Etching and Passivation Downstream of an O2-CF4-Ar Microwave Plasma

Edward Matuszak

Follow this and additional works at: http://scholarworks.rit.edu/theses

Recommended Citation
ETCHING AND PASSIVATION DOWNSTREAM
OF AN O₂-CF₂-AR MICROWAVE PLASMA

EDWARD A. MATUSZAK

June, 1986

THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE

APPROVED:

Vladimir Vukanovic
Project Advisor

Gerald A Takacs
Chemistry Department Head
and Project Advisor

Name Illegible
Director, Materials Science
and Engineering

Name Illegible
Library

Rochester Institute of Technology
Rochester, New York 14623
Materials Science and Engineering
ETCHING AND PASSIVATION DOWNSTREAM
OF AN O-CF Ar MICROWAVE PLASMA

I Edward A. Matuszak hereby grant permission to the
Wallace Memorial Library, of R.I.T., to reproduce my
thesis in whole or in part. Any reproduction will not
be for commercial use or profit.

July, 1986
# TABLE OF CONTENTS

ACKNOWLEDGEMENTS......................................................... i

1.0.  INTRODUCTION.......................................................... 1

2.0.  EXPERIMENTAL

2.1.  Microwave Etching System................................. 4

2.2.  Temperature Control and Measurement......... 7

2.3.  Pressure Measurement................................. 10

2.4.  Vacuum System........................................ 12

2.5.  Gas Flowrate........................................ 15

2.6.  The Microwave Discharge............................. 16

2.7.  Laser Interferometry.................................... 17

2.8.  Chemiluminescence.................................... 18

2.9.  Emission Spectroscopy................................. 19

2.10.  Computer Interface

2.10.1.  Photomultiplier Tube Bases................. 20

2.10.2.  Current-to-Voltage Amplifiers............. 20

2.10.3.  Instrumentation Amplifiers............... 23

2.10.4.  Active Filter Network......................... 23

2.10.5.  Analog-to-Digital Converters.............. 23

2.10.6.  Counter........................................... 26

2.11.  Substrate Analysis

2.11.1.  Infrared Spectroscopy......................... 26

2.11.2.  X-Ray Photoelectron Spectroscopy........ 26

2.11.3.  Scanning Electron Microscopy.............. 29
3.0. RESULTS AND DISCUSSION

3.1. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Gas Composition

3.1.1. Etch Rate Measurements................. 31
3.1.2. Emission Spectroscopy Measurements.. 34
3.1.3. XPS Measurements....................... 39

3.2. Etch Rate Parameters

3.2.1. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Reactor Pressure...................... 41
3.2.2. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Total Gas Flow Rate......................... 43
3.2.3. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Gas Flow Velocity......................... 48
3.2.4. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Microwave Power......................... 53
3.2.5. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Substrate Temperature....................... 53
3.2.6. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Reactor Geometry

3.2.6.1. Varying Injector Distance............ 57
3.2.6.2. Varying Injector Design.............. 61

3.3. Etch Rate Measurements at Different Locations on the Polyimide Wafer.............. 64

3.4. The Induction Effect........................ 64

3.5. Passivation of Polyimide..................... 77
3.5.1. XPS Studies.............................. 77
3.5.2. Deposition During Passivation........... 82
3.5.3. Depth Profile of a Passivated Polyimide Substrate............... 85
3.5.4. Transition Period Between the Removal of Passivation Stage and the Resumption of Etching Stage..... 91

4.0. CONCLUSION....................................... 95

APPENDIX I............................................... 98

APPENDIX II............................................... 100
FIGURE CAPTIONS

1. Schematic of the microwave plasma etching apparatus, front view.......................... 5

2. Expanded front view of the microwave cavity, injector tube and etching chamber (5-way cross). Dimensions are in centimeters................................. 6

3. Bottom view of the substrate holder................. 9

4. Vacuum system........................................ 13

5. Photomultiplier tube base diagram. K is photocathode; A is anode; Z1 is 150V 1W zener diode (RCA SK 3350); R2 through R10 are 100K ohm 1% 0.5 Watt resistors........... 21

6. Current-to-voltage amplifier. U1 is Texas Instruments TL081; R1 is a 1 megachm 1% 0.5 Watt resistor; C1 is a 47 pF monolithic capacitor; Iin is the photomultiplier anode current; Vout is the amplifier voltage output.......................... 22

7. Instrumentation amplifier. U2 is Analog Devices AD521JK; R1 is a 10.9K ohm 1% 0.5 Watt resistor; R2 is a 97.6K ohm 1% 0.5 Watt resistor; R4 is a 2K ohm ten turn pot; IN+ is a noninverting voltage input from current-to-voltage amp; V+ is +15V; V- is -15V; Vout is voltage output; Ref. is voltage output common.................. 24

8. Active filter network. U3 and U4 are Texas Instruments TL081; R1 and R3 are 20K ohm 1% 0.5 Watt resistors; R2 and R4 are 10.9K ohm 1% 0.5W resistors; C1 and C3 are 20,000 pF mylar capacitors; C2 and C4 are 10,000 pF mylar capacitors.......... 25

