Decomposition of Boron Trifluoride in the RF Plasma Environment

Ya-Fen Wang[1]*, Cheng-Hsien Tsai[2], Lien-Te Hsieh[3], Min-Liang Shih[1] and Wen-Ching Chang[1]

[1] *Department of Environmental Engineering and Science, Chia-Nan University of Pharmacy and Science, No. 60, Sec. 1, Erh-Jen Rd., Tainan 717, Taiwan*

[2] *Department of Chemical Engineering, National Kaohsiung University of Applied Sciences, No. 415, Chien Kung Road, 807 Kaohsiung, Taiwan*

[3] *Department of Environmental Engineering and Science National Pingtung University of Science and Technology, 1Hseuh Fu Rd., Nei Pu Hsiang, Ping Tung, 91201, Taiwan*

Boron trifluoride (BF_3) is the most commonly used gas for implanting ions of the N-type dopant boron. BF_3 is non-flammable and does not support combustion, but is toxic when inhaled and corrosive to the skin. A radio frequency (RF) plasma system used to decompose BF_3 was examined. The BF_3 decomposition fractions (η_{BF3}) were determined in effluent gas streams of $BF_3/CH_4/Ar$, $BF_3/O_2/Ar$ and $BF_3/O_{2(glass)}/Ar$ plasma systems. The by-products detected in the $BF_3/CH_4/Ar$ plasma system were CO, CO_2, SiF_4, HF and boron-carbon compounds. The by-products detected in the $BF_3/O_2/Ar$ plasma system were $B_2O_{3(s)}$ and SiF_4. The η_{BF3} in the $BF_3/CH_4/Ar$ plasma system was 49.8%, higher than that in the $BF_3/O_2/Ar$ and $BF_3/O_{2(glass)}/Ar$ plasma system. However, the amount of decomposed BF_3 divided by the input energy (E_{BF3}, energy efficiency) in the $BF_3/O_{2(glass)}/Ar$ plasma system was greater than that in the $BF_3/CH_4/Ar$ and $BF_3/O_2/Ar$ plasma systems. Moreover, the photo images of depositions of different reacting gases O_2, H_2 with BF_3 were also compared. The reaction in the $BF_3/O_2/Ar$ plasma system generated B_2O_3 fine particles and led to the deposition of a white substance on the surface of the reactor. The η_{BF3} was only around 25% for mixing with O_2, even when the input power exceeded 120 Watts, but the generation of fine particles in the system warrants much more investigation.

Keywords: BF_3, RF plasma, B_2O_3, fine particle

1. Introduction

Fluorides are effective and widely used as fire suppressants (Noto et al., 1996; Linteris et al., 1996), chemical extinguishers (Babushok et al., 1996) and ozone-depleting substances (Hayman et al., 1997; Holmes et al., 1996). Additionally, various fluorides have been used in the semiconductor industry, in such techniques as chemical vapor deposition (CVD) (Smith et al., 1998; Schmidt et al., 1998), chemical etching (Leech et al., 1998) and ion implantation (Josep et al., 1999). These hazardous and reactive materials raised environmental, safety and handling issues. Boron trifluoride (BF_3) is an inorganic fluorinated,

*Corresponding author:
Tel: +886-6-2660206
Fax: +886-6-2669090
E-mail address: yafen@ms17.url.com.tw

