Role of CF_2 in the etching of SiO_2, Si_3N_4 and Si in fluorocarbon plasma

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Abstract: The CF_2 density and etch rate of SiO_2, Si_3N_4 and Si are investigated as a function of gas pressure and O_2 flow rate in fluorocarbon plasma. As the pressure increases, the self-bias voltage decreases whereas the SiO_2 etch rate increases. Previous study has shown that SiO_2 etch rate is proportional to the self-bias voltage. This result indicates that other etching parameters contribute to the SiO_2 etching. Generally, the CF_2 radical is considered as a precursor for fluorocarbon layer formation. At a given power, defluorination of fluorocarbon under high-energy ion bombardment is a main source of fluorine for SiO_2 etching. When more CF_2 radical in plasma, SiO_2 etch rate is increased because more fluorine can be provided. In this case, CF_2 is considered as a reactant for SiO_2 etching. The etch rate of Si_3N_4 and Si is mainly determined by the polymer thickness formed on its surface which is dominated by the CF_2 density in plasma. Etching results obtained by varying O_2 flow rate also support the proposition.

Key words: CF_2; SiO_2 etching; fluorocarbon film
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1. Introduction

Fluorocarbon plasmas are widely used in the semiconductor industry for fabricating small structures. Selective dry etching of SiO_2 over Si or Si_3N_4 is a typical application. In this process, good selectivity and suitable profile are major concerns. To achieve appropriate etch property and optimize process, the etching mechanism has been studied by many researchers[1−3]. During etching, a steady state fluorocarbon film formed on etched material surface. The polymer thickness on the Si_3N_4 and Si surface is relative thick while a very thin polymer formed on the SiO_2 surface because the liberated oxygen reacts with carbon[4]. The different polymer thickness is the source of the selectivity of SiO_2 over Si. Recently, numerical experiments and simulations have been carried out to investigate the roles of ions and neutral radicals in surface reactions in fluorocarbon plasma etching[5,6].

In this study, we will focus on the role of CF_2 in the etching of SiO_2, Si_3N_4 and Si. The etch rate of SiO_2, Si_3N_4, Si as well as line critical dimension (CD) were investigated as a function of chamber pressure and O_2 flow rate. The polymer deposited on wafer surface is measured by spectroscopic ellipsometry (SE) and examined by X-ray photoelectron spectroscopy (XPS). The role of CF_2 in the etching of SiO_2, Si_3N_4, Si and plasma-surface interaction mechanism is interpreted.

2. Experiment

Experiments were performed in a capacitively coupled etching system. The power was supplied by a 13.56 MHz radio-frequency (RF) generator. A 200 mm wafer was placed on cathode with electrostatic chuck (ESC). In order to maintain good thermal contact between the ESC and the wafer, He gas at a pressure of 8 Torr was applied to the backside of the wafer. The temperature of ESC was kept at 15 °C. The chamber pressure was controlled by throttle valve and measured by capacitance manometer gauge.

Optical emission spectroscopy (OES) is one of the most convenient and non-intrusive diagnostic technologies of plasma characterization. The intensity of the optical emission was determined by both the density of the plasma species involved and the electron energy distribution function (EEDF)[7]. Since Ar is inert and will not be involved in reaction, Ar (750.4 nm) intensity was used to monitor plasma characteristics such as electron density, electron temperature. Thus the relative species concentration can be estimated by the ratio of species intensity to Ar intensity.

A $CHF_3/O_2/Ar$ gas mixture was used in this experiment. The flow rate of CHF_3 and Ar was 50 and 90 sccm respectively. The O_2 flow rate varied from 0 to 10 sccm. The RF power was kept at 300 W. The pressure varied from 50 to 100 mTorr. 3000 Å SiO_2, 2100 Å Si_3N_4 and 2100 Å poly silicon wafers formed by low-pressure chemical vapor deposition (LPVCD) were prepared for etch rate test. Line patterned wafers were prepared for CD test, which consist of photoresist/SiO_2/Si substrate stack with feature size of 0.15 μm.

