor process, micro-electro-mechanical system, microfluidic channel, surgical implant, food, beverage, and so on [1-4]. Transparent glass and plastics have been commonly used as substrate materials of chemical/biochemical analysis chips since light is used for detection and observation of samples [5]. The DLC is one of the promising materials for the chips since it gives its excellent properties to surfaces of the glass and plastics substrates [6, 7]. In use of the DLC for the chips, patterning and removal processes are required to fabricate highly functional bio-analysis systems. Plasma etching can be widely used for the processes [8]. The DLC and its related materials are usually etched in oxygen- and hydrogen-content plasmas [9-11]. This paper presents results of the etching of DLC thin films on Si substrates in inductively coupled fluorocarbon plasmas. Then we discuss performance of fluorocarbon plasmas in etching of the DLC, and try to understand etching mechanism by comparing with those of Si and SiO_2 well known in previous works [12-15].

2 Experimental

Samples for etching were 1000-nm-thick DLC films on Si substrates prepared by chemical vapor deposition (CVD), SiO_2 films formed by thermal oxidation, and bare Si. The samples were cleaved into 2 cm^2 pieces and attached on 2-inch-diameter Si wafer, which was then clamped on to a wafer stage. Etching experiments were performed in a low-pressure inductively coupled plasma (ICP) reactor supplied with 13.56-MHz powers [16, 17]. An rf power supply was coupled to plasmas via three-turn planar rf induction coil of 15 cm in outer diameter, positioned on the quartz window located at the top of the reactor. The distance from the bottom edge of the rf coupling window to a wafer stage was 5 cm. Gasmixtures of CF_4, O_2, and Ar were introduced into the reactor evacuated to a base pressure < 4×10^{-4} Pa, and gas pressure was typically maintained at 3 Pa. The total gas flow rate was 40 sccm (sccm denotes cubic centimeter per minute at the standard conditions). The discharge was established at a nominal rf power of 300 W, corresponding to net powers to the π-type matching circuit driving the induction coil. The wafer stage was capacitively coupled to another 13.56-MHz rf power supply for additional biasing; the rf bias power was varied between 0 and 20 W (net power), resulting in a dc self-bias voltage on the stage down to -100 V. In etching, the samples were partly covered with thin glass plates as masks and exposed to the plasmas for several minutes. A step appeared on a boundary between a part etched by the plasmas and the other covered with the plate. Etch depth was determined to be height of the step measured by stylus profilometry. The chemical composition of carbon, fluorine and oxygen was analyzed by x-ray photoelectron spectroscopy (XPS) using Mg $K\alpha$ x-ray radiation with a pass energy of 50 eV at a takeo□ angle of 90˚. The contents of carbon, fluorine, and oxygen were detected with assigning peaks of C_{1s}, F_{1s}, and O_{1s}, respectively. The atomic force microscopy (AFM) was employed with a tapping mode to observe surfaces of the samples and record their morphologies.

3 Results and Discussion

Figure 1 shows etch rates of the DLC, Si, and SiO_2 as functions of the gas-mixture ratio, $[CF_4]/([CF_4]+[Ar])$ with self-bias voltage constant at -100 V in CF_4/Ar plasmas. In fluorocarbon plasmas, F radical is a dominant etchant for Si and SiO_2.[12] Furthermore, CF_x radicals work effectively in etching of SiO_2 [13–15]. In Figure 1, the etch rate of Si has the same tendency as that of SiO_2. Therefore, the F radical is a main product in the CF_4/Ar plasmas. The etch rate of the DLC has the same tendency as those of Si and SiO_2, and is lower than other samples. This means that the F radical indeed etches the DLC, but it is not so effective as for Si and SiO_2.

XPS spectra of C_{1s}, F_{1s} and O_{1s} signals on surfaces of the DLC samples are shown in Figure 2. The contents of C and F were increased on the surfaces with increasing the gas-mixture ratio of $[CF_4]/([CF_4]+[Ar])$. In the regime of the ratio greater than 0.2 where the etch rate of the DLC decreased monotonically, chemical bond components of C–CF_x and CF were detected at 287.3 and 289.5 eV and intensity of those signals increased with increasing the ratio [18]. This indicated that the surfaces of the DLC were fluorinated, i.e., terminated by fluorine in the plasmas. Conversely, the pre-etched sample and surface of sputter-etched by a pure-Ar plasma were oxidized. Dangling bonds produced in CVD and sputter-etching combined with ambient oxygen. In the CF_4/Ar plasmas, the F radical works as an etchant of the DLC and terminates the dangling bonds produced in etching on the surface.