9. Analog-to-digital converter functional diagram (Reprinted with Permission)............. 27

10. Functional diagram of four stage 74191 16 bit binary counter. CP is clock pulse; CE is counter enable; U/D is direction control; RC is ripple clock........................................ 28
11. Etch rate if PI as a function of CF4 concentration downstream of O2-CF4-Ar MW plasma. Experimental conditions were total gas flow rate, 50 SCCM; reactor pressure, 0.3 Torr; absorbed MW power, 38 Watts; Y, 26.3 cm; Z, 13.5 cm; 5% Ar......................... 32

12. Interferogram for the etching of PI downstream of a MW discharge. Experimental conditions were the same as in Figure 11. Total gas flow rate was 50 SCCM, and gas composition was Run #4, Table 1............. 33

13. Ratio of atomic line intensities OI 845/ArI 750 nm and FI 704/ArI 750 nm as a function of CF4 concentration in O2-CF4-Ar plasmas with the same conditions as in Figure 11. Oxygen atom emission intensities must be multiplied by 23.17 to correct for spectral response.......................... 35

14. Etch rate of PI as a function of log (IO/IF) using OI 845 nm and FI 704 nm. Experimental conditions were the same as in Figure 11. Emission intensities have been corrected for the spectral response.............. 37

15. Relative intensity of ArI 750 nm spectral line as a function of O2 concentration in the gas feed. Experimental conditions were the same as in Figure 11.......................... 38

16. Etch rate of PI as a function of pressure. Experimental conditions were total flow rate, 65 SCCM; absorbed MW power, 60 Watts; Y, 26.3 cm; Z, 15.3 cm; gas composition, table 1, run #4................................. 42

17. Ratio of atomic spectral line intensities OI 845/ArI 750 nm, FI 704/ArI 750 nm and OI 845/FI 704 nm as a function of pressure. Experimental conditions were same as in Figure 16. Emission intensities have been corrected for spectral response..................... 44

18. Ratio of atomic spectral line intensities OI 845/ArI 750 nm, FI 704/ArI 750 nm and OI 845/FI 704 nm as a function of pressure. Experimental conditions were same as in Figure 16. Absorbed MW Power, 25 Watts. Oxygen atom emission intensities must be multiplied by 23.17 to correct for spectral response............................... 45
19. Etch rate of PI as a function of the total gas flow rate. Experimental conditions were the same as in Figure 16. Reactor pressure was 0.3 Torr.

20. Ratio of atomic spectral line intensities OI 845/ArI 750 nm, FI 704/ArI 750 nm and OI 845/FI 704 nm as a function of the total gas flow rate. Experimental conditions were the same as in Figure 19. Absorbed MW power was 58 Watts.

21. Etch rate of PI as a function of the gas flow velocity; X denotes data from Figure 16 and 0 denotes data from Figure 19. In all cases, the substrate temperature was 298K and r was taken to be 10 cm.

22. Etch rate as a function of absorbed MW power. Experimental conditions were same as in Figure 11. Gas composition was run #4, table 1 and distance Z was 15.3 cm.

23. Ratio of atomic line intensities OI 845/ArI 750 nm, FI 704/ArI 750 nm and OI 845/FI 704 nm as a function of MW power. Experimental conditions were same as in Figure 22. Number Density Ratio, O/F can be calculated by multiplying intensity ratio, IO/IF by 23.17.

24. Ratio of atomic line intensities OI 845/ArI 750 nm, FI 704/ArI 750 nm and OI 845/FI 704 nm as a function of MW power. Experimental conditions were same as in Figure 22, except that no PI coated the Si wafer. Number Density Ratio, O/F can be calculated by multiplying intensity ratio, IO/IF by 23.17.

25. Arrhenius plot for ln R versus 1000/T. Experimental conditions were same as in Figure 16. Reactor pressure was 0.3 Torr and absorbed MW power was 50 Watts.

26. Etch rate of PI as a function of distance, Z, between end of injector and substrate. Experimental conditions were same as in Figure 11. Gas composition was run #4, table 1.
27. Front view of MW apparatus with cavity in vertical position (dimensions in cm). .......... 62

28. Various locations on the PI wafer where etch rates were measured using a helium-neon laser. Experimental conditions were same as in Figure 11. Absorbed MW power was 19 Watts. ......................... 65

29. Etch rate and temperature as a function of exposure time for a new wafer. Experimental conditions were same as in Figure 19. Total gas flow rate was 65 SCCM, and absorbed MW power was 25 Watts. ................. 68

30. Etch rate and temperature as a function of exposure time for a new wafer after covering for two hours. Same experimental conditions as in Figure 29. .................. 69

31. Etch rate and temperature as a function of exposure time for a new wafer. Same experimental conditions as in Figure 29. .............. 71

32. Etch rate and temperature as a function of exposure time for a new wafer. Same experimental conditions as in Figure 29. Absorbed MW power was 42 Watts. ..................... 72

