

Solid particle production in fluorocarbon plasmas. I. Correlation with polymer film deposition

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Solid particles and agglomerates of the particles were found to be produced in octafluorocyclobutane (*c*-C₄F₈) plasmas used for reactive ion etching of SiO₂ and chemical vapor deposition of low dielectric constant fluorocarbon films. Analyses of the solid products elucidated a part of the chemical reactions related to the polymerization process in gas phase. The particle production depended strongly on the feed gas pressure in the plasma. A marked increase of the production was observed as the pressure became higher than 50 mTorr. The production accompanied the pressure depression at the steady state in the discharge, indicating the depletion of the gas species owing to polymerization. Furthermore, the partial pressure of stable molecules such as CF₄ and C₂F₆ produced in the plasma and the film deposition rate on surfaces changed drastically at the critical pressure. These pressure dependencies suggest that polymerization reactions between reactive species and source molecules in gas phase lead to the particle production. © 2001 American Vacuum Society. [DOI: 10.1116/1.1372901]

I. INTRODUCTION

Surface processing using low-pressure plasmas is one of the most important techniques in semiconductor manufacturing. Especially, reactive ion etching (RIE) and chemical vapor deposition (CVD) using plasmas with reactive gases are indispensable for fabrication of semiconductor devices. Since, recently, highly selective and anisotropic etching is required to obtain contact holes with high aspect ratio in ultralarge-scale integrated (ULSI) circuits. On the other hand, low permittivity intermetal dielectrics are investigated for the purpose of reducing the resistance capacitance time delay (RC delay), which is getting more conspicuous due to shrinkage of the spacing between metal lines in high-density multilayer integrated circuits. From these industrial requirements, fluorocarbons, e.g., C₄F₈, are being applied to plasma etching and CVD processes. In the fluorocarbon plasmas, it was shown that highly polymerized molecules were formed, which were detected by electron attachment mass spectrometry (EAMS).¹⁻³ Mechanisms analogous to cluster formation in silane discharges,⁴ polymerized molecules may have high sticking probability, and may cause formation of powder and dust particles in the gas phase as well as thin film on the surface.⁵⁻⁷ Since such dusts can damage semiconductor devices on the wafer, investigation of solid particle production is significant for purification of the processing plasmas for semiconductor fabrication. In this work, the particle production is examined by direct observation of solid particles dropped on the wafer prepared in the fluorocarbon plasmas. In addition, plasma-polymerized films (hereafter, polymer films) on the surface are sampled to measure deposition rate and to determine the chemical composition with x-ray pho-

toelectron spectroscopy (XPS). Finally, the correlation in polymerization between reactions in gas phase and on surface is studied, and the mechanism of the solid particle formation is discussed.

II. EXPERIMENTAL METHODS

Our experimental setup is shown in Fig. 1. A conventional parallel-plate type reactor was used in this study. The plasma reactor was evacuated by a turbomolecular pump and a rotary vane pump. The rf powered electrode at the upper side was a plate of 15 cm in diameter, surrounded by a grounded metal shield. This electrode also worked as a shower head to feed source gases. The other electrode was set below the rf electrode with a separation of 3 cm. The electrode was not grounded, having a floating potential in discharge. A load-lock chamber was attached to the plasma reactor, which was evacuated by another rotary vane pump. Si wafers were transported between the chamber and reactor when keeping the reactor at high vacuum. A capacitively coupled plasma was generated by a 13.56 MHz rf power source with a π -type matching network. The discharge power was measured at the output of the generator, so that the losses in the matching network and cables were not taken into account. The nominal value of the power density was typically maintained at 0.15 W/cm². Then, *c*-C₄F₈ gas was supplied by a mass flow controller to the upper shower-head electrode. The typical flow rate was 1.7 sccm. In this configuration, the residence time is relatively long being of the order of a few (1–10) min. This condition is preferable for the polymerization, since it allows the produced species to accumulate in the plasma. The gas pressure measured by a Baratron manometer was set in the range from 23 to 250 mTorr.