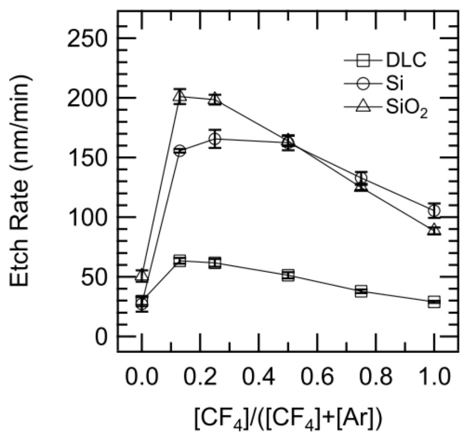

Figure 1 – Etch rate of the DLC in the CF_4/Ar plasmas plotted with those of Si and SiO_2 as a function of the gas-mixture ratio of $[CF_4]/([CF_4]+[Ar])$. The self-bias voltage was constant at –100 V. Error bars indicate variability in reproducing the experiments of etching and measuring the steps on the samples by stylus profilometry

Figure 3 shows etch rates of the DLC in CF_4/O_2 plasmas with self-bias voltage constant at -100 V. The rates increased drastically with increasing O_2 content from 0 to 0.125 of the gas-mixture ratio. Then the rates decreased drastically with the ratio varied to 0.875. In a pure-O_2 plasma, the sample of the DLC was etched at the highest rate of 120 nm/min. In the regime of small content of O_2 less than 0.2, the samples of Si and SiO_2 were etched by F radical produced in possible reaction, $CF_4 + O_2 \rightarrow 4F + CO_2$.[19] Here the F radical also contributed to etch the sample of the DLC.

In Figure 4, the XPS spectra on surfaces of the DLC etched in the plasmas are shown. Increasing the gas-mixture ratio of $[O_2]/([CF_4]+[O_2])$, intensity of the F_{1s} peak decreased and that of the O_{1s} peak was enhanced. Adding O_2 much more than 0.2 in the CF_4/O_2 plasmas, etching reaction on surfaces was suppressed, although fluorine content reached the surfaces. On the surfaces, C–O bond tends to be formed and stable rather than C–F, since energy of the C–O, 1076 kJ/mole is much higher than that of the C–F, 547 kJ/mole [20]. Moreover oxygen added to the plasmas did not result in etching of the DLC. This means that O radical is scavenged in a reaction before reaching surfaces, $CF_4 + O_2 \rightarrow COF_2 + 2F + O$.[21]

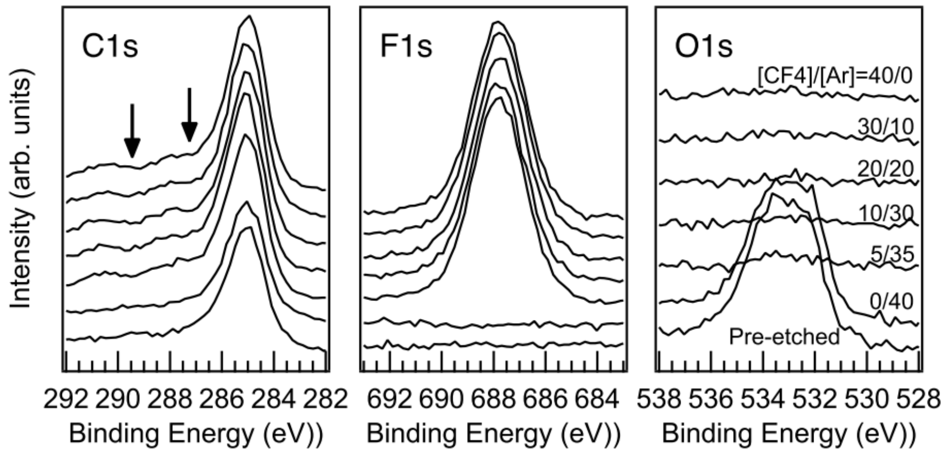

Figure 2 – XPS spectra of C_{1s}, F_{1s} and O_{1s} on surfaces of the DLC samples etched in the CF_4/Ar plasmas, and on that of a pre-etched one. The experimental conditions were the same as in Figure 1. Arrows show signals from chemical bond components of C–CF_x at 287.3 and CF at 289.5 eV

