PLASMA ETCHING OF SiO_2 USING NOVEL FLUORINATED MIXTURES

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Abstract

The plasma etching characteristics of SiO_2 have been investigated using perfluorobutadiene, hexafluoropropylene oxide and perfluoropropene in mixture with oxygen. Perfluorobutadiene has shown the best process performance and the lowest emission of greenhouse gases. Optical emission spectroscopy analysis suggested that these results are due to the higher tendency of perfluorocyclobuthane to polymerize, and consequently, to the higher oxygen concentration required for the etching process. In fact, oxygen reacts with perfluorcarbons and decreases the emission of greenhouse species.

1. Introduction

Dry etching processes using perfluorocarbon (PFC) gases are now required to reduce the use and emission of greenhouse gases because they are known to release in the atmosphere chemical species characterized by quite a high global warming potential (GWP) (> 6,500). Several low-GWP gases have already been proposed for replacing conventional reactants; namely, C_2F_4, C_3F_6, C_5F_8, CF_3I as well as some HFC's (hydrofluorocarbons) [1-4]. In this paper, we report the preliminary results on the utilization of two novel compounds characterized by low-GWP: perfluorobutadiene (C_4F_6) and hexafluoropropene (C_3F_6O), and that of a conventional gas, i.e. perfluoropropene (C_3F_6) for comparison.

Experiment

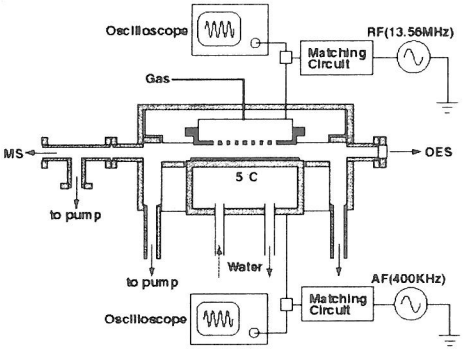

Fig.1 Schematic representation of experimental apparatus.

The etching reactor used in this study is schematically shown in Figure 1. It was a symmetrical parallel-plate reactor equipped with two electrodes (6 inches in diameter). The upper electrode was capacitively coupled to a RF (13.56 MHz) power supply while the thermally controlled lower electrode (5°C), on which the wafers to be etched were positioned during treatments, was connected to a 400 KHz power supply. A 6 inch

silicon shower, positioned on the upper electrode, allowed a uniform distribution of the feed gas during plasma processes. Etching experiments were performed on 6 inch Si and SiO_2 wafers that during plasma treatments were covered for a half area with a thin glass cover. The etching rate was calculated by the step height measured at the boundary of the masked region. Etching characteristics were mainly controlled by varying the fluorocarbon-O_2 ratio in the experimental conditions reported in Table 1. The system was equipped with three diagnostics: high impedance external electric probes, optical emission spectroscopy, and mass spectrometry. The electric probes, connected to a digital oscilloscope, allow control of the peak to peak voltage on both electrodes in order to detect variations of the electrical conditions, and therefore, of plasma characteristics, in particular that of bombardment energy. The optical emission of the plasma, sampled through a sapphire window by a quartz optical fiber, is analyzed with a monochromator (32 cm focal length) equipped with an intensified Optical Multichannel Analyzer (OMA). In order to obtain the relative concentration trends of emitting species in C_4F_6 containing plasma, Actinometric Optical Emission Spectroscopy (AOES) has been accomplished. For this reason a constant flow rate of He was added to the feed gas during the experiments as a supplemental actinometer at high excitation threshold energy (E_{th}= 23 eV) in addition to Ar (E_{th}= 13 eV). Since the emission of the two actinometers have been found to coincide in the experimental range investigated, it was possible to obtain the relative concentration trend even for those species with low excitation energy threshold (i.e. radicals) by simply dividing their emission intensity by that of the actinometer (i.e. Ar* at 751 nm) [5].

Mass spectrometric analyses of the gas emitted during experiments have been accomplished with a quadrupole mass spectrometer (Thermoquest Voyager). The gas was sampled at the exit of the plasma zone through an independently pumped stainless steel line (1 m long, 0.6 cm internal diameter) and entered the ionization chamber of the quadrupole through a leak valve. This

Table 1. Experimental conditions.