33. Etch rate and temperature as a function of exposure time for a new wafer. Same experimental conditions as in Figure 29. Absorbed MW power was 62 Watts. ..................... 73

34. Etch rate and temperature as a function of exposure time for a new wafer. Same experimental conditions as in Figure 33. Total gas flow rate was 75 SCCM. ................. 75

35. Etch rate, R, and substrate temperature, T, during etching, passivation, removal of passivation and resumption of etching. Experimental conditions were reactor pressure, 0.3 Torr; total gas flow rate, 65 SCCM; absorbed MW power, 25 Watts; Y, 7.3 cm; Z, 19.9 cm. ......................... 78

36. Relative atomic concentration (from XPS) during etching, passivation, removal of passivation and resumption of etching. Same experimental conditions as in Figure 35. ........ 80
37. Atomic ratios F/C, F/O and C/O (from XPS) during etching, passivation, removal of passivation and resumption of etching. Same experimental conditions as in Figure 35.......................... 81

38. Infrared spectrum of white precipitate from inside the MW apparatus, pressed into a KBr pellet.......................... 83

39. Infrared spectra standard of a teflon sample [36].......................... 84

40. Infrared spectrum of teflon sample.......................... 86

41. Values 1/Rx10³ during the removal of passivation as a function of time of removal of passivation for substrates passivated 20.4, 25.6 and 46.1 minutes. Experimental conditions were total gas flow rate, 52 SCCM; reactor pressure, 0.3 Torr; absorbed MW power, 49 Watts; Passivation: 11% O2, 84% CF4 and 5% Ar; Removal of passivation: 79.4% O2, 15.8% CF4 and 4.8% Ar; Y, 9.35 cm; Z, 3.45 cm........... 89

42. Values 1/Rx10³ during the removal of passivation as a function of thickness of fluorinated layers for substrates passivated 20.4, 25.6 and 46.1 minutes. Experimental conditions were the same as in Figure 41.......................... 90

43. Interferogram for the transition period between removal of passivation and resumption of etching conditions. Experimental conditions were the same as in Figure 41.......................... 92

44. SEM photograph of PI substrate during the removal of passivation stage. Magnification was 5000X....................... 93

45. SEM photograph of PI substrate during the resumption of etching stage. Magnification was 5000X....................... 94
I wish to express my appreciation and sincere thanks to my research advisors, Dr. Vladimir Vukanovic and Dr. Gerald Takacs for their continuous assistance and guidance on this project.

The project was funded by IBM Laboratories, Endicott. My thanks is also extended to Ron Horwath, Frank Egitto and Frank Emmi from IBM for their collaboration on the project.

Special thanks go to my lovely wife, Sue for her support and patience while I was in school.
1.0. INTRODUCTION

The mechanism of etching organic materials downstream of a microwave (MW) discharge with carbontetrafluoride (CF)$_4$-oxygen (O)$_2$-argon (Ar) gas mixtures was investigated in the literature [1-5]. Several investigators have reported no etching of polymers downstream of pure oxygen plasmas. However, in cases where etching has been observed, it occurred at elevated substrate temperatures, and/or in close proximity to the plasma [3,5].

The O/F atomic ratio is an important parameter influencing the etching of polyimide (PI) [6-8]. To initiate etching, in addition to oxygen atoms, fluorine atoms or oxygen ions (when the substrate is exposed to the plasma) are required. The presence of fluorine in small concentrations initiates and enhances the etching. At low CF$_4$ concentrations in oxygen, fluorine from the plasma interacts with the PI, breaking existing bonds and creating reactive sites. It has been proposed that fluorine can enhance etching via abstraction of hydrogen [9], indiscriminant abstraction [10] and addition to olephinic groups [11].

Fluorine atoms in excess inhibits etching and leads to fluorination of the polymer [6-8,12,13]. Passivation can be related to the fluorination of the polymer. At high CF$_4$ concentrations in an oxygen plasma, fluorine atoms
compete with oxygen atoms for the reactive sites [12]. Bonding of the type CF\textsubscript{2} form on the surface of the substrate which inhibits the etching process [6-8,12,13]. The fluorination of the polymer could be removed, after a period of time, by returning to the maximum etching conditions. The fluorine depth profile was obtained by measuring the small etch rates during the removal of passivation. These measurements are in good agreement with reference 12.

The role of different radicals, as well as the role of excited atoms and molecules on the etching process of organic materials, is still not well understood. In reference 16, ultraviolet photons are proposed to generate surface-free radicals.