Si wafers were rinsed by a solvent to remove the impurities such as house dust before the plasma treatment. A wafer

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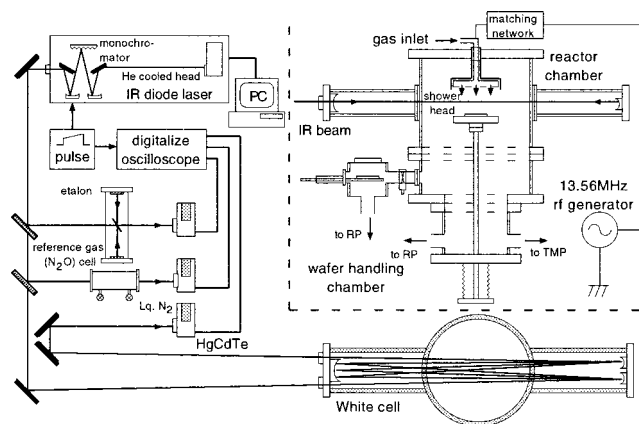


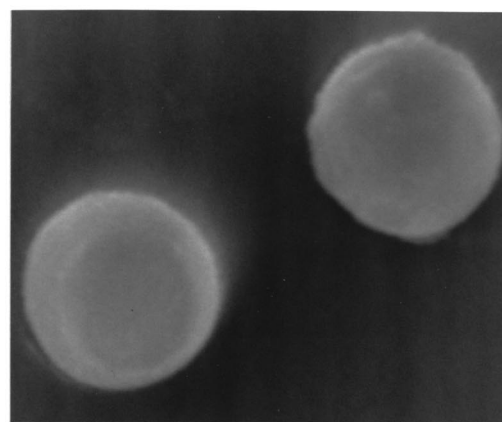
FIG. 1. Schematic of the experimental setup.

was mounted on the lower electrode and exposed to the discharge for 15 min with no external bias voltage. Thin film of fluorinated amorphous carbon (a -C:F) was deposited on the wafer surface, and particles and agglomerates fell down from the trapped region near the plasma-sheath boundary to the surface during the discharge. After the treatment, the surface morphology of the substrate was observed by an optical microscope (differential interference contrast microscope) and a scanning electron microscope (SEM). The chemical composition of the films and particles was also measured by XPS. The thickness of the polymer films deposited on the wafers was measured by stylus profilometry.

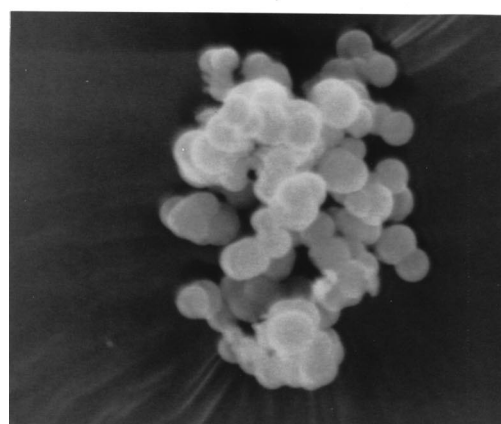
In C_4F_8 plasma, stable molecules such as CF_4 and C_2F_6 can be produced. Therefore the amount of these molecules was measured by using infrared laser absorption spectroscopy. The absorption lines of the ν_3 mode at 1283 cm^{-1} and the ν_7 mode at 1250 cm^{-1} were used for the measurement of CF_4 and C_2F_6 , respectively.⁸⁻¹⁰

III. RESULTS

In the observation by SEM, particles and agglomerates were found on the surface of a Si substrate treated in the pressure range higher than 50 mTorr. The particles were spherical and their diameter was distributed between 0.5 and $2.3\text{ }\mu\text{m}$. The shape of the particles, unlike flakes of films deposited on the electrode and the chamber wall, means that the particles were generated in the gas phase. As seen in Fig. 2, agglomerates composed of spherical primary particles were observed. Figure 3 shows the pressure dependencies of the particle diameter and the number of particles included in an agglomerate. As the figure shows, the number of particles composing an agglomerate increases as the pressure increases more than 50 mTorr. The aggregation mechanism seems to be complicated.¹¹ Particles in plasmas, generally, were charged owing to the difference in the mobility of electrons and ions. The mechanism can be strongly affected by Coulomb repulsion force between charged particles and kinetic energy. Therefore, it is difficult to grasp the pressure dependence of particle generation only from the number of component particles, as the charge state of particles varies