	C_3F_6O C_3F_6	C_4F_6
Power 13.56 MHz	400 W	400 W
Vpp 400 KHz	800 V	800 Vpp
Pressure	200mTorr	200mTorr
Ar	27 sccm	20.5 sccm
He	-	4.7 sccm
monomer + O_2	27 sccm	12 sccm

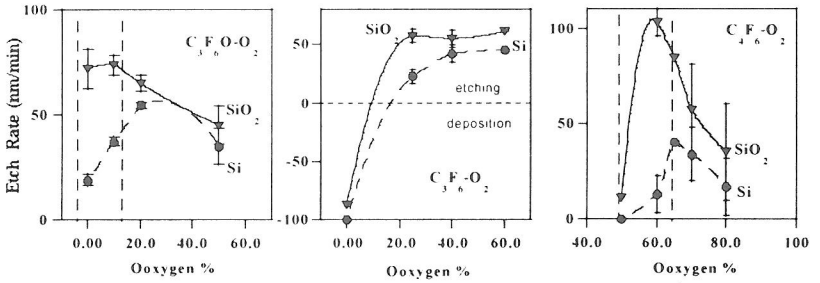

Figure 2. Etching rate of SiO_2 and Si for C_3F_6O/O_2, C_3F_6/O_2 and C_4F_6O/O_2 plasma

arrangement allows the detection of only the stable species formed after the plasma activation since radicals, ions, and other excited species are expected to recombine or to be quenched for gas-phase or gas-surface collisions in the sampling line. Quantitative analysis has been accomplished according the procedure reported in reference [6] and therefore, for analytical needs, the total flow rate was increased at 220 sccm (Ar 200 sccm, monomer + O_2 20 sccm).

2. Results and discussion

The etching rate of Si and SiO_2 is reported as a function of the oxygen percent in the gas feed in Figure 2. In the case of plasmas containing C_3F_6O, etching occurs even without O_2 and in this condition the best process performance in terms of etch rate and SiO_2-Si selectivity is obtained. On the contrary, with C_3F_6 and C_4F_6 consistent oxygen addition is necessary to suppress deposition in favor of etching. Plasmas fed with C_3F_6 show the best etching condition in proximity of the turning-point from deposition to etching (approximately at 25% O_2) because at higher oxygen content of feed gas, even though the SiO_2 etch rate trend reaches a plateau, that of Si increases leading to bud selectivity. C_4F_6 shows the highest etch rate and selectivity at quite a higher oxygen content (60%) with respect to the other two compounds because its polymerizing capability is higher. The best process intervals for SiO_2 etching is evidenced for each compound in Figure 2 by dashed lines: C_4F_6-60%O_2 fed plasma shows the best performances among the various mixture explored. The spectroscopic investigation performed with C_4F_6 containing plasma in the spectral region 200-800 nm show the typical features of fluorocarbon glow discharge. The characteristic species revealed are summarized in Table 2 along with their most important emission wavelength. As expected, massive addition of oxygen suppresses the signals of CF and CF_2 radicals and increases those of oxygen containing species (i.e. CO and CO_2). This is better shown in the actinometric concentration trends reported in Figure 3. The effect of oxygen is more evident on CF_2 than on CF radicals, by the comparison of Figures 2 and 3 it appears that in the concentration range where the etch rate grows and reaches the maximum, the concentration of CF decreases slowly, while that of CF_2 shows a steep

Table 2 Emission wavelength

Species	Wavelength (nm)
CF	203
CF_2	251.8
CF_2^*	240-320 cont.
CO	297.7
CO^*	218.9
CO_2^*	289.7
O	777.5
Si	288
Ar	750.4
He	388.9
F	703.7

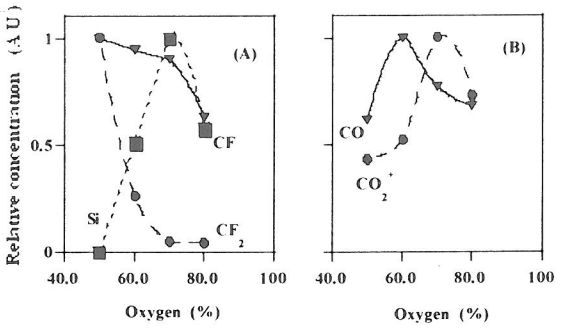

Fig. 3. Spectroscopic relative concentrations of some species in C_4F_6-O_2 plsamas vs. O_2 percent in the feed gas

