Application of Langmuir probe and optical emission spectroscopy for bromofluorocarbon plasma diagnostics

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Abstract. The Langmuir probe and optical emission spectroscopy were applied for diagnostics of C2F4Br2 low-pressure inductively coupled plasma. Electron temperature, plasma potential and concentrations of electrons, and positive ions, as well as fluorine and bromine radicals, were determined. An explanation of the results of experiments on the etching of low-k dielectrics in the studied plasma was proposed.

1. Introduction

Bromofluorocarbon plasmas (i.e. CF3Br, C2F4Br2) are of interest for research because of their possible applications in microelectronics. One of the usages of these plasmas is the process of low-damage etching of porous low-k dielectric films [1,2]. In the manufacturing of integrated circuits, the metallization system uses porous dielectrics with ultra-low dielectric constant to reduce signal transmission delays. The modern approach to the formation of metallization systems – dual-damascene, requires the formation of tranches in the dielectric layer with their subsequent filling with metal. However, the problem of reducing damage during plasma etching of dielectric films remains unresolved. Fluorine radicals penetrate the pores, where they can form a polar bond, which leads to an increase in the dielectric constant. Bromine does not spontaneously react with dielectric; therefore, bromine-containing compounds must protect the pore surface from the action of fluorine radicals. In [1,2], the study of cryogenic etching of films of dielectrics with a low dielectric constant in an inductively coupled plasma (ICP) of bromofluorocarbon was carried out. The results of these studies indicate that the degradation of films during etching in various fluorinated bromine-containing plasmas occurs for different reasons. In the present paper, to achieve a detailed understanding of the mechanisms of dielectric degradation, the ICP discharge of C2F4Br2 plasma was studied by Langmuir probe and optical emission spectroscopy.

2. Experimental

The experiment was carried out in a conventional commercial plasma etching tool Plasmalab 100 (Oxford Instruments). Inductively coupled plasma (ICP) was excited by an RF generator (2 MHz). The cylindrical process chamber (45 cm high and 38 cm in diameter) is made of aluminum. At the bottom of the chamber there is a table with wafer chuck. The chamber was pumped out by
A turbomolecular pump to base pressure $1 \cdot 10^{-6}$ Torr. Process gases are introduced into the chamber using mass flow controllers. $\text{C}_2\text{F}_4\text{Br}_2$ flow during experiments was 48 sccm.

2.1 Langmuir probe diagnostic

Langmuir probe diagnostic was performed using ESPion Advanced probe (Hiden Analytical) with RF compensation. Cylindrical tungsten probe (10 mm length and 0.15 mm in diameter) was used for measurements. The probe was placed in the center of the chamber 10 cm above the table. Metal walls of the chamber were used as a reference probe. Their surface area is much larger than the surface area of the measuring probe, which allows us to assume that the entire voltage drop across the measuring probe sheath. During I-V measurements in polymerizing plasmas a dielectric films can grow on the surface of the measuring probe. It leads to a distortion of the current-voltage characteristic and, as a consequence, the distortions of measured plasma parameters [3]. In order to remove non-conductive deposits, between the measurements probe was maintained at -30 V potential for ion sputtering of deposits. The cleaning mode was selected experimentally, ensuring the absence of film growth and, at the same time, the absence of etching of the tungsten probe. Good repeatability of experimental curves was obtained. A typical I-V curve is shown in figure 1.

![Figure 1](image_url)

**Figure 1.** A typical probe I-V curve for $\text{C}_2\text{F}_4\text{Br}_2$ plasma (p = 15 mTorr, $W_{\text{ICP}} = 2000$ W) a) overall view, plasma potential ($V_p$) is marked, b) ion branch

The IV-curves were processed as follows. Plasma potential ($V_p$) was determined as the inflection point of the IV-curve by numerical differentiation. The ion branch at high negative potentials, where electron current does not contribute to the current, was approximated using OML theory [4]. This approximation gives positive ion density ($N_{i+}$). Then ion current was subtracted from the measured total probe current to obtain electron current and calculate electron density ($N_e$). The electron temperature ($T_e$) was determined from the slope of the electron current graph at semi-log scale.