(a) $1\text{ }\mu\text{m}$



(b) $10\text{ }\mu\text{m}$

FIG. 2. SEM micrographs of (a) particles and (b) an agglomerate composed of many spherical particles. These were found on a wafer prepared at 250 mTorr in c - C_4F_8 plasma.

with plasma parameters depending on pressure, particle diameter, and density.¹² However, the collision frequency of particles increases as the particle density increases, so the number of component particles of an agglomerate corresponds to the amount of particle production in a certain regime. In these experiments, the particle charge is estimated to be on the order of 100 electrons and does not change much in the pressure range. Therefore, the increases of the component particle number with pressure can be correlated with increase of particles produced in the plasma. On the other hand, the deposition rate of the polymer films was measured. The rate shows complex dependence on feed gas pressure (Fig. 4). In the high pressure region where a large number of the particles were produced, the deposition rate decreased with rising pressure.

Furthermore, in order to understand plasma reactions, gas-phase products were observed. The total pressure monitored by the manometer was decreased for a few minutes after plasma ignition under every pressure condition. This pressure change was not caused by the fluctuations of pump-

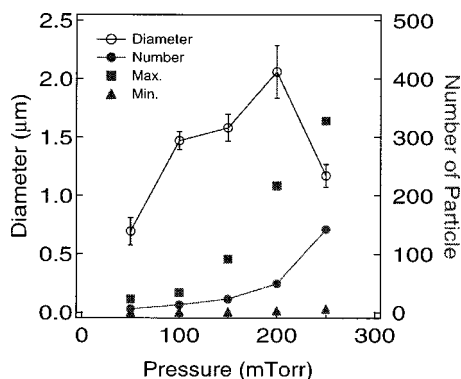


FIG. 3. Pressure dependence of the diameter of primary particles (open circles) and the number of particles composing an agglomerate (closed circles). For the diameter, the error bars indicate the values of dispersion. The maximum and the minimum values of the number of particles are also shown by squares and triangles, respectively.

ing and feeding of the gas but by chemical reactions in the plasma. The pressure depression increased with feed gas pressure as shown in Fig. 5. The depression meant the depletion of gas species due to polymerization reaction, that is, the transformation of gaseous components into solid matter. In addition, CF_4 and C_2F_6 molecules were found to be produced in C_4F_8 plasmas. The presence of these molecules has also been identified by measurements with Fourier transform infrared spectroscopy (FTIR).¹³ The density of these molecules was measured by infrared laser absorption spectroscopy at steady state after the initial pressure depression. The partial pressure of these molecules increased monotonously with feed gas pressure (Fig. 6). Figure 6 also shows the partial pressure of gaseous components except CF_4 and C_2F_6 molecules. It did not change monotonously but changed drastically as the feed gas pressure increased above a critical value of 50 mTorr for the particle formation.

The chemical bond composition of the polymer films deposited on the surface and the particles produced in the gas phase was analyzed by XPS. The measurement was done at two parts of a wafer prepared at 250 mTorr; a clean surface and a dirty one contaminated by particles (Fig. 7). The XPS spectra (Fig. 8) show that the chemical composition is different between the $\alpha\text{-C:F}$ films and the particles. In the spec-

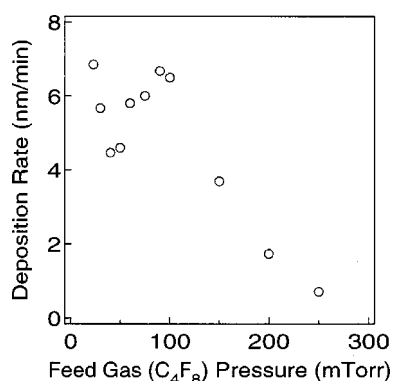


FIG. 4. Pressure dependence of the film deposition rate.