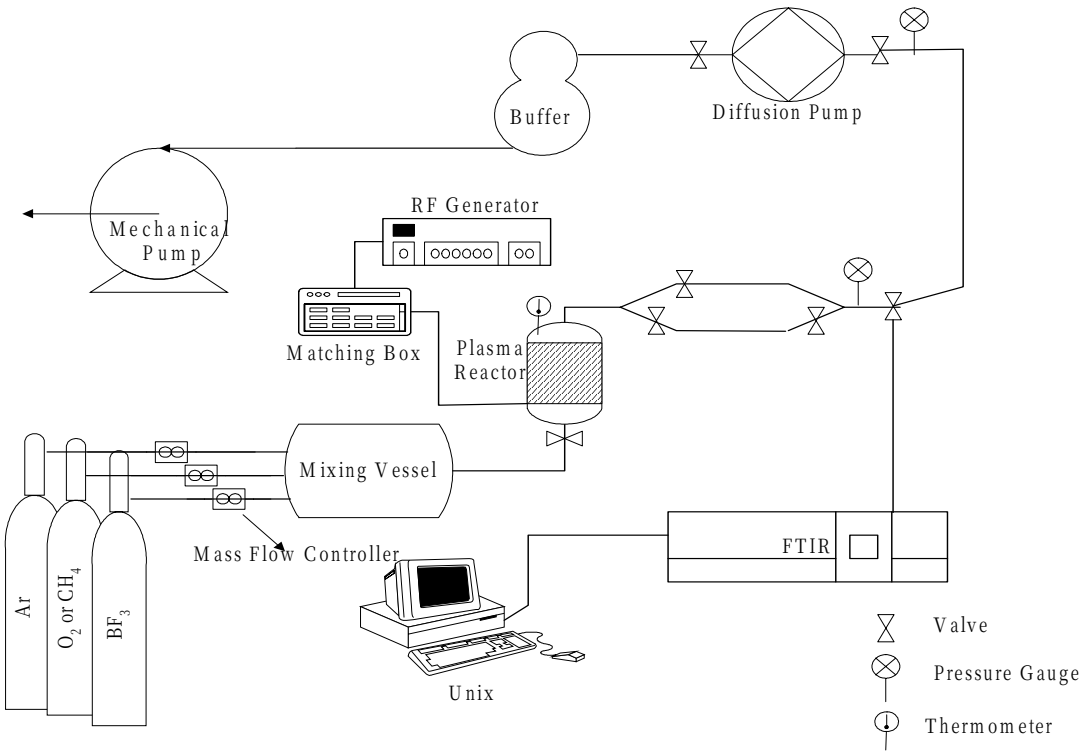


Figure 1. Schematic of the BF_3 RF plasma system

highly toxic, colorless and nonflammable has used to catalyze several chemical reactions, including polymerization, alkylation and acylation. It is also used to detector neutrons and is often used in ion implantation in the semiconductor industry (Schmidt et al., 1998; Boenig, 1988). Ion implantation is a process by which ionized atoms are accelerated directly into a substrate to selectively add dopant atoms. Although the requirements of clearance for semiconductor manufacturing, the generation of fine particles during the process of ion implantation warrants much more attention. The emissions of BF_3 must be controlled because at an immediate danger to live and health (IDLH) of 10 ppm and at a threshold level value (TLV) of 1 ppm, respectively (Josep et al., 1999).

A radio-frequency (RF) plasma environment with a high electrical and thermal conductivity constitutes an excellent energy conversion and heat transfer medium for reactants and products (Hsieh et al., 1998). The technology provides a more complete and a lower-temperature reaction environment for gas molecules than other methods. However, RF plasma exists out of equilibrium and is often called cold plasma (Boenig, 1988). The kinetic energy of electrons and ions exceeds that of molecules in the cold plasma system. The apparent operating temperature in an RF plasma reactor is generally below 400℃, while the real temperature of the electrons therein exceeds 2000 ℃. Consequently, conventional reactions that must proceed at a very high temperature can be completed at a lower temperature in the RF plasma reactor (Hsieh et al., 1998). Besides, RF plasma does not cause the erosion or corrosion of electrodes by by-products such as HCl or HF, unlike DC plasma (Breitbarth et al., 1997).

Although controlling and reducing the emission of perfluorocompounds (PFCs) has received considerable attention, the decomposition of BF_3 has seldom been addressed. This work compares

the depositions of various reacting gases, O_2, H_2 with BF_3 in an RF plasma system. Additionally, the effect of input power on the BF_3 decomposition fraction (η_{BF3}) in the $BF_3/CH_4/Ar$, $BF_3/O_2/Ar$ and $BF3/O_{2(glass)}/Ar$ (with glass beads added) RF plasma system was determined. Finally, the possible reaction equations in the $BF_3/CH_4/Ar$ and $BF_3/O_2/Ar$ RF plasma reactors were proposed.

