

Decomposition of Boron Trifluoride in the RF Plasma Environment

Ya-Fen Wang^{1*}, Cheng-Hsien Tsai², Lien-Te Hsieh³, Min-Liang Shih¹ and Wen-Ching Chang¹

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 (BF₃) is the most commonly used gas for implanting ions of the N-type dopant boron. BF₃ 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 BF₃ was examined. The BF₃ decomposition fractions (η_{BF_3}) were determined in effluent gas streams of BF₃/CH₄/Ar, BF₃/O₂/Ar and BF₃/O_{2(glass)}/Ar plasma systems. The by-products detected in the BF₃/CH₄/Ar plasma system were CO, CO₂, SiF₄, HF and boron-carbon compounds. The by-products detected in the BF₃/O₂/Ar plasma system were B₂O_{3(s)} and SiF₄. The η_{BF_3} in the BF₃/CH₄/Ar plasma system was 49.8%, higher than that in the BF₃/O₂/Ar and BF₃/O_{2(glass)}/Ar plasma system. However, the amount of decomposed BF₃ divided by the input energy (E_{BF_3} , energy efficiency) in the BF₃/O_{2(glass)}/Ar plasma system was greater than that in the BF₃/CH₄/Ar and BF₃/O₂/Ar plasma systems. Moreover, the photo images of depositions of different reacting gases O₂, H₂ with BF₃ were also compared. The reaction in the BF₃/O₂/Ar plasma system generated B₂O₃ fine particles and led to the deposition of a white substance on the surface of the reactor. The η_{BF_3} was only around 25% for mixing with O₂, even when the input power exceeded 120 Watts, but the generation of fine particles in the system warrants much more investigation.

Keywords: BF₃, RF plasma, B₂O₃, 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 (BF₃) is an inorganic fluorinated,

*Corresponding author:

Tel: +886-6-2660206

Fax: +886-6-2669090

E-mail address: yafen@ms17.url.com.tw

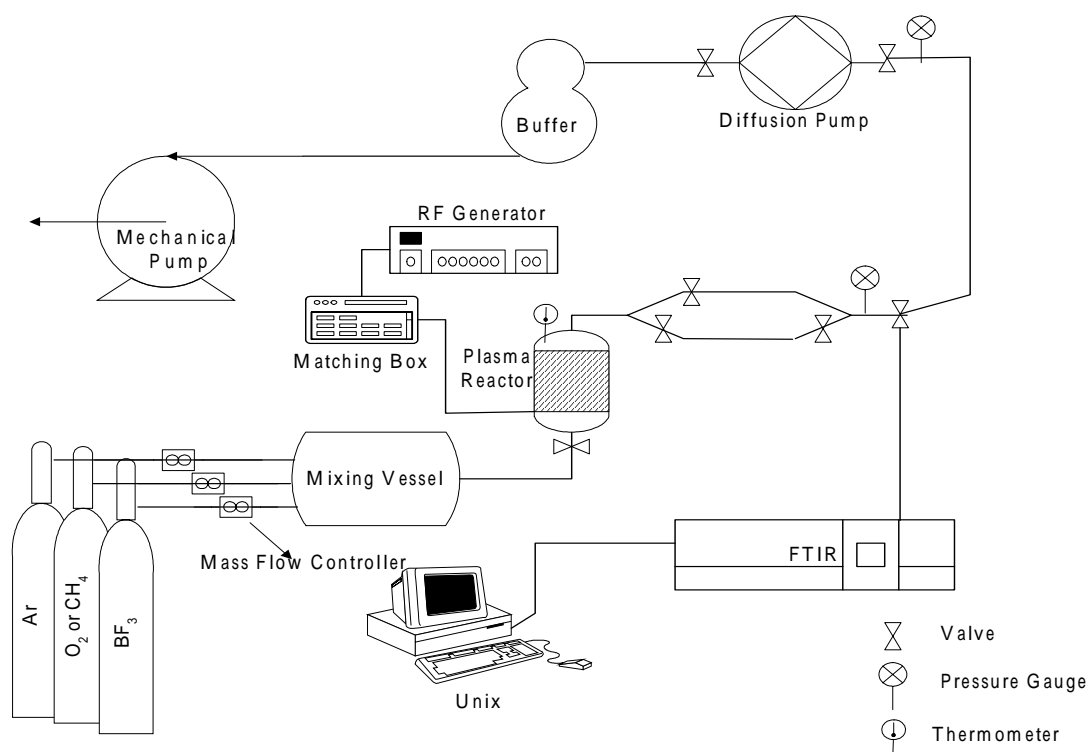


Figure 1. Schematic of the BF₃ RF plasma system

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 BF₃ 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 °C, while the real temperature of the electrons therein exceeds 2000 °C. 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 BF₃ has seldom been addressed. This work compares

the depositions of various reacting gases, O₂, H₂ with BF₃ in an RF plasma system. Additionally, the effect of input power on the BF₃ decomposition fraction (α_{BF_3}) in the BF₃/CH₄/Ar, BF₃/O₂/Ar and BF₃/O_{2(glass)}/Ar (with glass beads added) RF plasma system was determined. Finally, the possible reaction equations in the BF₃/CH₄/Ar and BF₃/O₂/Ar RF plasma reactors were proposed.

2. Experimental Apparatus

Figure 1 schematically depicts the experimental apparatus used in this study. The BF₃/CH₄/Ar or BF₃/O₂/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 CH₄/BF₃ or O₂/BF₃ ratio, the operational pressure and the BF₃ 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 BF₃ decomposition fraction (α_{BF_3}). The α_{BF_3} was defined as follows:

$$\alpha_{BF_3} (\%) = [(C_{in(BF_3)} - C_{out(BF_3)}) / C_{in(BF_3)}] * 100\% \quad (1)$$

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

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

$$\alpha_{CH_4} (\%) = [(C_{in(CH_4)} - C_{out(CH_4)}) / C_{in(CH_4)}] * 100\% \quad (2)$$

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

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

$$E_{BF_3} = (M_{BF_3} * N * 60 * 1000) / W \quad (3)$$

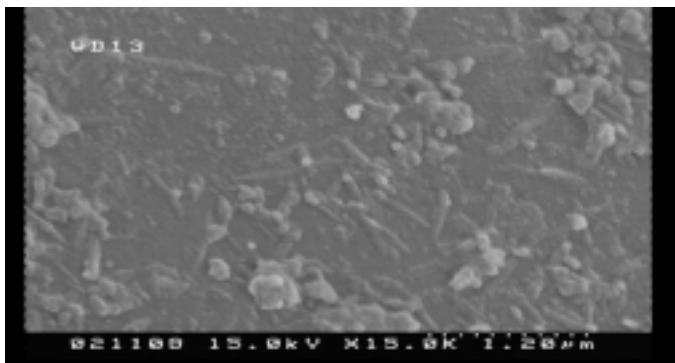
E_{BF_3} : energy efficiency, the amount of decomposed BF₃ divided by the input energy (molecules/kWh)

M_{BF_3} : number of moles of decomposed BF₃

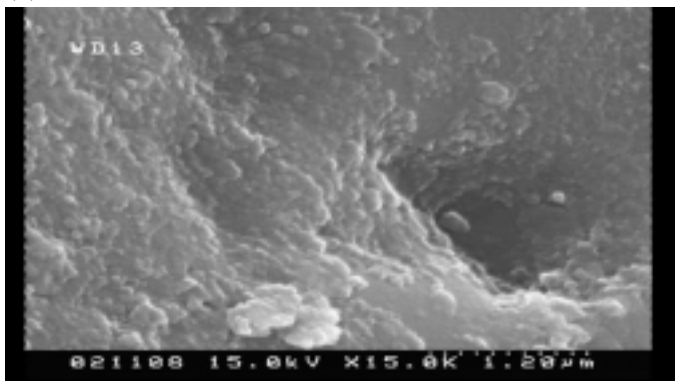
N : Avogadro's number, 6.02*10²³

W : input power (Watts)

$$F_{CO+CO_2} (\%) = [C_{CO} + C_{CO_2} / C_{in(CH_4)}] * 100\% \quad (4)$$



(a) before reaction



(b) after reaction

Figure 2. SEM image of glass bead (a) before and (b) after reaction in the BF₃/O₂(glass)/Ar system