The surfaces etched in pure-CF_4, Ar and O_2 plasmas were observed by AFM (Figure 5). Values of root mean square (RMS) indicating roughnesses on the surfaces was calculated from morphologies in the AFM images. The RMSs in the pure-CF_4, Ar and O_2 were 0.084, 0.094 and 1.7 nm, respectively. Conversely, the etch rates of the plasmas were 29, 30 and 120 nm/min. The higher etch rate gets the rougher surface. For fabrication and removing processes of the DLC, it is expected to get appropriate etch rate and roughness on the surface. The results mentioned above implies that processes require etching to use gas- mixture of CF_4, O_2 and Ar in order to control the morphologies on the surfaces as well as the etch rates. Samples of the DLC were etched in changing gas-mixture ratio of $[CF_4]/[O_2]$ with Ar dilution of 30 sccm (Figure 6). The total flow rate was constant at 40 sccm. Etch rates of Si and SiO_2 decreased with decreasing the flow rate of CF_4 i.e., increasing that of O_2. Etch rate of the DLC was enhanced with increasing the flow rate of O_2. The more content of O_2 gets the more reactive etching on surface of the DLC samples. It notes that roughness on the surface is expected to be also enhanced with increasing the content of O_2 according to the AFM images (Figure 5).

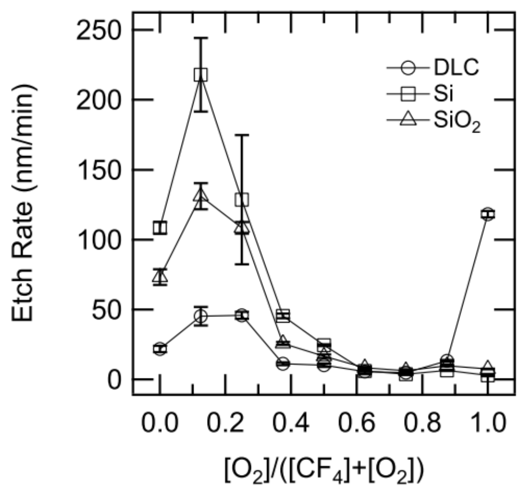

Figure 3 – Etch rate of the DLC in the CF_4/O_2 plasmas plotted with those of Si and SiO_2 as a function of the gas-mixture ratio of $[O_2]/([CF_4]+[O_2])$. The self-bias voltage was constant at 100V. The error bars are treated as in Figure 1

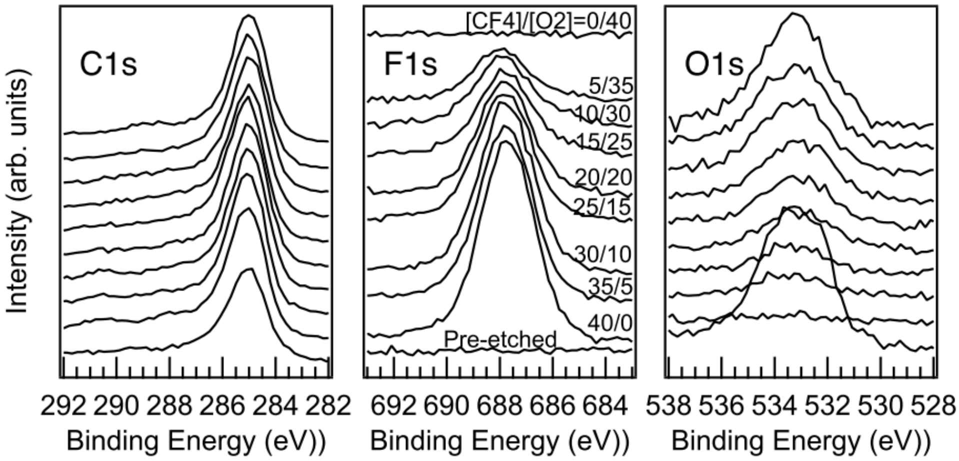

Figure 4 – XPS spectra of C_{1s}, F_{1s} and O_{1s} on surfaces of the DLC samples etched in the CF_4/O_2 plasmas, and on that of a pre-etched one. The experimental conditions were the same as in Figure 3