From the literature, the activation energy for the etching of photoresist has been shown to depend on the composition of the gas mixture. The values 0.5, 0.3 and 0.13 eV/mol were reported for pure oxygen, 0.048% CF\textsubscript{2}O\textsubscript{2} and 0.61% CF\textsubscript{2}O\textsubscript{2} respectively [14]. An independent study found 0.28 eV/mol for the etching of photoresist in pure oxygen [17]. The addition of 0.5% CF\textsubscript{2}O\textsubscript{2} to an oxygen 4 MW discharge reduced the activation energy for the etching of PI to 0.1 eV/mol from 0.58 eV/mol in pure oxygen [5].
This work discusses experimental factors which influence the etching of PI downstream of an O$_2$-CF$_2$-Ar$_4$ MW plasma. Of particular interest are the parameters gas feed composition, substrate temperature, reactor geometry, MW power, chamber pressure and total gas flow rate, the latter two determining the gas flow velocity. Etch rate measurements were compared with relative atomic concentrations of oxygen and fluorine in the plasma, obtained by optical emission spectroscopy. Surface analysis of unetched, etched and passivated polyimide were performed by X-ray Photoelectron Spectroscopy (XPS).

The etching of PI downstream of a MW discharge was found to be rather homogeneous. This would be expected from the isotropic behaviour involved with etching downstream of any glow discharge [18].
2.0. EXPERIMENTAL

2.1. Microwave Etching System

The reactor chamber used to investigate the etching and passivation of PI downstream of a MW discharge consisted of a special conical 5-way pyrex 7740 cross, with each arm extending 7" (17.78 cm) from the center of the cross and having a 4" (10.16 cm) i.d. A schematic of the MW etching apparatus is shown in Fig. 1. The substrate was a 5.7 cm diameter silicon (Si) wafer coated with a layer of PI. A detailed description of the substrate preparation is given in Appendix I.

An expanded front view of the MW etching apparatus is shown schematically in Figure 2. Experiments were done with two positions of the substrate in the apparatus. In the first position, substrates (lowered) were placed on an aluminum substrate holder situated in the middle of the reaction chamber. The position of the holder in the glass cross was stable and no change in the angle of the substrate to the oncoming stream of activated gas species was possible. In the second position, substrates (raised) were placed on top of a 24" (5.715 cm) glass tube raised into the upper arm of the glass cross. All experiments were performed with the substrate in the lowered position, unless mentioned otherwise.

The geometry of the reactor could be varied in
Figure 2
several ways to change the distance between the plasma and the substrate. The distance between the end of the glass injector (2.05 cm i.d. and 2.54 cm o.d.) and the substrate, Z, could be varied by moving the injector and/or the substrate. The movable injector was made possible with the use of a 1" stainless steel cajon ultra-torr male connector. This type of fitting threads into the aluminum plate on the top of the apparatus (Figure 2) and provided a vacuum-tight seal using a Viton o-ring. The inside of the fitting has been bored through to allow a glass tube to pass through and enter into the system. The cajon fitting provided a vacuum-tight seal with quick finger-tight assembly, and allowed reusability on glass tubing. Various tube lengths, Y, (Figure 2) could also be used for varying the distance between the plasma and the substrate. The distances Z and Y were kept constant at 15.3 cm and 26.3 cm respectively, unless otherwise stated.

2.2. Temperature Control and Measurement

The temperature of the substrate in the lowered position was varied and controlled using a Forma Scientific, model 2095 refrigerated and heated circulating bath. The circulating bath provided a stream of controlled temperature fluid to the substrate holder. The
fluid passed through a valve on the unit, through ¼" tubing coupled to ⅛" stainless steel tubing and entered the right side of the MW apparatus. A vacuum tight seal was achieved using a bored through ¼" stainless steel cajon ultra-torr male connector. The bath had a temperature range of -20°C to +70°C with a temperature uniformity of ±0.02°C. The capacity of the bath was seven gallons. There was approximately 5°C heat loss from the bath to the substrate.

The tubing was wound in a circular pattern below the substrate holder before returning to the circulating bath. The tubing was held in direct contact with the substrate holder for maximum heat transfer using a metal plate. A schematic of the substrate holder, showing the bottom view, is in Figure 3. A chromel-alumel thermocouple with a type 304 stainless steel sheath passed through the bottom of the substrate holder and touched the underside of the lowered substrate. On the right side of the cross (Figure 1) the thermocouple passed through a 1/16 in. swagelok male connector into the chamber. The end of the thermocouple probe was held in position underneath the substrate holder using the same type of swagelok tube fitting. This type of fitting has threads on one end and a compression type fitting on the other end. A vacuum-tight seal was achieved with a nut and ferrule inside the fitting, and a Viton o-ring on the outside of
the fitting.

The chromel-alumel thermocouple used was recommended for oxidizing atmospheres, in the temperature range from -330°F to 2300°F. The sheath protected the thermocouple from the corrosive environment within the reaction chamber. The thermocouple was connected to a digital recorder which featured selectable scales (°C, °F), 0.1° resolution up to 200°C, and an ice point referenced analog output.

The temperature of the raised substrate could not be controlled because of the geometry of the apparatus. An iron-constantan Omegaclad thermocouple wire with a type 304 stainless steel sheath and magnesium oxide insulation (.062 in. diam.) was used to measure the temperature of the raised substrate. This type of thermocouple wire bends rather easily. The thermocouple passed into the reactor chamber in a similar fashion as before and touched the underside of the substrate. The thermocouple was connected to a model HH-707C pocket thermometer for temperature measurement.