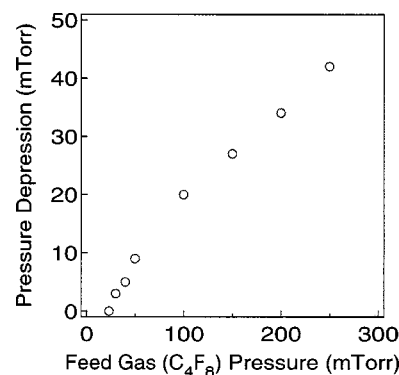


FIG. 5. Pressure dependence of the pressure depression caused by polymerization reaction at an initial state of the discharge.

tra, five peaks assigned by chemical shift correspond to five chemical bond components, C-C at 285.0 eV, C- CF_x at 287.3 eV, CF at 289.5 eV, CF_2 at 292.1 eV, and CF_3 at 294.0 eV.^{14,15} The spectrum of particles as dropped on the surface during the treatment was the same as that of the film, because the particles were covered with $\alpha\text{-C:F}$ films after dropping on the wafer. In order to remove the films found on particles, Ar ion sputtering was performed in the XPS system, using a low-energy ion beam to avoid the change of the chemical composition. The spectra after sputtering indicate that the particles include a larger amount of C- CF_x bond than the films, implying that the particles were formed by cross-linked molecules.

IV. DISCUSSION

The deposition rate of the polymer film on the surface depended on feed gas pressure. The pressure dependence of the rate was changed drastically by the presence of the particles in the pressure region higher than 50 mTorr. Especially, the deposition rate was reduced by the particle production. This fact indicates that polymer film precursors can be consumed mainly in the particle formation in the gas phase. In addition, the feed gas pressure dependence of the deposition rate was similar to that of the partial pressure of

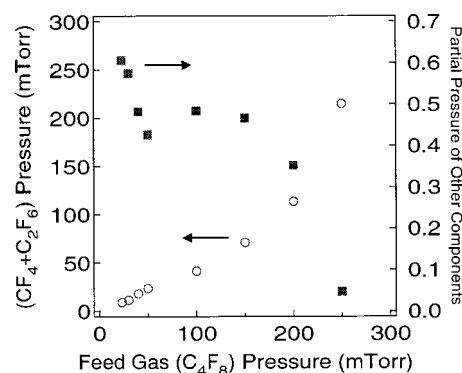


FIG. 6. Pressure dependence of the partial pressure of CF_4 and C_2F_6 produced in $c\text{-C}_4\text{F}_8$ plasmas. Also shown on right axis is the dependence of the partial pressure of gaseous components except CF_4 and C_2F_6 molecules.

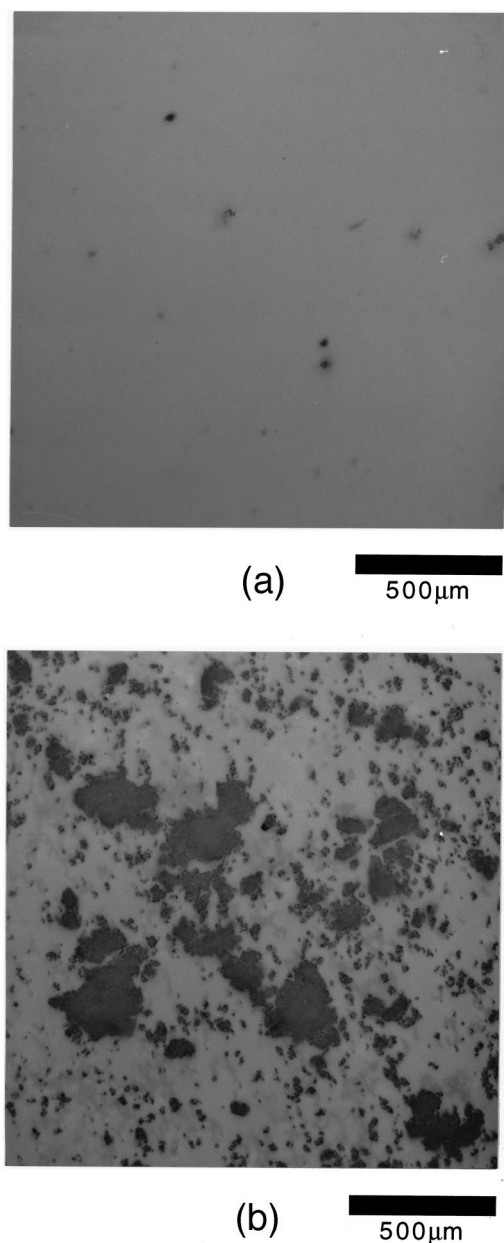


FIG. 7. Surface morphology of a wafer treated at 250 mTorr, observed by an optical microscope. The wafer included two parts of (a) a clean and (b) a dirty surface contaminated by the particles. In these images, black spots and parts indicate the contaminated regions.

