ETCHING CHARACTERISTICS OF CARBON FILMS BY RF PLASMA

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Diamond films made by the hot-filament method and hydrogenated amorphous carbon (a-C:H) films made by plasma chemical vapor deposition were etched using an RF plasma system. After the etching by the RF plasma, an etched step between a masked and an etched area was studied with a scanning electron microscope. The etching rate of hard amorphous carbon film (nearly 6 nm/min) was three times larger than that of diamond film (nearly 2 nm/min) by Ar plasma at 5 × 10⁻² Torr. From the results of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD), the surface of the diamond samples was modified by species in the plasma. The relationship between the etching rate of a-C:H films and the hydrogen content of the film was investigated and it was concluded that the hardness of a-C:H film was directly related to the hydrogen content.

1. Introduction

Recently, diamond films and hydrogenated amorphous carbon (a-C:H) films have been investigated by many researchers because of their many interesting properties. Usually diamond films have been prepared from hydrocarbon gases by the hot-filament method,¹ microwave CVD,² or hot plasma CVD.³ The plasma-CVD method,⁴⁻⁶ ion-beam deposition⁷⁻⁹ and ion-beam sputtering⁹ are available to produce a-C:H film which has similar diamond properties at a relatively low temperature. These a-C:H films have very different properties especially in terms of hardness, depending on preparation conditions and methods. In our previous work, mechanically soft (easily scratched by tweezers) and hard films were obtained at higher and lower gas pressure regions, respectively.⁶ It might be thought that hydrogen atoms contained in a-C:H films should have a big influence on film properties. We thought that there was a close relation between the hydrogen content of a-C:H film and its etching properties. Further, etching characteristics of diamond and a-C:H films will be important for applications of these films in the future.

In this work, the etching of diamond films and a-C:H films were attempted by RF plasma to investigate their degrees of hardness related to the etching gas pressure. Diamond surfaces before and after etching were observed by SEM, and analyzed by XPS and XRD analyses. The hydrogen content (C/H) in a-C:H film was measured by infrared (IR) spectra in order to discover the relationship between these films’ etching rate and their hydrogen content.

2. Experimental Procedures

A parallel-plate RF plasma system was utilized for the etching of both carbon films. For the vacuum background, a vacuum chamber was evacuated by a diffusion pump to a level of about 10⁻⁶ Torr after the sample was set on the upper cathode electrode of 10 cm diameter. As etching samples, a-C:H films and diamond films on Si substrate were utilized. The a-C:H film samples were prepared by RF (13.56 MHz) plasma decomposition from methane gas; diamond film samples were deposited by the hot-filament method⁹ from methane gas mixed with hydrogen (CH₄:H₂ = 1:99). The thicknesses of most of the a-C:H and diamond films were about 0.5 μm and 1.0 μm, respectively. Ar and CF₄ gases were introduced into the reaction chamber through mass flow controllers for the etching. Etching conditions
were adjusted by the gas pressure \( (2 \times 10^{-2} - 0.5 \) Torr); the other etching parameter, the input power was kept constant at 50 W. The etching rates were calculated from the etching time and etched depth of the sample. The samples before and after etching were observed with a JEOL JSM-1200 scanning electron microscope. The surfaces of diamond samples with and without the etching treatment were measured by XPS and XRD analyses.

For investigating the properties of a-C:H films, the relations between sample preparation conditions such as CH\(_4\) pressure \( (2 \times 10^{-2} - 0.5 \) Torr) and etching properties were also studied. The IR spectra of carbon films were observed using a FTIR spectrometer. The hydrogen content in a-C:H films was calculated from the integral of the IR spectrum near 2900 cm\(^{-1}\).

3. Results and discussion

3.1 Etching properties of carbon films

The etching characteristics of diamonds and a-C:H films by Ar plasma as a function of Ar etching pressure are shown in Fig. 1. It was seen that the etching rates of diamond and a-C:H films monotonously increased with Ar etching pressure. The behaviors of these rates are closely related to the volume of Ar molecules in the chamber. By comparing both lines in Fig. 1, the etching rate of a-C:H film by Ar plasma is three times larger than that of diamond film at around these pressure regions. Figure 2 shows SEM photographs of the step between an etched area and a masked area for a diamond sample(a) and an a-C:H sample(b). An etching depth for the diamond sample was observed to be about 600 nm from Fig. 2(a), treated in Ar \( (5 \times 10^{-3} \) Torr) plasma for 300 minutes. The surface morphology of a-C:H film still remained after etching by the Ar plasma; the diamond samples will be described in detail in the next section.