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

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

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

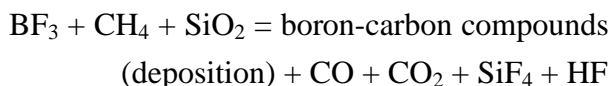
$$F_{SiF_4} (\%) = [C_{SiF_4} * 4 / C_{in(BF_3)} * 3] * 100\%$$

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

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

3.1 Deposition in the BF₃/CH₄/Ar Plasma System

A possible reaction equation of BF₃/CH₄/Ar RF plasma system is as follows.



SiF₄ was formed in the well-known plasma-

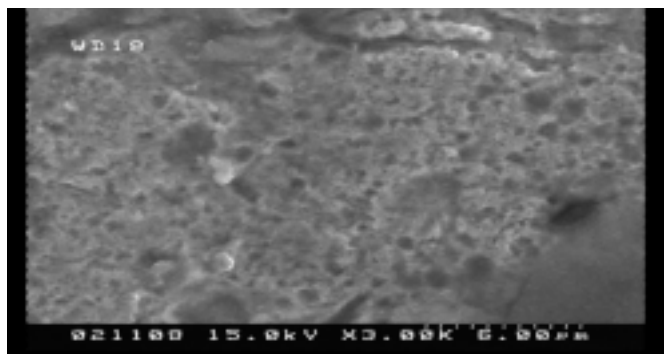


Figure 3. SEM image of deposition in the BF₃/O₂/H₂/Ar system

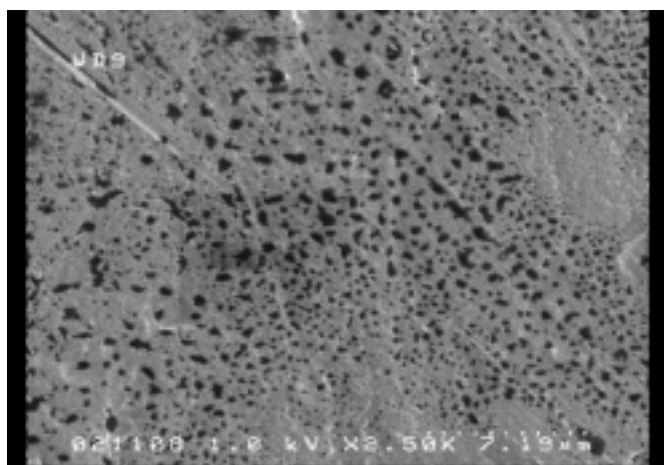


Figure 4. SEM image of deposition in the BF₃/H₂/Ar system with tungsten as catalyst

chemical etching reaction : SiO₂ + 4F = SiF₄ + O₂. The SiF₄ was converted into CaF₂ according to the results proposed by Breitbarth, et al. (1997). Additionally, the produced O₂ will react further with CH₄, resulting in the formation of CO and CO₂ in the RF plasma system. HF was formed because of the high bond strength of H-F (567.9 ± 0.1 D₂₉₈⁰/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.

3.2 Deposition in the BF₃/O₂/Ar Plasma System

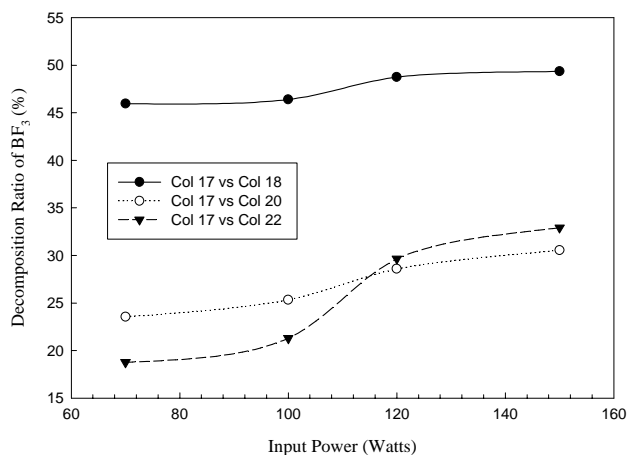
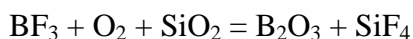


Figure 5. Comparison of variation of BF_3 decomposition ratio with input power among $\text{BF}_3/\text{CH}_4/\text{Ar}$, $\text{BF}_3/\text{O}_2/\text{Ar}$ and $\text{BF}_3/\text{O}_2(\text{glass})/\text{Ar}$ RF plasma systems

A possible reaction equation of the $\text{BF}_3/\text{O}_2/\text{Ar}$ RF plasma system is as follows.