the gaseous components except molecules such as CF_4 and C_2F_6 , where molecules can be formed by the three-body association given by the following equations:



where M is the third body. These reactions have relatively high rates of 2.8×10^{21} and $1.0 \times 10^{25} \text{ cm}^6/\text{mol}^2 \text{ s}$, respectively.^{16,17} These reactions are effective even at low pressure below 750 mTorr.¹⁸ The production of such molecules is a chain termination reaction forming a nonreactive site for polymerization. These molecules are chemically

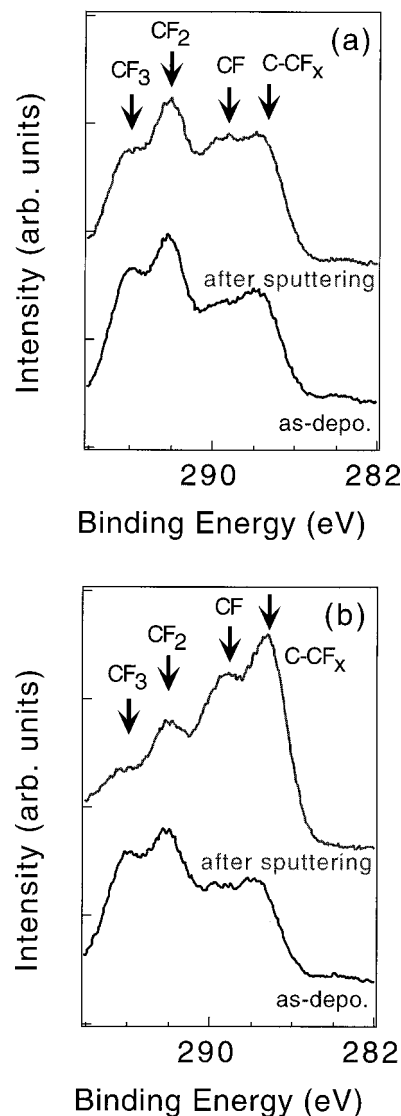


FIG. 8. XPS spectra of (a) polymer films on the surface and (b) particles produced in the gas phase. The XPS measurements were done before and after Ar ion sputtering to remove the polymer film on the particles. Five peaks were assigned to correspond to five chemical bond components, C–C at 285.0 eV, C– CF_x at 287.3 eV, CF at 289.5 eV, CF_2 at 292.1 eV, and CF_3 at 294.0 eV.

stable compared with C_4F_8 . The stable molecules easily accumulate in the plasma and their loss rate is close to a time constant determined by the pumping speed. In the present study, pure CF_4 and C_2F_6 plasmas produced neither polymer films nor particles. Therefore, it can be safely said that the film formation results from chemical reactions related to the reactive gaseous components except CF_4 and C_2F_6 . On the other hand, the particles were found to be formed by the cross-linked molecules as suggested in the XPS measurement. These molecules have molecular weights distributed around 100 000 (Ref. 19) and sizes of a few nanometers, which should be a cluster of solid matter. The cluster formation caused the depression of total pressure. Since the cluster can be charged and trapped in the discharge, they are grown up to micron-sized particles owing to the deposition of reac-

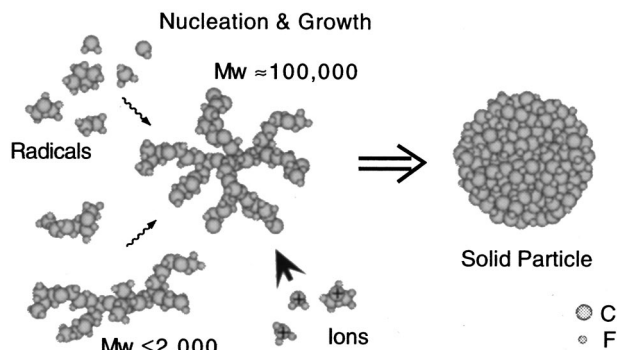
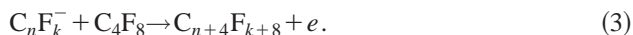