2. Experimental Apparatus

Figure 1 schematically depicts the experimental apparatus used in this study. The $BF_3/CH_4/Ar$ or $BF_3/O_2/Ar$ mixing gas was metered using Brooks type 5850E mass flow controllers, at a total flow rate of 700 sccm : the gas entered a mixing vessel and was introduced perpendicularly into a 4.14 × 15 cm cylindrical glass reactor. The RF plasma discharge was produced using a plasma generator (PFG 600 RF, Fritz Huttinger Elektronik Gmbh) at 13.56 MHz and with a matching network (Matchbox PFM). RF power was delivered through the power meter and the matching unit to an outer copper electrode that was wrapped around the reactor, the other electrode was earthed. The system was inductively coupled : the external electrode and the glass reactor wall beneath it, together with the conductive plasma inside the reactor, generated a capacitor that enabled capacitive coupling of RF power into the discharge (Biederman et al., 1992).

Before the experiment, a diffusion pump was used to maintain the pressure of the system below 0.001 Torr to clean up contamination. Under each designed experimental condition, the input power, the CH_4/BF_3 or O_2/BF_3 ratio, the operational pressure and the BF_3 feeding concentration were measured more than three times within five minutes to ensure that steady-state conditions had been reached. Both reactants and final products were first identified by gas chromatography/mass spectrometry (HP5890A PLUS GC/MS). Then, all species were identified and quantified using an on-line Fourier Transform Infrared (FTIR) spectrometer (Thermo Nicolet AVATRA 360).

Gaseous reactants and products were calibrated by withdrawing unreacted gases and passing them through the sampling line connected to the FTIR. The mass of species was calculated by comparing the response factor (absorbance height/ concentration) of standard gas and reaction gas at given IR wave number. Each run of the experiment took 20 min and the results indicated that the steady-state conditions were reached in the effluent after 10 min. The data presented herein are mean values measured after a steady-state condition had been reached.

3. Results and Discussion

Experiments were performed to determine the dependence of the BF_3 decomposition fraction (η_{BF3}). The η_{BF3} was defined as follows:

$$\eta_{BF3}\ (\%) = [(C_{in(BF3)}-C_{out(BF3)})/(C_{in(BF3)})]* 100\% \quad (1)$$

$C_{in(BF3)}$：feeding concentration of BF_3 (%)
$C_{out(BF3)}$：effluent concentration of BF_3 (%)

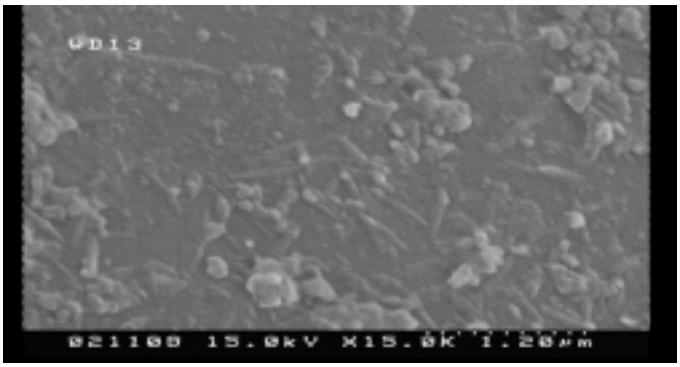
$$\eta_{CH4}\ (\%) = [(C_{in(CH4)}-C_{out(CH4)})/(C_{in(CH4)})]*100\% \quad (2)$$

$C_{in(CH4)}$：feeding concentration of CH_4 (%)
$C_{out(CH4)}$：effluent concentration of CH_4 (%)

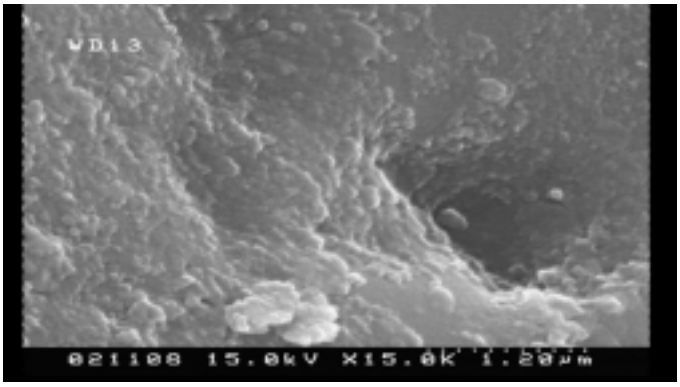
$$E_{BF3} = (M_{BF3}* N*60*1000) / W \quad (3)$$

