Smooth Surface Dry Etching of Diamond by Very High Frequency Inductively Coupled Plasma

Hiromichi Yoshikawa*,1,2, Shinichi Shikata2, Naoji Fujimori2, Naoyuki Sato1 and Takashi Ikehata1

1Department of Applied Beam Science, Graduate School of Science and Engineering, Ibaraki University, 4-12-1 Nakanarusawa, Hitachi, Ibaraki 316-8511, Japan
2National Institute of Advanced Industrial Science and Technology, 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

(Received 14 November 2005; accepted 18 April 2006)

Key words: diamond, RIE, etching, VHF, ICP

In this study, the effect of ion species in oxygen plasma on the surface morphology of diamond is reported to optimize reactive ion etching (RIE) for diamond devices. Oxygen gas was excited by inductively coupled plasma (ICP) with excitation in a very high frequency (VHF) range of 60–230 MHz under a pressure of 0.05–5 Pa. The results of optical emission spectroscopic analysis confirmed the presence of oxygen atoms and molecules. Also, the results obtained by quadrupole mass spectroscopy (QMS) analysis confirmed that the existence ratio of each ion species is dependent on the combination of pressure, magnetic field and excitation frequency. The substrate surfaces of single-crystal diamond, which were etched by plasma with different flux ratios of ionic oxygen atoms to oxygen molecules, have different morphologies. The results of optical emission spectroscopy (OES) indicate that the surface, which was etched by plasma with strong emission from oxygen molecules and with high-ionic-oxygen-molecule flux determined by QMS, has dome-shaped protrusions approximately 0.2 μm in size. In contrast, on the substrate surface etched by plasma with strong emission from ionic oxygen atoms and with high-ionic-oxygen-atom flux, grooves that originally existed due to machining and etch pits with a diameter of 0.2 μm or less were formed. Using plasma in which both ionic oxygen molecules and atoms coexist, an etched surface with good flatness and suppressed etch-pit formation can be obtained. In addition, since it was possible to obtain a flat surface with a long etching duration without introducing etchant gases such as CF3 (generally used to flatten surfaces) for metals, the possibility of improving the selectivity of hard masks during lithographic pattern formation and the development of a system in which an exhaust gas treatment facility is unnecessary have been demonstrated.

*Corresponding author: e-mail: h-yoshikawa@aist.go.jp
1. Introduction

Wide-band-gap electronic devices and sensors based on diamond are some of the most promising devices that can operate under high-temperature, high-power and high-frequency conditions where Si-based devices cannot work.\(^1\) However, there are several problems in the realization of diamond devices. In particular, due to the inertness of diamond to wet chemical processes, processability by high-resolution and low-damage dry etching using oxygen plasma is desired. Although many dry etching systems using high frequency (HF), microwave, ECR plasma and gas mixture have been proposed to satisfy these requirements, in many cases, a damaged surface, microcolumns and trenching of the etched diamond substrate have been observed.\(^4\) To control these shape defects, a technique for obtaining a smooth surface by physical sputtering with argon ions or oxygen ions under a low-pressure condition is proposed.\(^10\)–\(^13\) However, for dry etching in which physical sputtering is employed, there is a practical problem due to the low selectivity between diamond and a hard mask materials, such as SiO\(_2\) and Al, and the improvement in the processing speed is difficult. Moreover, the damage formed on the surface is also reported for the conventional dry etching system because it is processed with ionic oxygen atoms with an energy range of 100–700 eV.\(^14\)–\(^19\)

In this research, ion energy was controlled at around 10 eV under low-pressure conditions by suppressing the reduction in plasma density using a guiding magnetic field and reducing the electronic temperature using a VHF plasma of 60–230 MHz. VHF plasma has the advantage of maintaining high-density plasma with low potential and to stabilize etching even at low pressure. Damage of the etched surface due to the ions was controlled, and the shape defect on the etched surface formed by the impurity of adhesion that came flying from the mask material and the vacuum chamber was decreased, and the stability of plasma was confirmed under a low-pressure condition.