FIG. 9. Schematic describing a scheme for the particle production. Here, Mw means a molecular weight.

tive gaseous components of molecular weights below 2000, which form the surface films on the substrate as well as on the particles.¹⁸ Figure 9 shows the particle production scheme as mentioned above. The particle production and the total pressure depression strongly depend on feed gas pressure. The fact that the particle production increased monotonously with feed gas pressure may imply that the polymerization reaction correlates with the density of source gas molecules or the products resulted from first order reactions. As a scheme to grow a polymer chain, the following reaction is suggested:¹⁸



This reaction means that polymerization by associative electron detachment can proceed in C_4F_8 plasmas. At high pressures, supersaturation of the source gas molecule and other polymer precursor causes nucleation for the particle production.

Here, reaction products are generated in the transformation from source gas (C_4F_8) molecule to plasma-polymerized polymers. In this study, the reaction products are divided into three groups (Fig. 10). The first group are such stable molecules as CF_4 and C_2F_6 . These molecules are insufficiently reactive to form plasma polymers. Gaseous components except the stable molecules are included in the second group.

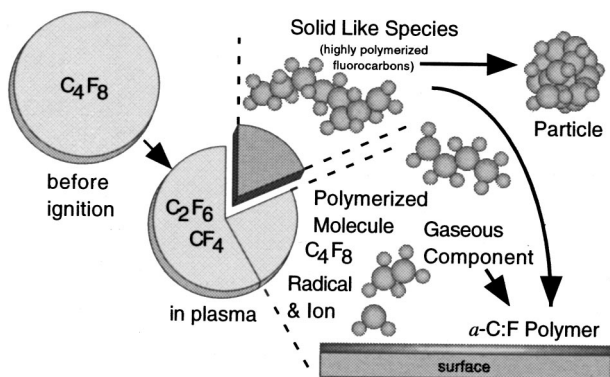


FIG. 10. Schematic for the transformation from source gas molecules to polymers. Components before and after ignition of the plasma are represented by pie charts.

This group is composed of radicals, ions, and molecules larger than source gas in molecular weight. These products are reactive and candidates for the polymer formation of the film deposition and the particle growth. Solid-like species, whose formation causes the pressure depression belong to the last group. The species are high molecular weight fluorocarbon compounds and a solid matter acting as the particle nuclei.

V. CONCLUSIONS

In $c-C_4F_8$ plasma, particle production was caused at high pressures above a critical value of 50 mTorr. The production should be noted especially in CVD processes, e.g., for the formation of films with low dielectric constant. In order to avoid contamination of process plasmas, it is necessary to maintain reactors at low pressures. On the other hand, it is possible to use the fluorocarbon particles as a material with low dielectric constant. Since more C- CF_x bond content was included in the particles rather than in the films, the particles are expected to have high thermal stability required in semiconductor processing. Furthermore, a composite of the particles can be porous media suitable for low permittivity materials. The composite is one of promising interlayer dielectrics for ULSI circuits.

From observation of particles, polymerization reactions were partly elucidated in the gas phase. The particle production accompanied by pressure depression was induced by the formation of clusters acting as nuclei of the particles. The nuclei trapped in the plasma can be grown up to micron-size particles, owing to the deposition of polymer film precursors. According to the feed gas pressure dependence of the deposition rate, it is suggested that these precursors must be reactive gaseous components and not stable molecules such as CF_4 and C_2F_6 . The presence of clusters was confirmed in chemical characterization with XPS, but their formation mechanism is not clear. Since the source gas ($c-C_4F_8$) molecule and products dissociated in first order reactions can form plasma polymer, other measurements detecting such molecules, e.g., FTIR spectroscopy, are required. Furthermore, it is indispensable to confirm the nuclei formation in gas phase diagnosis in order to elucidate the whole mechanism of the particle production in fluorocarbon plasmas. These subjects will be studied in the following work.

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