3. Results and discussion

3.1. Effects of pressure

Figure 1 shows the self-bias voltage as a function of pressure. The self-bias voltage decreases with pressure. When

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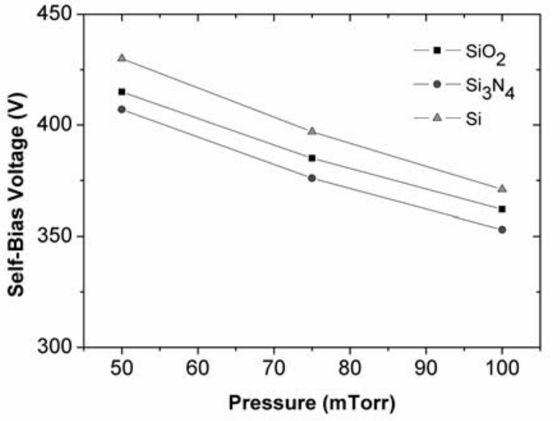

Fig. 1. Self-bias voltage as a function of pressure. The power is 300 W and O_2 flow rate is 5 sccm.

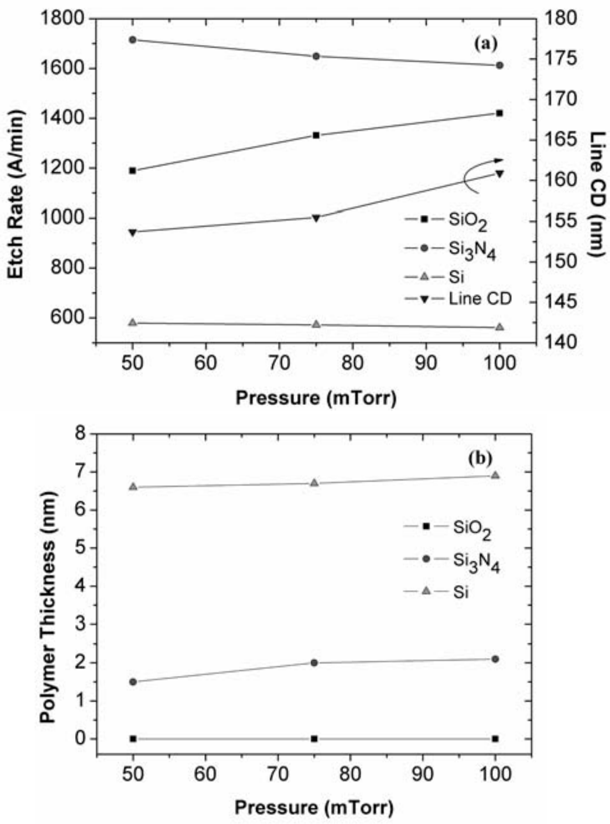

Fig. 2. (a) Etch rate, CD and (b) polymer thickness as a function of pressure. The power is 300 W and O_2 flow rate is 5 sccm.

the pressure increases, the collision rate between particles increases and mean free path (MFP) of ions decreases. Thus the self-bias voltage decreases. Figure 2(a) shows the etch rate of SiO_2, Si_3N_4 and Si as a function of pressure. The SiO_2 etch rate increases with pressure. Although the self-bias voltage decreases with the pressure, the self-bias voltage is comparatively high (> 300 V). Under this condition, SiO_2 etching is in the reactive sputtering regime[8], and the SiO_2 etch rate is proportional to the square root of the ion energy[1, 9]. However, the result in this experiment shows that SiO_2 etch rate increases with pressure in spite of decrease of self-bias voltage. This result indicates that other parameters contribute to the SiO_2 etching. It is an opportunity to study the more detailed mechanism of SiO_2 etching.

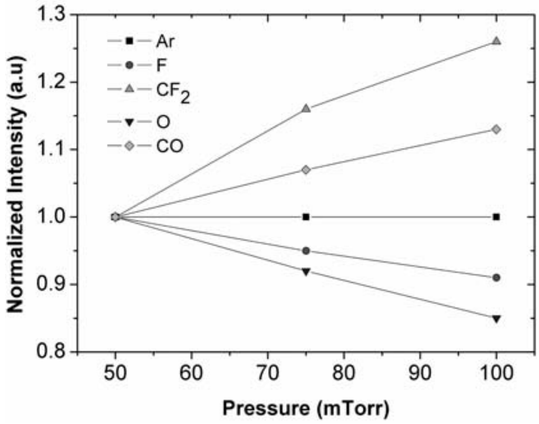

Fig. 3. Normalized optical emission intensity as a function of pressure. The power is 300 W and O_2 flow rate is 5 sccm.