2.3. Pressure Measurement

The pressure in the reaction chamber was measured \( \frac{1}{4} \) (between 10\(^{-4} \) and 1.0 Torr) by a Type 310 BHS-1 Torr absolute capacitance manometer pressure sensor. Pressure in the reaction chamber deflected the sensor diaphragm
towards electrodes which changed the capacitance between the diaphragm and each adjacent electrode on the reference side. The change in capacitance between the electrodes in the sensor produced a signal which was amplified by the sensor electronics. The sensor was maintained at 45°C by the internal heaters, which were controlled by a DC proportional control. This helped to minimize the effects of ambient temperature change on the sensor zero and span coefficients [19]. The sensor was connected to a MKS Baratron Type 170-M-27D digital readout unit for a visual display of the pressure.

The capacitance manometer was connected to the reaction chamber using a ¼" stainless steel ultra-torr male connector. One end of the fitting threaded into an aluminum plate on the right side of the MW apparatus (Figure 1), providing a vacuum-tight seal using a Viton o-ring. The other end of the fitting connected to ¼" stainless steel tubing, which went to, and was connected to the sensor using a VCR to swagelok connector. The reactor pressure during the experiments was 0.3 Torr, unless otherwise stated.

A NRC 524-2 cold cathode ionization gauge connected to a NRC 855 vacuum ionization gauge controller was used to measure the pressure in the range from $1 \times 10^{-9}$ to $5 \times 10^{-3}$ Torr. The cold cathode ionization gauge is similar to the Redhead Magnetron Gauge. The cold cathode gauge
attached to the vacuum system (IG in Figure 4) using an o-ring compression adaptor.

2.4. Vacuum System

The pumping system mentioned above and illustrated in Figure 4 has been connected to the MW etching system using a 2" (5.08 cm) i.d. copper tubing and elbows. A Type SL-in line Viton o-ring sealed, brass Veeco valve, that was used for throttling the gas flow (to vary the pressure in the system), was installed using silver solder connections in the middle of the copper tubing. All of the connecting plumbing and the throttle valve were cleaned with an oakite solution, rinsed with distilled water and alcohol, then baked in Freon at 375°F for 1.2 hours, and leak tested with a helium leak detector.

The vacuum pumping system consisted of a water-cooled, 6 in. oil diffusion pump, backed by a Leybold-Heraeus model D30A Dual-Stage Rotary Vane mechanical pump. To avoid a possible explosion when pure oxygen was pumped through the mechanical pump, the pump was disassembled and all the parts were cleaned with a trichloro-trifluorocethane (Freon TF) solvent. New seals, gaskets, o-rings and rotary vanes were used when reassembling the pump. The gas ballast valve was intentionally plugged in order to prevent oxygen from the room from entering the pump. The pump was then filled
Captions for Figure 4

B.V. Bleed Valve; Manual Control
C.V. Controller Valve for LN$_2$
D.P.H. Diffusion Pump Heater
D.P.W. Diffusion Pump Water
F.V. Foreline Valve
H.V. High Vacuum Valve
I.G. NRC 524-2 Cold Cathode Ionization Gauge
LN$_2$ Liquid Nitrogen Tank
M.P. Mechanical Pump; Model D30A Dual Stage Leybold-Heraeus Rotary Vane Pump
R.V. Roughing Valve
T.C. Thermocouple Gauges #1, #2 and #3 (Varian Type 0531)
T.V. Brass Veeco Throttle Valve
with a perfluoropolyether (Fomblin) pump fluid, which does not polymerize when exposed to oxygen.

The valves (roughing, foreline and high vacuum) and the diffusion pump on the vacuum system (Figure 4) were controlled using an IBM Central Scientific Auto-Manual Vacuum Control System. The liquid nitrogen fill into the diffusion pump trap was controlled with a Model 100L Cryotrol Controller.

The ends of the 5-way conical glass cross are flared with an o-ring groove in the glass. A vacuum-tight seal was achieved with a ¼" thick aluminum plate pressed against the end of the cross. A #245 Viton o-ring sat firmly between the groove in the glass cross and a groove in the aluminum plate. The aluminum plates were held in place against the ends of the glass cross with metal flanges, inserts, nuts and bolts.

2.5. Gas Flowrate

The flow rate of the gases Ar, CF and O were 4 2 controlled by Tylan FC-260 mass flow controllers. Mass flow control is a means of measuring and automatically controlling the weight flow rate of a gas. A sensor tube externally wound with two heated resistance thermometers is used to measure the gas flow. A bridge circuit senses the temperature differential and develops a linear output signal of 0 to 5 Vdc proportional to the gas flow rate
over the calibrated range. The output signal is then compared to a command voltage from a voltage source. This comparison generates an error signal that alters the valve power, thereby changing the flow rate until the set point is reached. [20]

The total flow rate of the gases was kept constant (65 SCCM) during the experiments, unless otherwise stated. The gas mixture consisted of different concentrations of $\text{O}_2$ and CF with a constant 5% addition of Ar. During the etching, removal of etching and resumption of etching experiments, the gas composition was $71.2\% \text{ O}_2, 23.8\% \text{ CF}_4, 5\% \text{ Ar}$ and during the passivation experiments, the gas composition was $9.5\% \text{ CF}_4, 85.5\% \text{ O}_2$ and 5% Ar unless noted differently.