2. Experiment

Etching was performed on the surfaces of 3×3×0.5 mm synthetic Ib(100) diamond crystals from Sumitomo Electric Industries, Ltd. The diamond surfaces were covered with grooves in the polishing direction and the roughnesses were approximately Ra: 1.5 nm. SiO\(_2\) or Al films of 500 nm thickness were deposited on these samples by cathodic sputtering. Line and dot patterns were drawn using lithography.

Samples were mounted in a discharge chamber of a vacuum system as shown in Fig. 1. 6N purity oxygen gas was introduced into the quartz tube at a flow rate of 5–10 std cc/min from the side flange, its pressure was controlled by a gas flow rate and pressure control valve. Oxygen gas was excited by inductively coupled plasma (ICP) in a pressure range of 0.05–5 Pa. The plasma was produced inside a 4-turn antenna, which was set around an 84-mm-diameter quartz tube installed in a 304ss chamber along the uniform magnetic field. The driving frequencies of the ICP were changed to examine the effect of frequency on plasma production from 60 to 250 MHz using a signal generator (RF SIGNAL GENERATOR HP 8648B). RF power amplified by an RF power amplifier (RF POWER AMPLIFIER ASTECH ALA2728-100) was supplied to the ICP antenna using a coaxial cable. The 304ss
substrate holder was set down-flow of the plasma coaxially inside the quartz tube and its holder was electrically connected to ground. The processing conditions are described in Table 1. For stable plasma under a low-pressure condition, the resonance frequency of this system was measured using a network analyzer (RF NETWORK ANALYZER Agilent 8714ET), and excited frequency for the plasma was determined.

Among the dry etching processes for diamond, energetically excited species such as ionic oxygen atoms O⁺ and oxygen molecules O₂⁺ are believed to act as etchants, although the role of each active species is not clear. For the optimization of oxygen plasma, the measurement of the flux ratio between O⁺ and O₂⁺ in oxygen plasma is important. A quadrupole mass analyzer system (QMS, Quadrupole Gas Analyzer, ANELVA AQA-100 MPX) was used to observe these active gases through an orifice plate with a 0.7-mm-diameter hole for species sampling. For the measurement of photons emitted by excited state species in the plasma, light emitted by the plasma was collected into an optical fiber and the emitted spectra were analyzed by optical emission spectroscopy (OES, USB2000 Miniature Fiber Optic Spectrometer: Ocean Optics Inc.). It was positioned at the center of the plasma through a view port. The plasma potential ϕ, the electron temperature Te and the electron density ne were measured using a Langmuir probe. The collector surface was set at 20 mm over the substrate holder and the exposed area was 3.1×10⁻⁶ m².

A d.c. magnetic field of 0–100 mTesla was applied parallel to the axis of the plasma column with magnetic coils located on either side of the antenna.

The flux ratio of O⁺ to O₂⁺ in oxygen plasma changed with driving frequency, pressure and magnetic field strength.

Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to observe diamond surface morphology, etching depth and surface roughness.

![Fig. 1. Schematic of experimental apparatus.](image-url)
3. Results and Discussion

Figure 2(a) shows an SEM image of a diamond surface etched by oxygen plasma using the conventional HF-ICP RIE system. Oxygen gas was excited by a high-frequency-band (13.56 MHz) power supply unit, and 1000 W RF power was introduced to the double-loop antenna. The substrate holder was connected to another RF power supply unit for the addition of self-bias. In this case, the self-bias was 700 V. As a result, many nanosize rods were observed on the etched surface. The nanorod growth is often attributed to the presence of nano- and micromasks that originate on the chamber wall or hard mask. Fluorocarbon gases efficiently removed these contamination materials.\(^{16,20}\) To avoid such nanorod formation, a 2% tetrafluoromethane (CF\(_4\)) / oxygen (O\(_2\)) mixture was introduced into the same HF-ICP RIE system for etching. Although the cleaning of the diamond surface resulted in a smooth surface without nanorod formation, dimples were observed on the etched surface. An AFM image of the etched surface is shown in Fig. 2(b). From this image, the mean density of the dimples was estimated to be approximately \(7.0 \times 10^7\) cm\(^{-2}\) in the 10×10 mm\(^2\) area and their distribution was not uniform. Since a higher etching rate is expected at the defects, this morphology is ascribed to etching at a higher rate at dislocations in the (100) surface of the sample. The relationship between dislocations and residual defects in diamond has been reported and the density described above is in agreement with a previously estimated dislocation density of approximately \(10^9\) cm\(^{-2}\).\(^{21–23}\)