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 $\text{BF}_3/\text{O}_2/\text{H}_2/\text{Ar}$ system. The competitive reaction between O_2 and BF_3 and O_2 and H_2 made the deposition thinner than in the $\text{BF}_3/\text{O}_2/\text{Ar}$ RF plasma system, in which fewer B_2O_3 particles were formed. Figure 4 presents the deposition in the $\text{BF}_3/\text{H}_2/\text{Ar}$ system, with tungsten as a catalyst in the reactor. Interestingly, cobweb deposition formed on the surface of the reactor. Although the BF_3 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

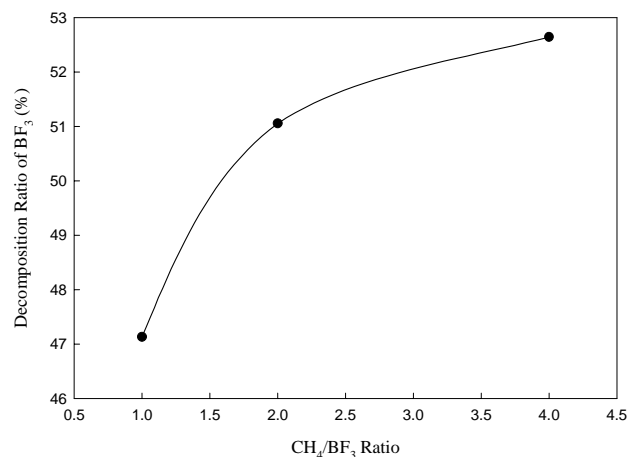


Figure 6. Relationship between BF_3 decomposition ratio and CH_4/BF_3 ratio

particles in such systems in the ion implantation industry.

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

Figure 5 indicated that the values of BF_3 were 49.8%, 30.5% and 32.9% for $\text{BF}_3/\text{CH}_4/\text{Ar}$, $\text{BF}_3/\text{O}_2/\text{Ar}$ and $\text{BF}_3/\text{O}_2(\text{glass})/\text{Ar}$ plasma system, respectively, at an input power of 150 Watts. Accordingly, for a given input power, BF_3 of the $\text{BF}_3/\text{CH}_4/\text{Ar}$ plasma system exceeded that of the $\text{BF}_3/\text{O}_2/\text{Ar}$ or $\text{BF}_3/\text{O}_2(\text{glass})/\text{Ar}$ plasma system. Moreover, BF_3 increased when a catalyst (glass beads) was added to the system, when the input power exceeded 120 Watts. The value of BF_3 increased with the input power, BF_3 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 BF_3 is not high enough, the CH_4 was almost 100% under all experimental conditions. However, the results for E_{BF_3} revealed that the energy efficiency was 2.63×10^{23} in the $\text{BF}_3/\text{O}_2(\text{glass})/\text{Ar}$ plasma system, better than that in the $\text{BF}_3/\text{O}_2/\text{Ar}$ ($E_{\text{BF}_3} = 1.77 \times 10^{23}$) and $\text{BF}_3/\text{CH}_4/\text{Ar}$ ($E_{\text{BF}_3} = 1.48 \times 10^{21}$) plasma systems, respectively.