The application of the Langmuir probe method requires a check of the correctness of the conditions and the correctness of processing under the theory applicable to the given plasma parameters. In this case, studies show that in the region where the samples are subjected to etching and in the region where the probe was located in the experiment there are no directional particle fluxes (no drift), there are no significant magnetic fields. This makes it possible to apply the methods of analysis of probe curves for unperturbed cases. The gas temperature is less than 1000K, hence the assumption of cold ions applies: $T_i << T_e$. The plasma tool used is optimized for precision microelectronic processes and is characterized by low electron temperatures of 1.5–3 eV and characteristic electron concentrations in the range $10^{10}$-$10^{11}$ cm$^{-3}$. Calculations show that the Debye length in this case is about 50–100 µm.
While operating pressures are 5-50 mTorr and the mean free path is about few centimeters. So, plasma sheath, which can be estimated as few Debye length, is much thinner than mean free path and sheath is collisionless. The radius of the probe is 75 μm, which is significantly less than the size of the probe layer.

### 2.2 Optical emission spectroscopy

The concentrations of neutral fluorine and bromine were determined using optical emission actinometry [5]. The idea of this method is to determine the concentration of particles by intensity of their emission relative to the intensity of emission of particles, which concentration is known, called an actinometer. For this purpose, small addition of noble gas (i.e. Ar) usually used, because it does not form stable molecular particles so in weakly ionized plasma concentration of neutral argon can be found from ideal gas law. A small amount (4%) of argon was added into C₂F₆Br₂ plasma and optical emission spectra were measured. Following atomic lines were used for actinometry: Ar – 750.4 nm, F – 685.6 nm and Br – 700.5 nm. Spectroscopy was carried out using acousto-optic spectrometer “Quartz 2000”. The ratio of concentration of radicals and actinometer is proportional to the ratio of intensities of their atomic lines:

\[
\frac{[X]}{[Ar]} = \frac{I_X}{I_{Ar}}
\]

Where \([X]\) is the concentration of radical (Br or F) and \([Ar]\) is the concentration of argon atoms; \(I_X\), \(I_{Ar}\) are intensities of atomic lines and \(C^{X}_{Ar}\) is an actinometric coefficient. As intensity of atomic line emission proportional to the concentration of atoms in upper excited state corresponding to the line, the actinometric coefficient depends on the rates of excitation and deexcitation processes of this state. According to [6] main excitation process of upper atomic states of the selected for actinometry lines in similar conditions is direct electron excitation. Deexcitation processes are photon emission and collisional quenching. At low pressures (<1 Torr), collisions of excited particles rarely occur in comparison with photon emission; therefore, the quenching process can be neglected. Thus, actinometric coefficient \(C^{X}_{Ar}\) depends on the rates of direct electron excitation of upper state and Einstein coefficients for atomic transitions:

\[
C^{X}_{Ar} = \sum_k A^{X}_{ik} \frac{\lambda^{X}_{ij}}{\lambda^{Ar}_{mm}} \frac{k^X_{e}}{k^e_{X}}
\]

Where \(\lambda^{X}_{ij}, \lambda^{Ar}_{mm}\) - wavelengths of the selected atomic lines of X atom (F or Br) and Ar respectively, \(A^{X}_{ik}, A^{Ar}_{ik}\) - Einstein coefficients for X atomic transitions from the selected upper level to the selected lower level and all possible lower levels respectively. \(k^X_{e}, k^{Ar}_{e}\) - rates constants of excitation by direct electron impact into the selected upper atomic state for X and Ar respectively. Values of Einstein coefficients were taken from [7]. Rate constants for Ar (\(k^X_{e}\)) for different electron temperatures were determined in [5]. Rates constants of F and Br (\(k^X_{e}, k^{Br}_{e}\)) were determined from the cross sections calculated in the same approximation:

\[
k^X_{e} = (2/m_e)^{1/2} \int_0^\infty \sigma^X(\epsilon) f(\epsilon) \sqrt{\epsilon} \, d\epsilon
\]

Where \(f(\epsilon)\) - electron energy distribution function, \(\sigma^X(\epsilon)\) - electron impact excitation cross section for the X atomic transition to the selected upper atomic state at scattering electron energy \(\epsilon\). According to electron current determined from Langmuir probe diagnostics, the electron energy distribution function is in a good accordance with Maxwellian distribution. Rate constants of excitation by direct electron impact of F and Br were calculated with Maxwellian electron energy distribution function with electron temperature determined by Langmuir probe.