In general, most etching processes employ a chemical reaction and/or physical sputtering.\(^{24,25}\) In general, ion beam etching employs mainly a physical reaction, the etching rate of which is low; however, the obtained surface is flat. In contrast, wet etching and plasma etching are mainly based on chemical reactions, in which the etching rate is high, but the formation of etch pits is observed. A good balance of anisotropy, selectivity and smooth surface will be achieved by employing both physical sputtering and chemical reactions in the same dry etching process. Understanding the roles of these reactions and control technique is particularly important for inhibiting etch pit formation.

To recognize the active species in the plasma, the emission spectrum was measured using OES, in which continuum emission is separated from molecular bands and atomic lines. Compared with the emission from the first negative band system (\(b^1Σ_g - a^1Π_u\), 499.2–786.1 nm) of ionic oxygen molecules observed at 500 nm – 700 nm, the emission from free radicals of oxygen atoms observed at 777 nm (3p-3s) has a high intensity. Therefore, it is expected that the dissociation of oxygen molecules proceeds, and the number of oxygen atoms is

<table>
<thead>
<tr>
<th>Plasma type:</th>
<th>Inductively coupled plasma (ICP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>antenna</td>
<td>4 turns, $\phi$ 84 mm</td>
</tr>
<tr>
<td>Power/frequency:</td>
<td>30 – 90 W / 60 – 240 MHz</td>
</tr>
<tr>
<td>Pressure:</td>
<td>0.05 – 5 Pa</td>
</tr>
<tr>
<td>Gas:</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Flow rate:</td>
<td>5–10 sccm</td>
</tr>
</tbody>
</table>
extremely high. However, for etching by RIE, the effect of positive ions on etching should
be considered; the determination of the flux ratio of ionic oxygen atoms to molecules (O+/ O₂⁺) on the basis of the optical emission spectrum alone may lead to an incorrect result.²⁶ It is desirable that the results obtained from vacuum ultraviolet absorption spectroscopy, laser-induced fluorescence (LIF) and mass analysis also be used.

Next, three plasmas with different O+/O₂⁺ ratios were produced by ICP-RIE with a VFH
power source and used for diamond etching. The ion flux ratio was calculated using the
results obtained by quadrupole mass analysis (Fig. 4). The following O+/O₂⁺ ratios of the
plasmas were used. Condition A: ionic oxygen atoms dominant, O+/O₂⁺ = 400%. Condition

Fig. 2. SEM and AFM images of single-crystal diamond surface after etching using HF (13.56 MHz)
ICP RIE system; (a) O₂ plasma, SEM; (b) O₂/CF₄ plasma, AFM.

Fig. 3. Optical emission spectrum of O₂/CF₄ plasma for single-crystal diamond etching using
conventional ICP RIE system.
B: balanced ionic oxygen atoms and molecules, $O^+/O_2^+ = 69\%$. Condition C: ionic oxygen molecules dominant, $O^+/O_2^+ = 16\%$. The excitation frequency, magnetic field strength and power of these plasmas were as follows: condition A: 170 MHz, 0.08 Tesla, and 76 W; condition B: 79 MHz, 0.03 Tesla and 29 W; and condition C: 170 MHz, 0.1 Tesla and 28 W. The pressure was 50 mPa in all cases. The plasma potential, electron temperature and electron density of the three plasmas were measured using a Langmuir probe (condition A: 43.4 V, 5.8 eV and $8.9 \times 10^{15}$ m$^{-3}$; condition B: 65.2 V, 12.7 eV and $1.1 \times 10^{15}$ m$^{-3}$; and condition C: 34.0 V, 5.5 eV and $5.4 \times 10^{15}$ m$^{-3}$). Since the substrate was electrically grounded, the plasma potential governs the maximum energy of the ion energy under very low pressure. Although the relationship between the generation ratio of ionic species and these plasma parameters has not yet been clarified, the plasma potentials obtained under the three conditions were subsequently lower than that adopted in HF-ICP RIE.