A Tylan RO-14 readout unit provided control and monitoring of the mass flow controllers. The flowrates of the gases were calibrated using a constant volume technique. The gases passed through the MW cavity (Figure 1) and were introduced into the chamber from the upper part of the apparatus.

2.6. The Microwave Discharge

A KIVA Instrument Corporation 2.45 GHz MW power supply, with an output power rating from 0-120 Watts, supplied the MW energy to an Ophthos Instruments "Evenson" type air-cooled MW, clip-on cavity by means of a
coaxial cable (Figure 1). The MW cavity could be inductively tuned for minimizing the reflected power. The absorbed MW power was taken as the difference between the forward and the reflected power. The position of the MW cavity in relation to the substrate was configured to minimize the interaction of UV photons and ions from the MW plasma with the substrate. A Sola constant voltage normal-harmonic type transformer was used to stabilize the MW power. The absorbed MW power remained at 38 Watts, unless otherwise stated.

2.7. Laser Interferometry

A laser interference method was used to monitor the etch rate of PI. A helium-neon laser beam (Figure 1) with a wavelength of 632.8 nm was focused onto the substrate surface at nearly normal incidence. The beam was directed down through the same glass tube in which the active species were introduced into the chamber from the upper part of the MW apparatus. A 1" cajon fitting had been attached to the top of the open glass tube. Inside the other end of the cajon fitting was fitted a polished Pyrex window, held in place with two Viton o-rings. This provided a vacuum-tight seal.

The reflected laser beam from the substrate was detected by a Metrologic Photometer. The photodiode detector was connected to an ammeter and then to a strip
chart recorder for recording the etch rates.

Interferometry is a general term that refers to measurements of changing reflectivity associated with constructive and destructive optical interference produced from the front and rear surfaces of the film. With a fixed wavelength ($\lambda$), the consecutive maxima (or minima) in the reflectivity in the equation:

$$\Delta d = \lambda / 2n$$

is related to the change in the film thickness ($\Delta d$) where $n$ is the refractive index of the film [21]. By measuring the reflectivity (in arbitrary units) as a function of time during the experiments, the distance between two adjacent maxima (or minima) could be related to the change in the film thickness by using equation 1. A value of 1.76 was taken for the index of refraction of PI. 

2.8. Chemiluminescence

Nitric oxide gas was introduced into the MW system, downstream of the discharge, from the right side of the apparatus (Figure 1). The reaction of oxygen atoms with nitric oxide was accompanied by a visible emission that is a continuum, extending from 388 nm into the infrared, with a maximum intensity at about 650 nm. The intensity of the "yellow-green" chemiluminescence from the reaction:

$$^{*} \text{O} + \text{NO} \rightarrow \text{NO} \rightarrow \text{NO} + h\nu$$

(2)
is proportional to the concentration of atomic oxygen and nitric oxide, i.e., \( I_{\text{[O][NO]}} \). The resulting chemiluminescence was followed by an EMI 9761R photomultiplier tube connected to a recorder. The photomultiplier tube and housing were situated on the left side of the apparatus (Figure 1). A 4" hole was cut into the center of the aluminum plate. A polished Pyrex plate (5 11/32" o.d., 4" thick) was attached to the aluminum plate over the hole. With the use of a Viton o-ring between the glass and the aluminum plate, a vacuum-tight seal was achieved.

2.9. Emission Spectroscopy

A Minuteman spectrometer model 310 SMP was used to monitor the radiation from the plasma. A 4" cajon ultratorr union was installed onto the injector before the gases are introduced into the MW cavity (Figure 1). A polished quartz window was positioned between two Viton o-rings inside the cajon fitting. The radiation from the plasma was focused onto the entrance slit of the spectrometer. The spectrometer operated in the monochromatic, polychromatic or spectrographic mode. A Bausch and Lomb grating of 1200 grooves/mm was used. The wavelength of the monochromator and the spectral sensitivity of the spectrometer (photomultiplier and grating) were calibrated with a low pressure Hg lamp and
an Eppley Laboratory Standard irradiance lamp, respectively.

The etching of PI was studied with comparative measurements of relative oxygen and fluorine atomic concentrations in the plasma using emission spectroscopy with argon actinometry. According to the literature [23-25], the spectral line intensities of OI 845, FI 704 and ArI 750 nm could be used.

The spectrometer has been interfaced with a LSI-11 digital computer for storage of the spectral line intensities. The signals could be stored in the computer with a time resolution of 0.1 ms or higher.

2.10. Computer Interface

2.10.1. Photomultiplier Tube Bases

Four photomultiplier tube bases were constructed with the resistor networks shown in Figure 5. This design provided for a voltage drop across the photo cathode to the first dynode of 150 V.