E_{BF3}：energy efficiency, the amount of decomposed BF_3 divided by the input energy (molecules/kWh)
M_{BF3}：number of moles of decomposed BF_3
N：Avogadro's number, $6.02*10^{23}$
W：input power (Watts)

$$F_{CO+CO2}\ (\%) = [C_{CO} + C_{CO2}/C_{in(CH4)}]*100\% \quad (4)$$



(a) before reaction



(b) after reaction

Figure 2. SEM image of glass bead (a) before and (b) after reaction in the $BF_3/O_{2(glass)}/Ar$ system

F_{CO+CO2} : fraction of total input carbon converted into CO and CO_2 (%)

C_{CO} : effluent concentration of CO (%)

C_{CO2} : effluent concentration of CO_2 (%)

$$F_{SiF4}(\%) = [C_{SiF4}*4 / C_{in(BF3)}*3]*100\%$$

F_{SiF4} : fraction of total input fluorine converted into SiF_4 (%)

C_{SiF4} : effluent concentration of SiF_4 (%)

3.1 Deposition in the $BF_3/CH_4/Ar$ Plasma System

A possible reaction equation of $BF_3/CH_4/Ar$ RF plasma system is as follows.

$$BF_3 + CH_4 + SiO_2 = \text{boron-carbon compounds (deposition)} + CO + CO_2 + SiF_4 + HF$$

SiF_4 was formed in the well-known plasma-chemical etching reaction : $SiO_2 + 4F = SiF_4 + O_2$. The SiF_4 was converted into CaF_2 according to the results proposed by Breitbarth, et al. (1997). Additionally, the produced O_2 will react further with CH_4, resulting in the formation of CO and CO_2 in the RF plasma system. HF was formed because of the high bond strength of H-F (567.9 ± 0.1 D^0_{298}/kJ mol^{-1}), and reduces the opportunities for reaction between F and C atoms to generate other fluorinated compounds. However, scrubbing or neutralizing easily removed the HF.

A little deposition occurred on the inside of the plasma reactor. The result of Electron Spectroscopy for Chemical Analysis (ESCA, ESCA-210) analysis revealed that carbon, boron, fluorine and silicon were present in the deposition.

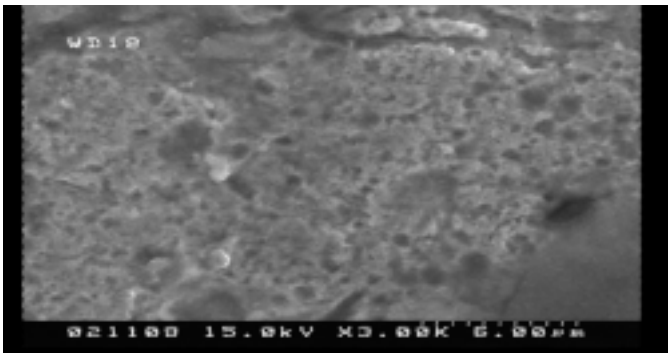


Figure 3. SEM image of deposition in the $BF_3/O_2/H_2/Ar$ system

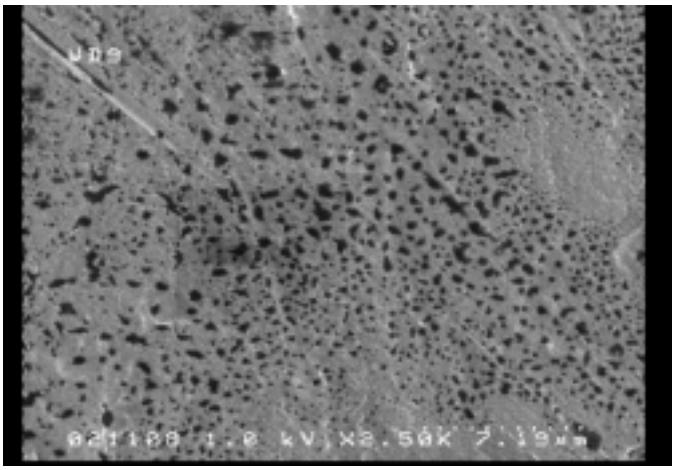


Figure 4. SEM image of deposition in the $BF_3/H_2/Ar$ system with tungsten as catalyst