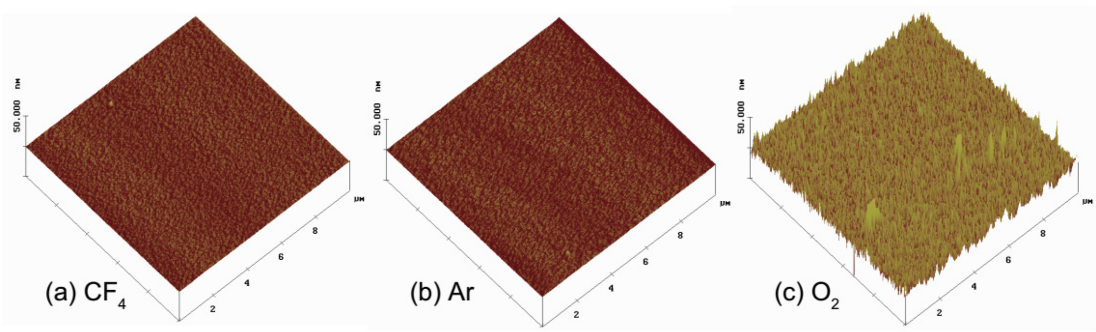

Figure 5 – AFM images on surfaces of the DLC samples etched in the (a) pure-CF_4, (b) Ar and (c) O_2 plasmas. The RMSs indicating roughness on the surfaces in the pure-CF_4, Ar and O_2 plasmas were 0.084, 0.094 and 1.7 nm, respectively

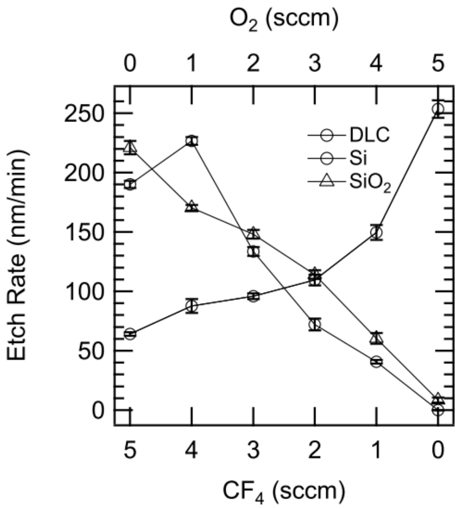

Figure 6 – Etch rate of the DLC in the CF4/O2/Ar plasmas plotted with those of Si and SiO2 as a function of the gas flow rates of CF4 or O2. Etching was performed in changing gas-mixture ratio of [CF4]/[O2] with Ar dilution of 30 sccm. The total flow rate was constant at 40 sccm. The error bars are treated as in Figure 1

4 Conclusions

The DLC was etched in the CF_4/Ar, CF_4/O_2 and CF_4/O_2/Ar plasmas. In the plasmas, F radical worked as an etchant of the DLC in addition to O radical well-known as the etchant in other works. Adding O_2 to the plasmas enhanced etch rates of the DLC. Furthermore, the pure-O_2 plasma had the etch rate highest in all the plasmas. However, it made surface of the DLC rough, implying that highly reactive etching with high etch rates tended to have marked roughness. Conversely, the Ar plasmas could be a candidate of process for etching the DLC with a smooth surface. Its sputter-etching produced abundant dangling bonds on the surface after treatment. The dangling bonds combining with ambient oxygen led the surface of the DLC oxidized. In the fluorine-content plasmas, the dangling bonds were terminated by fluorine atoms, and oxidation on the surface was suppressed by the atoms. In practical processes for fabrication and removing of the DLC, etch rate, its depth, roughness and chemical composition on the surface are required to be controlled well. The present study gives a way to control the etch rate and depth by changing the gas-mixture ratio of CF_4, O_2 and Ar, which also modifies the roughness and suppresses oxidation on the surface preferable to devices of the DLC.

Acknowledgements

This work was partly supported by Toyo Advanced Technologyies Co., Ltd.

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