The etch rate of Si_3N_4 and Si decreases slightly with the pressure, as shown in Fig. 2(a). The polymer thickness formed on etched material surface as a function of pressure is shown in Fig. 2(b). The polymer thickness on SiO_2 surface is rather thin (< 1 nm) even it is unmeasured. The polymer thickness on Si_3N_4 and Si surface is about 2 and 7 nm respectively. The typical ion penetration depth is about 1 nm. When the polymer thickness is smaller than the ion penetration depth, ion can go through the film and ion physical sputtering occurred. If the polymer thickness increases beyond the ion penetration depth, the physical sputtering is suppressed, and the etch rate is strongly dependent on the thickness of the polymer film. In this experiment, the etch rate of Si_3N_4 and Si is strongly dependent on the fluorocarbon film thickness. As pressure increases, the film thickness increases therefore etch rate decreases.

Figure 2(a) also shows the line CD after etching as a function of pressure. The line CD can be used as an indicator of the polymerizing nature of the plasma. Because the etched line CD is determined by the polymer formed on line lateral sidewall, which is dominated by CF_2 radical in plasma. The increase of line CD with pressure indicates that polymerization of plasma is enhanced as pressure increases.

Figure 3 shows the normalized species emission intensity as a function of pressure. As pressure increases, Ar (750.4 nm) intensity almost does not change, which means that the plasma characteristics such as electron density and electron temperature are kept constant. However, the CF_2 (251.9 nm) intensity changes greatly with pressure, and the variation is up to 27%. The increase of CF_2 will depress the F, O radical density because the F and O radical will be consumed by polymer precursor like CF_2. Consequently the intensity of F (704 nm) and O (777.5 nm) decreases with the pressure. The CO is one of the SiO_2 etching byproducts. The increase of CO (483 nm) intensity with pressure is consistent with the enhancement in the oxide etch rate.

The role of CF_2 in oxide etching can be interpreted by the following way. The CF_2 radical has been proposed as the dominant precursor for polymer formation[10]. When CF_2 radical increases with pressure, polymer formation on the oxide