reduction. The variation of fluorine atom concentration is very low, because the wide silicon area of the gas-shower head on the RF electrode, constantly exposed to the plasma, acts as scavenger of fluorine atoms. These data confirm the importance of CFx radicals in oxide etching and allow to make some interesting hypotheses on their role during SiO_2 treatment in C_4F_6–O_2 plasmas. In particular, it seems that the etch rate increases due to the reduction of gas-phase concentration of CF_2 radicals since the surface contamination of fluoropolymer decreases and CF radicals (and eventually F atoms) can more easily react with the oxide surface. When the oxygen content of the feed gas is raised above 70%, the decrease of CF radical concentration in the etching reactions is high, the effect of fluorine becomes predominant, the silicon surface is oxidized and consequently, a sensible loss of SiO_2-Si selectivity is detected. Spectroscopic measurements also show that due to the particular experimental set-up utilized and in particular to the wide silicon area exposed to the plasma (the shower head), the gas phase relative concentration of silicon atoms (i.e. the silicon emission rationed by that of the actinometer) is correlated with the etch rate of silicon, but with that of silicon dioxide.

The mass spectrometric quantitative analysis of the off-gas emitted in the atmosphere by plasmas fed with the three fluorocarbons investigated in mixture with oxygen is reported in Figure 4. The following PFC's have been detected in the off-gas: CF_4, C_2F_6, and C_3F_8 and their concentration decreases with the oxygen content of the feed gas. As confirmed by the spectroscopic measurements performed for C_4F_6 containing plasmas, this can be explained considering that oxygen converts the fluorocarbon species to CO and CO_2, and therefore, reduces the probability of PFC formation for radical recombination or radical-neutral

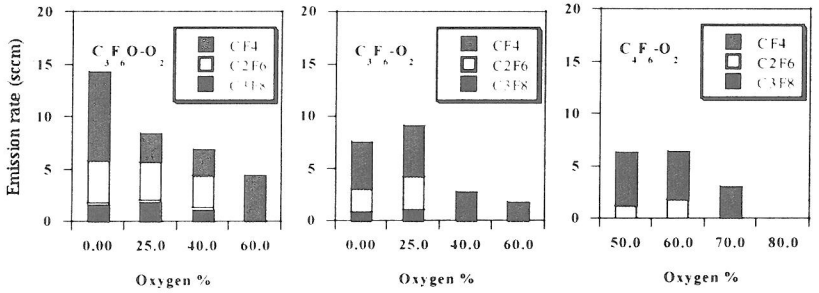

Fig. 4. Mass spectrometric evaluation of the PFC's emitted in the atmosphere

reactions.

The cumulative PFC emissions, expressed as Carbon Equivalent Emission Rate (CE) (gCE/min) according to: $CE = \frac{12}{44}\sum_{i=1}^{N}\left(Q_i \times GWP_{100i}\right)$, are reported for the best conditions of etch rate and SiO_2-Si selectivity in Figure 5. The lowest CE is registered for C_4F_6 because it shows the best etching performances when 60% of oxygen is added to the feed gas, and therefore, a more efficient removal of fluorocompounds occurs with respect to the other two compounds that show the best etching performances at lower oxygen percent.

4. Conclusions

The evaluation of the dry etching of SiO_2 thin film in C_3F_6, C_3F_6O, and C_4F_6 plasmas in mixture with oxygen have shown that the best results of etch rate and SiO_2-Si selectivity are obtained with C_4F_6. Since the polymerizing tendency of this compound is high, the best performances are detected when the feed gas contains 60% of oxygen. Spectroscopic measurements have shown that oxygen reduces considerably the concentration of CF_2 radicals, and therefore, the degree of surface contamination, but has a lighter effect on CF radicals which with F atoms can etch SiO_2. C_4F_6 plasmas are also characterized by the lowest contribution to global warming because the elevated quantity of oxygen contained in the gas mixture reduces the formation of PFC's.

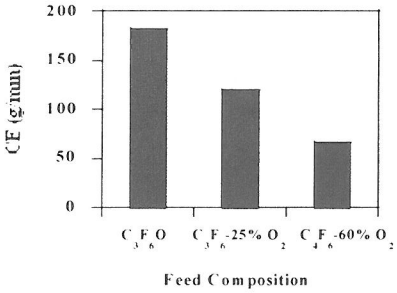

Fig. 5. CE *Vs.* feed composition

5. References

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