3.2 Deposition in the $BF_3/O_2/Ar$ Plasma System

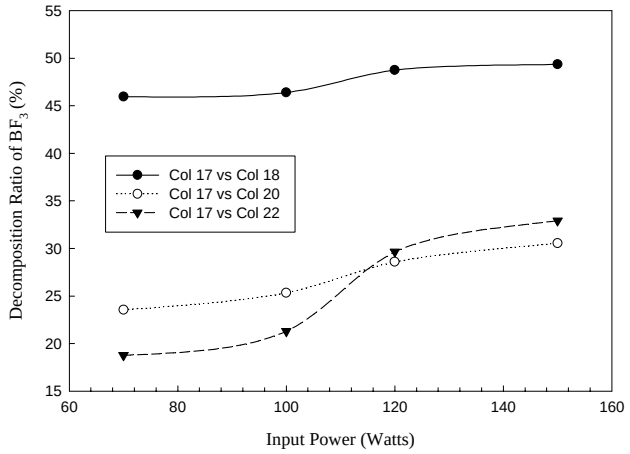


Figure 5. Comparison of variation of BF_3 decomposition ratio with input power among $BF_3/CH_4/Ar$, $BF_3/O_2/Ar$ and $BF_3/O_{2(glass)}/Ar$ RF plasma systems

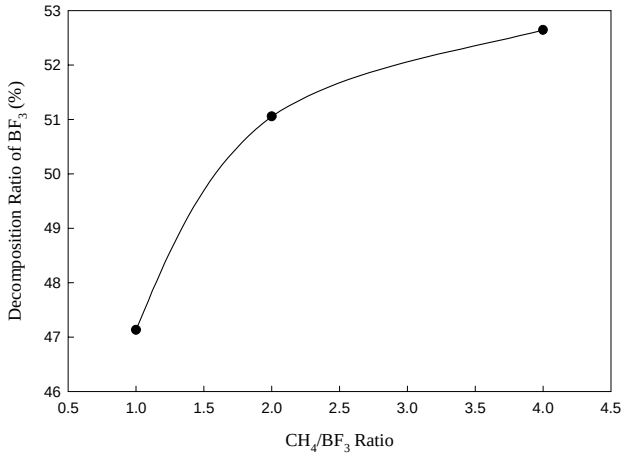


Figure 6. Relationship between BF_3 decomposition ratio and CH_4/BF_3 ratio

A possible reaction equation of the $BF_3/O_2/Ar$ RF plasma system is as follows.

$$BF_3 + O_2 + SiO_2 = B_2O_3 + SiF_4$$

Generated B_2O_3 particles will adhere to the surface of the reactor and inhibit further plasma-chemical etching. Interestingly, the increased reaction surface area provided by the addition of glass beads increases the decomposition ratio of BF_3. The results in Fig 2 display SEM (SEM, JXA840A) images of the glass beads before and after the reaction between BF_3 and O_2 in the RF plasma system. The etching in Fig 2(b) was obvious and the deposition of film on the surface of the glass beads was increased. Figure 3 depicts the deposition of $BF_3/O_2/H_2/Ar$ system. The competitive reaction between O_2 and BF_3 and O_2 and H_2 made the deposition thinner than in the $BF_3/O_2/Ar$ RF plasma system, in which fewer B_2O_3 particles were formed. Figure 4 presents the deposition in the $BF_3/H_2/Ar$ system, with tungsten as a catalyst in the reactor. Interestingly, cobweb deposition formed on the surface of the reactor. Although the η_{BF3} was not favorable, many fine particles were still generated in the system, resulting in the formation of deposition on the surface of the reactor. Accordingly, much more attention should be paid to the generation of fine particles in such systems in the ion implantation industry.