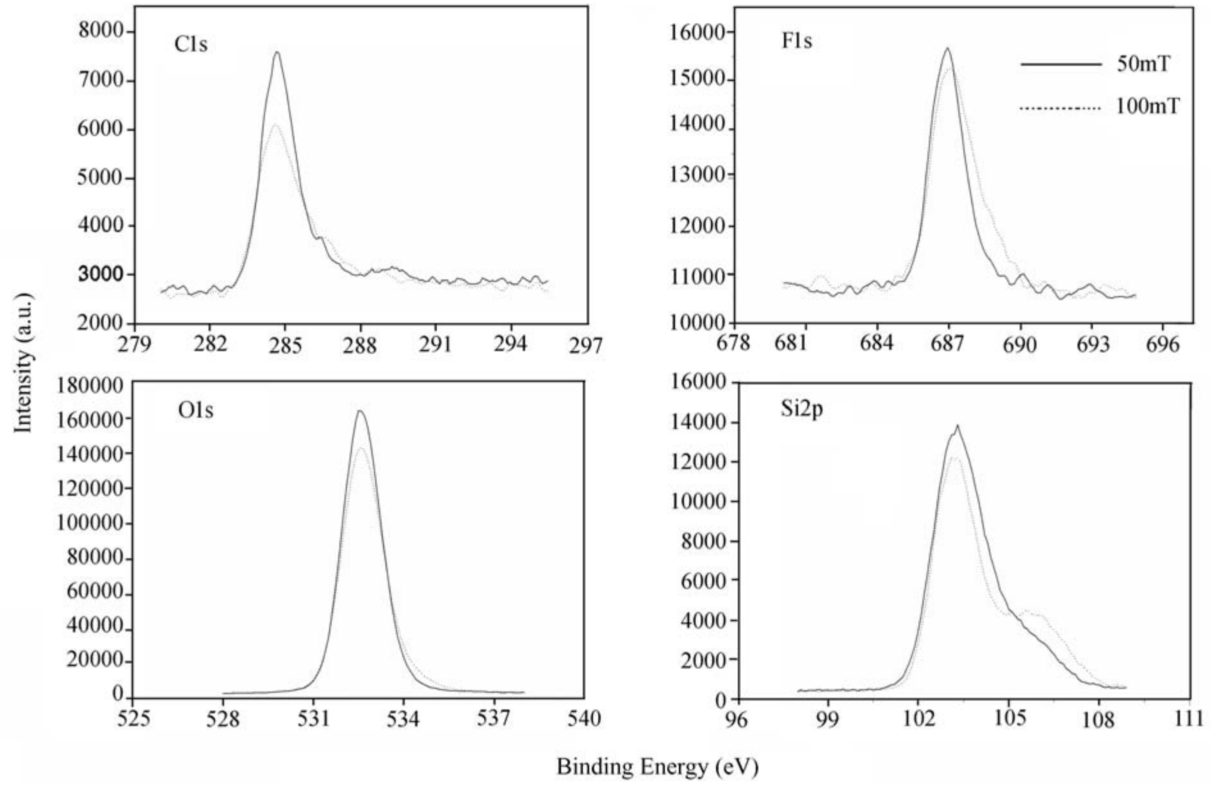

Fig. 4. XPS analysis result of partial etched SiO_2 samples.

Table 1. Summary of atomic percentages.

Atom%	C	F	O	Si	F/C
50 mT	6.3	2.0	70.9	20.9	0.31
100 mT	5.9	2.6	71.3	20.3	0.44

surface is enhanced. However, the fluorocarbon film is exposed to high energy ion bombardment promptly. Under the high ene-rgy ion bombardment, the fluorocarbon film is dissociated into CF or C and F radical, which provide fluorine for oxide etching. The ion-induced defluorination of the polymer can be a predominant source of the fluorine used for etching of the substrate[11]. When more CF_2 radicals exist in plasma, polymer formation on SiO_2 surface is enhanced and more fluorine source is released therefore SiO_2 etch rate is increased. In this case, CF_2 is considered as reactant, which is also proposed by Barela *et al*.[12]. This result is consistent with the observation made by Takada *et al*.[13], who found that a significant contribution of direct SiO_2 etching by fluorocarbon molecules under ion bombardment.

To validate the defluorination of the polymer film, two partial etched SiO_2 samples at 50 and 100 mT were examined by XPS, whose result is shown in Fig. 4. Four elements, C1s, F1s, O1s and Si2p are presented on SiO_2 surface. The Si and O element mainly comes from SiO_2. Table 1 shows the summary of atomic percentages calculated with atomic sensitivity factors. The C element decreases from 6.3% to 5.9% while F element increases from 2.0% to 2.6%. The ratio of F/C increases from 0.31 to 0.44. Obviously, F concentration in fluorocarbon layer is increased with pressure. This result supports that more F source is provided when more CF_2 exists in plasma.

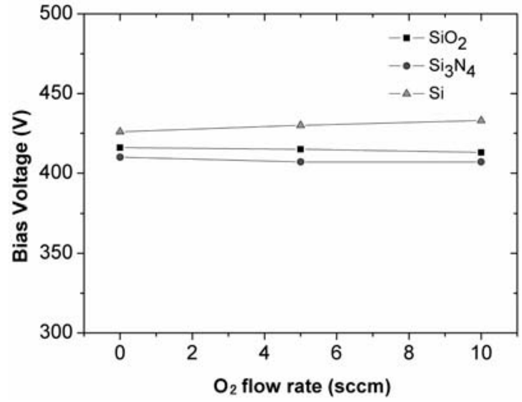

Fig. 5. Self-bias voltage as a function of O_2 flow rate. The power is 300 W and pressure is 50 mTorr.

3.2. Effects of O_2 flow rate

Figure 5 shows the self-bias voltage as a function of O_2 flow rate. The self-bias voltage essentially remains constant with O_2 flow rate. Small addition of O_2 (0–10 sccm) does not change the plasma property significantly. Thus the self-bias voltage is insensitive to the O_2 addition.

Figure 6(a) shows the etch rate of SiO_2, Si_3N_4, Si and line CD as a function of O_2 flow rate. With O_2 addition, SiO_2 etch rate decreases while the etch rate of Si_3N_4 and Si increases. The polymer thickness formed on etched material surface as a function of the O_2 flow rate is shown in Fig. 6(b). The polymer thickness on Si_3N_4 and Si surface decreases with O_2 flow rate. O_2 is well known as a primary gas to eliminate carbon containing polymer precursor by forming volatile CO, CO_2 and COF_2. When O_2 is added to the plasma, SiO_2 etch rate will decrease due to the reduction of CF_2. The etch rate of Si_3N_4