Electron impact excitation cross section of upper states of F and Br were calculated as a function of electron energy in Born approximation [8]. The upper states are excited from the ground states of the atoms. The transition from the ground state to selected upper state occurs with a change in spin by 1 for both atoms. Slater-type orbitals were used for approximation of atom radial functions in ground and excited states [9] (in atomic units).
\[ p_{n_0l_0}^F(r) = 12.5864 \cdot r \cdot \exp(-2.6 \cdot r), \quad p_{nl}^F(r) = 0.0851 \cdot r^2 \cdot \exp(-0.633 \cdot r) \]
\[ p_{n_0l_0}^{Br}(r) = 1.4063 \cdot r^{2.7} \cdot \exp(-1.649 \cdot r), \quad p_{nl}^{Br}(r) = 0.0040 \cdot r^3 \cdot \exp(-0.475 \cdot r) \]

Plane wave functions were used as wave functions of a scattered electron, which can be applied for excitation of a neutral atom.

3. Results and discussion

3.1 Langmuir probe diagnostic

Langmuir probe measurements of \( \text{C}_2\text{F}_3\text{Br}_2 \) plasma were carried out at chamber pressure in the range 5-20 mTorr and ICP power 2000 W. Electron temperature and plasma potential are shown in the figure 2 as a function of chamber pressure. Electron temperature decreases with increasing pressure, what is typical for ICP discharges. The temperature values are in the range 1.6-2.6 eV. The plasma potentials decrease with increasing pressure, which is associated with a decrease in the electron temperature. Values of plasma potential are 9-14 V.

![Figure 2](image)

**Figure 2.** a) Electron temperature, b) plasma potential depending on chamber pressure for ICP power of 2000 W

The concentration of electrons and positive ions is determined from the probe characteristics and is shown in figure 3. The concentration of charged particles decreases with increasing pressure, which is caused by a drop in the electron temperature and the decrease in the rate of the ionization processes. The concentration of electrons sharply decreases with pressure growth. The concentration of positive ions at high pressures is about an order of magnitude higher than the concentration of electrons, which indicates a significant concentration of negative ions.
Figure 3. The concentration of a) electrons, b) positive ions depending on chamber pressure for ICP power of 2000 W

3.2 Optical emission spectroscopy

The concentrations of fluorine and bromine atoms in the C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> plasma obtained at various pressures and power of 2000 W using actinometry are shown in figure 4. The concentration of F in the C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> plasma increases with increasing pressure, which can be explained by an increase in the number of particles in the chamber. It was found that the F concentration in the C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> plasma is almost an order of magnitude higher than the Br concentration; this may be due to the consumption of atomic bromine for the formation of bromine-containing particles stable at low electron temperatures.

Figure 4. The concentration of F and Br radicals depending on chamber pressure for ICP power of 2000W

4. Conclusion

In the present work, the inductively coupled plasma of C<sub>2</sub>F<sub>4</sub>Br<sub>2</sub> was studied in a typical commercial plasma etching tool applied in the microelectronic industry. A detailed actinometric model for determining the concentration of F and Br radicals in plasma was developed. A significant concentration of negative ions in the plasma was found. The concentration of atomic fluorine exceeds the concentration of bromine. These results can explain the degradation of dielectrics during etching.
in the $\text{C}_2\text{F}_4\text{Br}_2$ plasma, which is also observed for $\text{CF}_3\text{Br}$ plasma in an ICP discharge [1,2] as exposure of fluorine radicals leads to an increase in dielectric constant.

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