3.3 η_{BF3} and E_{BF3} in the BF_3 RF Plasma System

Figure 5 indicated that the values of η_{BF3} were 49.8%, 30.5% and 32.9% for $BF_3/CH_4/Ar$, $BF_3/O_2/Ar$ and $BF_3/O_{2(glass)}/Ar$ plasma system, respectively, at an input power of 150 Watts. Accordingly, for a given input power, η_{BF3} of the $BF_3/CH_4/Ar$ plasma system exceeded that of the $BF_3/O_2/Ar$ or $BF_3/O_{2(glass)}/Ar$ plasma system. Moreover, η_{BF3} increased when a catalyst (glass beads) was added to the system, when the input power exceeded 120 Watts. The value of η_{BF3} increased with the input power, η_{BF3} also increased from 47.1% to 52.6% as the CH_4/BF_3 ratio increased from 1.0 to 4.0 (Fig 6). Although the η_{BF3} is not high enough, the η_{CH4} was almost 100% under all experimental conditions. However, the results for E_{BF3} revealed that the energy efficiency was $2.63 * 10^{23}$ in the $BF_3/O_{2(glass)}/Ar$ plasma system, better than that in the $BF_3/O_2/Ar$ ($E_{BF3} = 1.77 * 10^{23}$) and $BF_3/CH_4/Ar$ ($E_{BF3} = 1.48 * 10^{21}$) plasma systems, respectively.

3.4 Detecting Products in the $BF_3/CH_4/Ar$ Plasma System

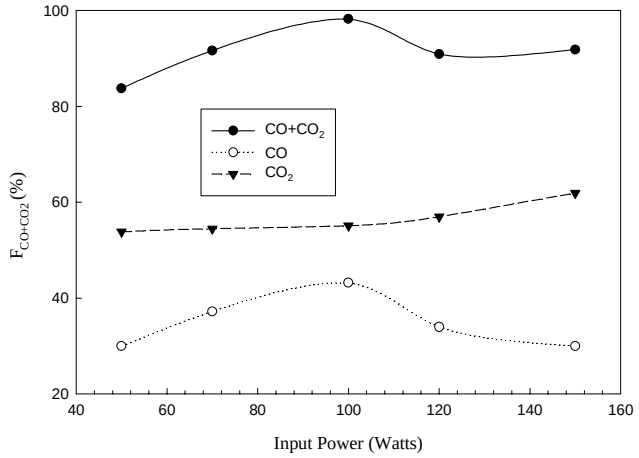


Figure 7. Fraction of total input carbon converted into CO and CO_2 in the $BF_3/CH_4/Ar$ RF plasma system

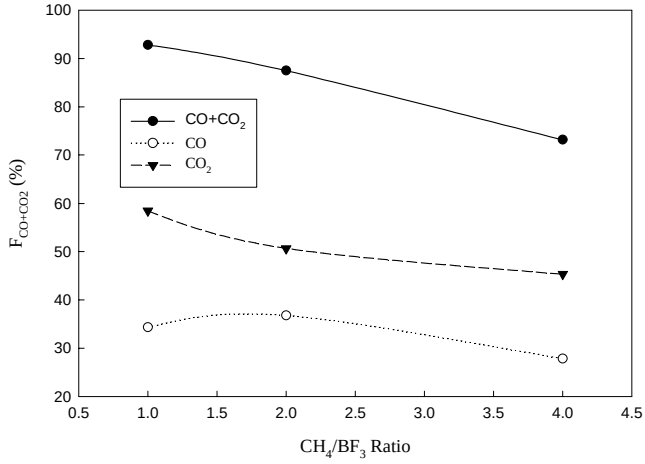


Figure 8. Relationship between fraction of total input carbon converted into CO and CO_2 and the CH_4/BF_3 ratio

According to Fig 7, the fraction of total input carbon converted into CO (F_{CO}) increased from 29.9% to 43.1%, and then declined to 29.9% as the input power increased from 50 to 150 Watts. The fraction of total input carbon converted into CO_2 (F_{CO2}) increased from 53.8% to 61.9% as the input power increased from 50 to 150 Watts. The value of F_{CO+CO2} increased from 83.7% to 98.2% and then declined to 91.8% as the input power increased. However, Fig. 8 indicated that F_{CO} increased from 34.4% to 36.8% and then fell to 27.9% as the CH_4/BF_3 ratio increased from 1.0 to 4.0. The value of F_{CO2} fell from 58.4% to 45.3% as the CH_4/BF_3 ratio increased from 1.0 to 4.0. The value of F_{CO+CO2} declined from 92.8% to 73.2% as the