3.4 Detecting Products in the $\text{BF}_3/\text{CH}_4/\text{Ar}$ Plasma System

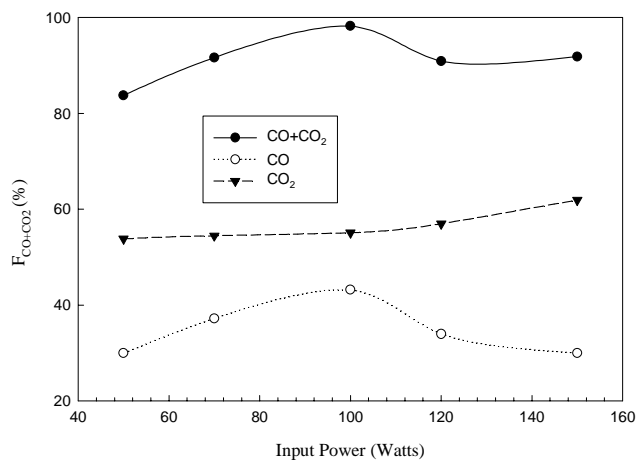


Figure 7. Fraction of total input carbon converted into CO and CO₂ in the BF₃/CH₄/Ar RF plasma system

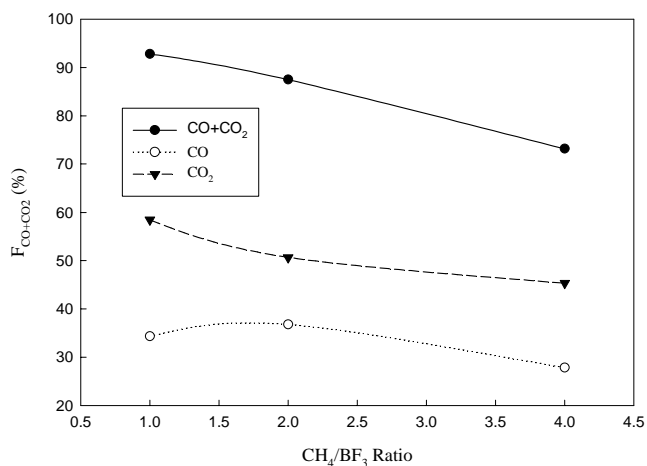


Figure 8. Relationship between fraction of total input carbon converted into CO and CO₂ and the CH₄/BF₃ ratio

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 CO₂ (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 CH₄/BF₃ ratio increased from 1.0 to 4.0. The value of F_{CO₂} fell from 58.4% to 45.3% as the CH₄/BF₃ ratio increased from 1.0 to 4.0. The value of F_{CO+CO₂} declined from 92.8% to 73.2% as the

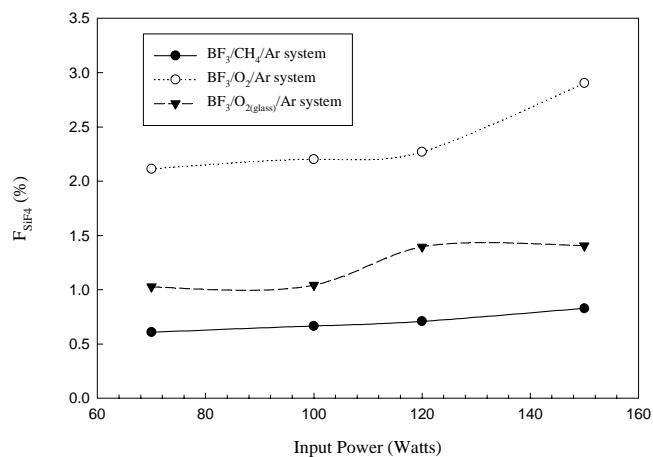


Figure 9. Comparison of the fraction of total input fluorine converted into SiF₄ with input power among BF₃/CH₄/Ar, BF₃/O₂/Ar and BF₃/O_{2(glass)}/Ar RF plasma systems

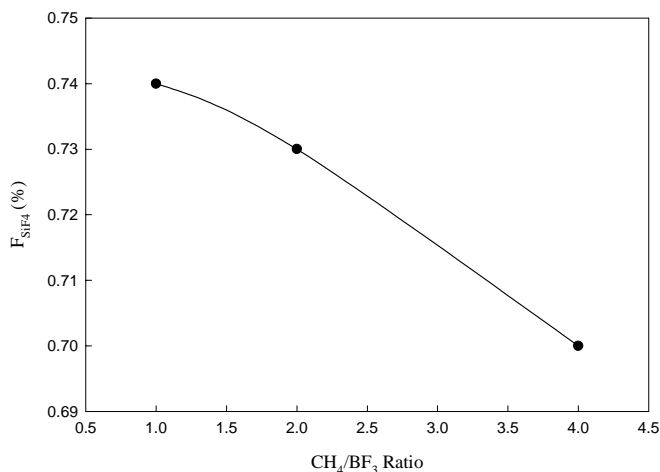


Figure 10. Relationship between the fraction of total input fluorine converted into SiF₄ and the CH₄/BF₃ ratio