Figure 5 shows the OES of each of the oxygen plasmas obtained under conditions A–C. The intensity ratio of emission from the free radicals of oxygen atoms $O^+$ observed at 777.3
nm (3p-3s) to emission from the first negative band system (b^4 Sigma_g - a^4 Pi_u, 499.2–786.1) of ionic oxygen molecules O_2^+ was greatly increased compared with the ratio obtained by HF-ICP RIE which means that the existence ratio of oxygen molecules in the plasma was high. The intensity of O^* at 777 nm and that of O_2^+ at 625 nm are reversed under conditions A and B (Fig. 5). Under condition C, in addition to the emissions observed under condition B, a second negative band system (4Pi_u –> 4Pi_g, 200 nm–610.3 nm) of oxygen molecules is observed. Since the results of OES indicate emission from the plasma as a whole, they do not directly indicate each ion flux on the sample, which is measured separately by quadrupole mass spectroscopy. Nevertheless, the results of OES clearly show a change in bulk plasma under different conditions.

Figures 6(a) and 6(b) shows AFM images of the Ib(100) single-crystal diamond surface after O_2 plasma etching for 90 min in the VHF ICP system under conditions A–C. Under condition A, in which ionic oxygen atoms are dominant, the shapes of the grooves caused by polishing during substrate preparation still remain, the pattern of which is different from that obtained by physical sputtering. In addition, many etch pits are observed on the surface, similar to the surface obtained by HF-ICP RIE. These results indicate that chemical reaction plays the main role in etching by ionic oxygen atoms. In contrast, under condition C, in
which ionic oxygen molecules are dominant, the initial grooves disappear after etching, and the etched surface has a convex shape, which is an indication that the surface morphology is due to a physical reaction. This finding indicates that the ionic oxygen molecules are mainly related to the physical reaction. To realize optimal etching, we carried out etching under condition B. As shown in Fig. 6(b), a smooth surface, with neither etch pit formation nor convex shape, was obtained.

The etching of a diamond substrate with a line pattern formed by lithography using SiO₂ as a mask was carried out under condition B, which is considered to be optimal for diamond etching. Figure 7 shows the AFM image of the etched single-crystal diamond surface. The etching duration, etching depth and etching rate were 90 min, 350 nm and 3.9 nm/min, respectively. The selectivity of SiO₂ with respect to diamond was 35. The surface roughnesses before and after etching were 1.35 nm and 1.95 nm, respectively. No decrease in the flatness of the surface due to etching was observed. Similarly, when the etching duration was 90 min under condition C, the etching depth was 59 nm, the etching rate was
0.66 nm/min, and the selectivity was 9.8. Both etching rate and selectivity are low under condition C compared with those obtained under condition B. These results also suggest that ionic oxygen molecules play a role in the physical reaction.

When etching was carried out using oxygen plasma alone without a fluorine compound gas such as CF₄, minute masks are formed on the etched surface due to scattered hard-mask materials. However, no rods were formed under any conditions. The scattering of plasma used in this study was suppressed due to the existence of a magnetic field. Furthermore, since a frequency higher than that conventionally used in HF (13.56 MHz) plasma was used in this study, it was possible to maintain a stable plasma under a low pressure. Therefore, in this study, etching was carried out under a pressure (50 mPa) lower than that in the conventional RIE system (>1 Pa). As a result, a smooth etched surface was obtained by the suppression of the reattachment of hard-mask material and the removal of the attached hard-mask material by sputtering in the presence of an appropriate amount of ionic oxygen molecules.

4. Conclusions

Inductively coupled plasmas with different ions flux ratios of oxygen atoms to molecules were formed under a low pressure of 50 mPa with excitation frequency in the range of VHF. Under a condition of dominant ionic-oxygen-atom flux, etch pits were formed on the surface, suggesting that etching proceeds mainly by chemical reaction. In contrast, under a condition of dominant ionic-oxygen-molecule flux, etching proceeds mainly by physical reaction. Under conditions where the two reactions proceed in a balanced manner, a smooth surface without etch pits was obtained. It is considered that a surface free of columns and pits was obtained by etching with only oxygen without CF₄, because etching was carried out under a low pressure.
Acknowledgment

This work was supported by the ADD Project, which was consigned from NEDO.

References