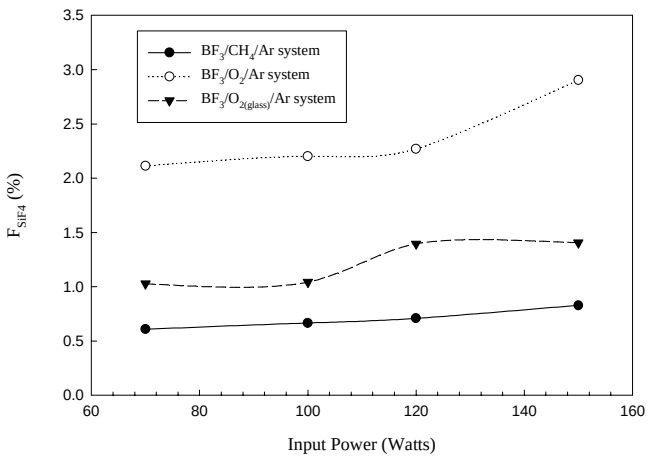


Figure 9. Comparison of the fraction of total input fluorine converted into SiF_4 with input power among $BF_3/CH_4/Ar$, $BF_3/O_2/Ar$ and $BF_3/O_{2(glass)}/Ar$ RF plasma systems

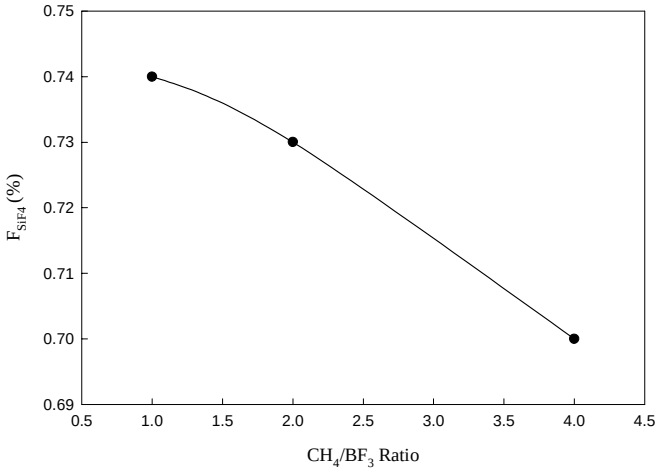


Figure 10. Relationship between the fraction of total input fluorine converted into SiF_4 and the CH_4/BF_3 ratio

CH_4/BF_3 ratio increased from 1.0 to 4.0.

The value of F_{SiF4} increased from 0.61% to 0.83%, from 2.11% to 2.90% and from 1.03% to 1.41% for $BF_3/CH_4/Ar$, $BF_3/O_2/Ar$ and $BF_3/O_{2(glass)}/Ar$ plasma systems, respectively, as the input power increased from 70 to 150 Watts (Fig 9). The F_{SiF4} was higher in the $BF_3/O_2/Ar$ plasma system than in the $BF_3/CH_4/Ar$ plasma system, because of the competition between the etching process and the formation of HF. Additionally, the value of F_{SiF4} declined from 0.74% to 0.70% as the CH_4/BF_3 ratio increased from 1.0 to 4.0 (Fig 10). The value of η_{BF3} was around 50% during mixing

with the CH_4, but near only 29% during mixing with O_2, even when the input power exceeded 120 Watts. Although the value of η_{BF3} in the $BF_3/O_2/Ar$ plasma system was lower than that in the $BF_3/CH_4/Ar$ plasma system, the generation of fine particles and their deposition were more serious in the $BF_3/O_2/Ar$ plasma system, which fact warrants further investigation.

Acknowledgements

The authors would like to thank the National Science Council of the Republic of China, Taiwan for financially supporting this research under Contract No. NSC90-2211-E-041-003.

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Received for review, March 12, 2003
Accepted, June 10, 2003
AAQR-2003-06