CH₄/BF₃ 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 BF₃/CH₄/Ar, BF₃/O₂/Ar and BF₃/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 BF₃/O₂/Ar plasma system than in the BF₃/CH₄/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 CH₄/BF₃ ratio increased from 1.0 to 4.0 (Fig 10). The value of F_{BF₃} was around 50% during mixing

with the CH₄, but near only 29% during mixing with O₂, even when the input power exceeded 120 Watts. Although the value of BF_3 in the BF₃/O₂/Ar plasma system was lower than that in the BF₃/CH₄/Ar plasma system, the generation of fine particles and their deposition were more serious in the BF₃/O₂/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.

References

- Arno J., Boyd W., Rendon M. J. and Romig T. (1999), Abatement of Hazardous Ion Implant Gases: Experimental Results. IEEE. pp.243-246.
- Babushok V., Noto T., Burgess D. R. F., Hamins A. and Tsang W. (1996), Influence of CF₃I, CF₃Br and CF₃H on the High-Temperature Combustion of Methane. *Combust. Flame*. 107: 351-367.
- Biederman H. and Osada Y. (1992), *Plasma Polymerization Processes*, Elsevier Science Publishers, New York.
- Boenig H. (1988), *Fundamentals of Plasma Chemistry and Technology*, Technomic Publishing Co., Inc.
- Breitbarth F. W., Berg D., Dumke K. and Tiller H. J. (1997), Investigation of the Low-Pressure Plasma-chemical Conversion of Fluorocarbon Waste Gases. *Plasma Chem. Plasma Process.* 17: 39-57.
- Hayman G. D. and Derwent R. G. (1997), Atmospheric Chemical Reactivity and Ozone-Forming Potentials of Potential CFC Replacements. *Environ. Sci. Technol.* 31: 327-336.
- Holmes K. J. and Ellis J. H. (1996), Potential Environmental Impacts of Future Halocarbon Emissions. *Environ. Sci. Technol.* 30: 348A-355A.
- Hsieh L. T., Lee W. J., Chen C. Y., Chang M. B. and Chang H. C. (1998), Converting Methane by Using an RF Plasma Reactor. *Plasma Chem. Plasma Process.* 18: 215-239.
- Hsieh L. T., Lee W. J., Chen C. Y., Wu Y. P. G., Chen S. J. and Wang Y. F. (1998), Decomposition of Methyl Chloride by Using an RF Plasma Reactor. *J. hazard. mater.* B63: 69-90.
- Leech P. W. (1998), Reactive Ion Etching of Piezoelectric Materials in CF₄/CHF₃ Plasma. *J. Vac. Sci. Technol., A, Vac. Surf. Films.* 16: 2037-2055.
- Linteris G. T. and Truett L. (1996), Inhibition of Premixed Methane-Air Flames by Fluoromethanes. *Combust. Flame*. 105: 15-27.
- Noto T., Babushok V., Hamins A. and Tsang W. (1998), Inhibition Effectiveness of Halogenated Compounds. *Combust. Flame*. 112: 147-160.
- Schmidt I. and Benndorf C. (1998), Mechanisms of Low-Temperature Growth of Diamond Using Halogenated Precursor-Gases. *Diamond and Related Materials* 7: 266-271.
- Smith B. K., Sniegowski J. J., Lavigne G. and Brown C. (1998), Thin Teflon-Like Films for Eliminating Adhesion in Released Polysilicon Microstructure. *Sensor Actuation A-Physics* 70: 159-170.

Received for review, March 12, 2003

Accepted, June 10, 2003

AAQR-2003-06