2.10.2. Current-to-Voltage Amplifiers

Four current-to-voltage amplifiers were constructed with the design shown in Figure 6. The capacitor C1 could be varied for the appropriate bandwidth of sampling. The frequency of the 3dB attenuation occured at \( f = \frac{1}{6.28} \) (R1
Figure 5
$V_{OUT} = -I_{IN} \times R_i$

Figure 6
x C1). The voltage gain of the amplifier was determined by R1, as shown in Figure 6. The amplifiers required both positive and negative 15 volt supplies. Coaxial miniplugs were used to connect the amplifiers to the photomultiplier tube bases, and to connect the output of the current-to-voltage amplifiers to the instrumentation amplifiers.

2.10.3. Instrumentation Amplifiers

The output of the current-to-voltage amplifier was connected to the noninverting input of the instrumentation amplifier, shown in Figure 7. These amplifiers could be modified to provide voltage gains from 1 to 1000 by changing the value of R1.

2.10.4. Active Filter Network

A two stage active filter with butterworth characteristics was provided with the data acquisition modules. The design of the filter network is shown in Figure 8. The bandwidth of the filter was adjusted to the same bandwidth selected for the current-to-voltage amplifiers.

2.10.5. Analog-to-Digital Converters

The AD574 ADC's are described in the Analog Devices' product literature. These components expect an incoming
signal level of 0-10 V. This ten volt range, coded into a 12 bit binary output, is shown in Figure 9. The digital output was connected to one of several channels of the DRV11J parallel interface module.

2.10.6. Counter

A 16 bit binary counter (Figure 10) was used for time keeping. A signal generator was attached to the clock pulse of the timer, and the cycles of a periodic waveform was counted.

2.11. Substrate Analysis

2.11.1. Infrared Spectroscopy

Material deposited onto the walls of the reactor chamber was analyzed using a Perkin-Elmer Infrared Spectrophotometer Model 681. The sample was pressed into a KBr pellet, following the procedure outlined in Appendix II.

2.11.2. X-Ray Photoelectron Spectroscopy

The atomic percentage of elements present on the surface (0.5-2 nm deep) of PI were analyzed using X-ray Photoelectron Spectroscopy (XPS). XPS analysis was carried out at IBM, Endicott. Surface analysis of PI were performed on substrates before and after etching, with
Figure 9
Figure 10
different gas feed mixtures, and at various stages of passivation and removal of passivation.

A complete description of the XPS instrumentation and experimental techniques employed are given in reference 6.

2.11.3. Scanning Electron Microscopy

Photographs of the PI surface for different experiments were obtained using an ISI-40 International Scientific Instrument Scanning Electron Microscope. The filament voltage was kept at 15kV, and the magnification was 5000X.
3.0. RESULTS AND DISCUSSION

3.1. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Gas Composition

3.1.1. Etch Rate Measurements

The gas mixture introduced into the MW discharge consisted of different concentrations of O, CF and a constant 5 percent of Ar. The concentrations of the gas mixtures that were used are given in Table 1.

The etch rate of PI was measured as a function of the CF - O - Ar composition in the MW discharge, and the results are shown in Figure 11. The total gas flow rate was 50 SCCM and distance Z was 13.5 cm. The etch rate of PI was measured using laser interferometry. A copy of an interferogram for the etching of PI downstream of a MW discharge containing Ar, O and CF (Table 1, Run #4) is shown in Figure 12. An etch rate of 513 A/min was calculated for this example.

Passing 95% oxygen mixed with 5% argon (Table 1, Run #1) through the MW discharge resulted in no measurable etch rate of the PI. Under these conditions, addition of nitric oxide gas resulted in an intense chemiluminescence radiation, confirming the presence of oxygen atoms in the vicinity of the substrate. Increasing the temperature of the substrate to 50°C did not initiate the etching of PI with an O - Ar plasma.
Table 1

<table>
<thead>
<tr>
<th>Run Number</th>
<th>%O</th>
<th>%CF</th>
<th>%Ar</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>95.0</td>
<td>0</td>
<td>5.0</td>
</tr>
<tr>
<td>2</td>
<td>85.5</td>
<td>9.5</td>
<td>5.0</td>
</tr>
<tr>
<td>3</td>
<td>76.0</td>
<td>19.0</td>
<td>5.0</td>
</tr>
<tr>
<td>4</td>
<td>71.2</td>
<td>23.8</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>66.5</td>
<td>28.5</td>
<td>5.0</td>
</tr>
<tr>
<td>6</td>
<td>57.0</td>
<td>38.0</td>
<td>5.0</td>
</tr>
<tr>
<td>7</td>
<td>47.5</td>
<td>47.5</td>
<td>5.0</td>
</tr>
<tr>
<td>8</td>
<td>38.0</td>
<td>57.0</td>
<td>5.0</td>
</tr>
<tr>
<td>9</td>
<td>28.5</td>
<td>66.5</td>
<td>5.0</td>
</tr>
<tr>
<td>10</td>
<td>23.8</td>
<td>71.2</td>
<td>5.0</td>
</tr>
<tr>
<td>11</td>
<td>19.0</td>
<td>76.0</td>
<td>5.0</td>
</tr>
<tr>
<td>12</td>
<td>9.5</td>
<td>85.5</td>
<td>5.0</td>
</tr>
<tr>
<td>13</td>
<td>0</td>
<td>95.5</td>
<td>5.0</td>
</tr>
</tbody>
</table>
Figure 12