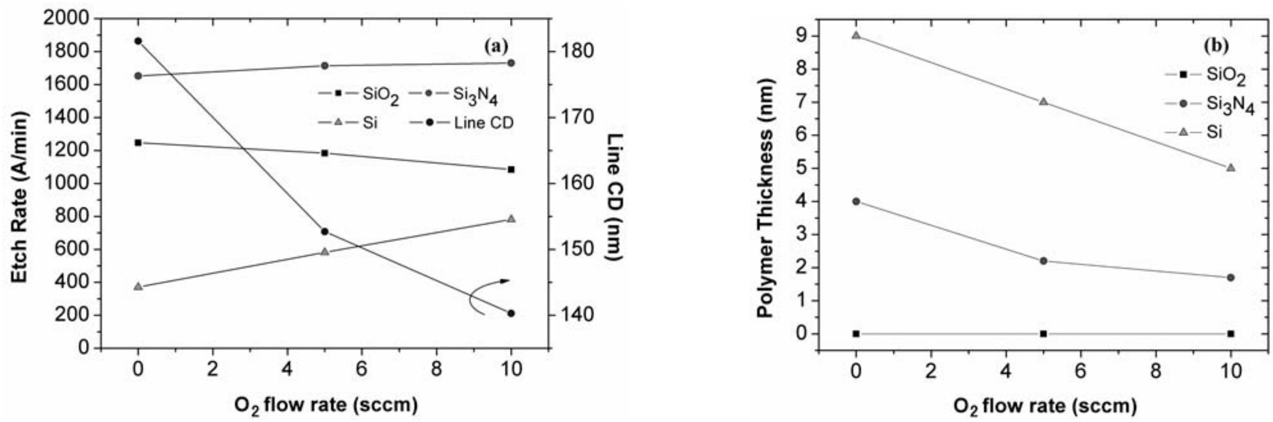

Fig. 6. (a) Etch rate, CD and (b) fluorocarbon thickness as a function of O_2 flow rate. The power is 300 W and pressure is 50 mTorr.

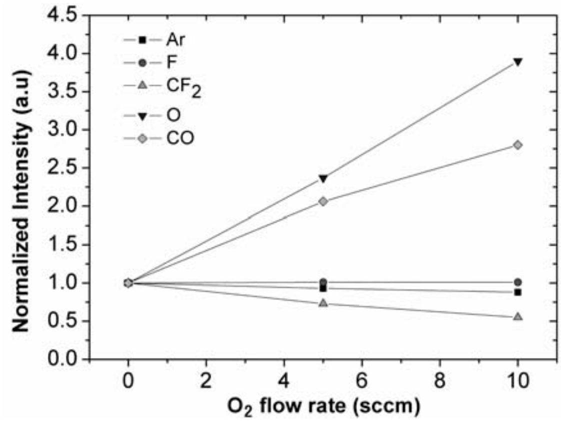

Fig. 7. Normalized optical emission intensity as a function of O_2 flow rate. The power is 300 W and pressure is 50 mTorr.

and SiO_2 is enhanced due to reduction of polymer thickness with O_2 addition. The decrease of line CD also indicates that polymerization of plasma is reduced with O_2 addition.

The normalized species emission intensity as a function of O_2 flow rate is shown in Fig. 7. With O_2 addition, O intensity increases greatly which is in expected. The intensity of Ar and F varies little. The CF_2 intensity decreases significantly with O_2 addition and the variation of CF_2 intensity is up to 45%. The intensity of CO, which is a byproduct of CF_2 consuming by O, increases with O_2 addition. This is consistent with the reduction of CF_2 intensity and increase of O intensity.

4. Conclusion

The role of CF_2 in the etching of silicon dioxide, silicon nitride and silicon is studied in fluorocarbon plasma. During etching a thin fluorocarbon film formed on SiO_2 surface while a relative thick polymer is formed on Si_3N_4 and Si surface. CF_2 is the predominant precursor for fluorocarbon film formation. The fluorocarbon film plays different roles in the etching of SiO_2, Si_3N_4 and Si due to different fluorocarbon film thickness. At a given power, the SiO_2 etch rate is determined by the fluorine source provided. When more CF_2 exists in plasma, more fluorine source can be released for SiO_2 etching through the defluorination of fluorocarbon film. In this case, CF_2 is considered as a reactant for oxide etching. The etch rate of Si_3N_4 and Si is mainly determined by the polymer thickness formed on its surface, which is dominated by the CF_2 density in plasma. Both etching results obtained by gas pressure and O_2 flow rate support the proposition. For practical application, pressure and O_2 flow rate are two key parameters modulating CF_2 density in plasma gas phase to achieve appropriate etch properties such as etch rate, selectivity and CD profile.

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