The etching gas was renewed CF\(_4\) gas with reactive molecules. Figure 3 shows the etching rate of both films by CF\(_4\) plasma as a function of the CF\(_4\) etching gas pressure. The etching rate increased with a decrease of CF\(_4\) gas pressure, different from Ar gas plasma etching. This difference is thought to be because activated species are increaed in lower pressure regions. On the other hand, the etching rate of a-C:H film was also three times larger than that of diamond film, similar to when both were etched by Ar plasma. The etching rate evaluated from this experiment seems to
depend on the hardness value of these films, because diamond film and hard a-C:H film have micro Vickers hardnesses of about 7000–10000 kg/mm²⁰¹ and approximately 3500 kg/mm²¹², respectively.

3.2 Surface observation of diamond films with etching treatment

The surface after etching was analyzed by X-ray photoelectron spectroscopy (XPS). The plasma ion loss spectra of diamond film is shown in Fig. 4. The loss energy at the 35 eV peak is due to diamond, the 27 eV peak due to graphite and 23 eV peak due to amorphous carbon. It is clear that the diamond signal is decreased with an increase of Ar plasma etching time. The amorphous and graphite phases are increased on the surface of the diamond sample, and the diamond surface may be modified by the Ar plasma etching. The valence band X-ray photoemission spectra before and after Ar plasma etching are shown in Fig. 5. A broad peak located between about 10 eV and 0 eV is due to p-like bands in diamond and graphite, and the 13 eV peak is due to the diamond’s s and p character. It can be seen in Fig. 5 that the diamond peak (near 13 eV) is decreased by the Ar plasma etching treatment. Figure 6 shows SEM photographs of a masked area and an etched area in the diamond sample with Ar plasma etching. As shown in Fig. 6(a) and
(b), the etched surface of the sample became smooth in comparison with the masked area. It was found that the diamond film surface was improved in flatness as a result of the removal of sharp points on the film by the excited Ar⁺ species in the plasma.

The structure before and after Ar etching was identified by X-ray diffraction. XRD data shows four peaks which mainly correspond to the spacings of the (111), (220), (311) and (400) planes in diamond,\textsuperscript{15} as well as some peaks due to the silicon substrate. The intensity of the (111) and (400) planes signals of the diamond sample as a function of Ar etching time is shown in Fig. 7. The intensity of the (400) plane signal in the diamond sample increased with Ar etching time. This may be related to the flattening of the diamond surface after Ar etching, because (111) and (100) plane diamond particles are relatively sharp and relatively flat, respectively. Photographs of the diamond surface after CF₄ etching are shown in Fig. 8. The diamond sample surface is sharper after being etched by the CF₄ RF plasma. From this result, it seem that active species, such as CFₙ and F radicals, in the plasma attacked and reacted with the diamond surface.
3.3 The relation between the etching rate and hydrogen content of a-C:H film

Figure 9 shows the etching rate of carbon film as a function of the CH₄ pressure during the film deposition; the etching condition was kept constant (Ar: 5 × 10⁻² Torr, power: 50 W). In our previous work, a-C:H films with various hardnesses were obtained by changing the CH₄ pressure. As the hardness of the relatively hard a-C:H films could not be easily distinguished, the film hardness was studied from the viewpoint of the film deposition conditions. The hardness of a-C:H films is estimated from the Ar plasma etching rates because this etching reaction depends only on a sputtering mechanism. Furthermore, the ratio of different etching rates in the different films is related directly to the ratio of the hardness of both films. It can be seen that the film hardness may be increased by decreasing the deposition pressure.

For an examination of the relationship between the etching rate and hydrogen content in a-C:H films, hydrogen contents were measured from IR spectra (the CH₄ bond near 2900 cm⁻¹). Hydrogen content in a-C:H films as a function of the deposition pressure is shown in Fig. 10. This indicates that the hydrogen contents in a-C:H films increases with CH₄ deposition pressure. Soft carbon films prepared under 0.25 Torr or higher include a vast volume of hydrogen in contrast with hard a-C:H films. The construction of soft films should be completely different from that of hard ones, and it appears that soft films become polymer-like carbon films. However, the etching rate depends upon the hydrogen contents in the films at the suitable CH₄ pressure for masking the hard films.

4. Conclusions

The etching rate of a-C:H films was three times larger than the diamond film's etching rate. From the etching rate obtained from these experiments, the hardness of the films can be evaluated to a certain extent. Part of the etched surface of the Ar plasma-etched diamond film became smooth as the result of removing sharp points on the film, while the CF₄ plasma etched surface was sharpened by the etching treatment. A close correlation between the etching rate and hydrogen content of the hard a-C:H films may exist, because the etching rate of a-C:H films increased with greater hydrogen content.

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