1 minute

Time
Addition of CF to an O – Ar MW plasma initiated the etching. The presence of fluorine in small concentrations initiated and enhanced the etching. The addition of CF to O – Ar resulted in an increase in the O dissociation, as will be seen from the increase in the intensity of the oxygen spectral line, in section 3.1.2.

The maximum etch rate occurred at about 75% O in CF (Table 1, Run #4). After a maximum etch rate was achieved, the addition of CF at higher concentrations inhibited the etching of PI. Fluorine in excess inhibited etching and led to the fluorination of the polymer (confirmed by XPS analysis of the PI surface in section 3.1.3.). No etching was observed using a CF plasma with the addition of 5% Ar (Table 1, Run #13).

3.1.2. Emission Spectroscopy Measurements

During the above etching experiments, the intensities of the spectral lines FI 703.7 nm, ArI 750.4 nm and OI 844.6 nm in the plasma were measured. The spectral line intensities OI 845 and FI 704 nm were corrected for the spectral response of the spectrometer. The ratio of the oxygen to the fluorine atom concentration in the plasma was O/F = 23.17 IO/IF after making the correction. Using argon actinometry, both lines were measured relative to the same ArI 750.4 nm spectral line.

Figure 13 shows the relative ratio of the spectral
lines intensities IO/IAr and IF/IAr as a function of the CF gas concentration in an O – Ar MW plasma. The addition of CF to an O – Ar MW plasma caused, at low concentrations, an increase in the oxygen atom concentration; the addition of O to a CF – Ar MW plasma had a similar effect on the fluorine atom concentration. These effects are discussed in references 26-31. It is important to note that the atomic concentrations in the vicinity of the substrate, downstream of the MW plasma, might be different from the atomic concentrations in the plasma. This difference could be caused by mass transport properties and by the rates of formation and removal of radicals in the region between the plasma and the substrate. Among the factors which influence these rates are the gas flow rates, the reactor pressure and the reactor wall conditions [32-35].

The etch rate plotted as a function of log (IO/IF) is given in Figure 14. The existence of an optimum O/F ratio to obtain a maximum in etch rate seems to be essential in the etching process, in agreement with references 6-8, when etching in an RF plasma.

The spectral line intensity of the argon actinometer was measured as a function of the oxygen gas composition in Figure 15. The argon line intensity is nearly constant from 100% to 70% oxygen and increases almost linearly at compositions less than 70% oxygen (Figure 15). The
increase in the Argon line intensity below 70 % oxygen may be due to an increase in the electron number density and/or the electron temperature.

3.1.3. XPS Measurements

The atomic percentage of elements present on the surface of PI wafers exposed downstream of a MW plasma using different gas compositions, were analyzed by XPS, and are reported in Table 2. These results are similar to results obtained at IBM, Endicott for the etching in a radio-frequency (RF) plasma [6].

Compared with an un-etched substrate, XPS analysis showed an increase of fluorine atom concentration in the surface layers of PI after etching downstream of a MW plasma containing CF in O – Ar (Table 2, Sample 2). The beginning of the etching was characterized with a sharp decrease in the C/O ratio. Similar results were obtained with the etching in a RF plasma [7,8]. Results of etching downstream of a MW plasma confirmed that PI etched downstream of an O – CF – Ar discharge, with a low concentration of CF, essentially changed the surface composition.

An increase in the fluorine concentration in the surface of PI was found when the substrate was exposed downstream of the MW plasma with a high concentration of CF in O – Ar (Table 2, Sample 4). Passivation of the
Table 2

Results of XPS Analysis of Relative Atomic Concentrations at the Surface of Polyimide

<table>
<thead>
<tr>
<th>Sample</th>
<th>Elements</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
<td>F</td>
<td>N</td>
<td>Na</td>
<td>Al</td>
</tr>
<tr>
<td>1. Unetched PI</td>
<td>76.1</td>
<td>19.1</td>
<td>0</td>
<td>5.9</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2. Exposed</td>
<td>65.3</td>
<td>25.6</td>
<td>2.7</td>
<td>6.1</td>
<td>0.3</td>
<td>0</td>
</tr>
<tr>
<td>4 mins. (Table 1, Run #4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3. Exposed</td>
<td>61.9</td>
<td>24.1</td>
<td>5.2</td>
<td>5.6</td>
<td>3.2</td>
<td>0</td>
</tr>
<tr>
<td>10 mins. (Table 1, Run #4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4. Exposed</td>
<td>38.0</td>
<td>13.9</td>
<td>43.6</td>
<td>3.8</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>2 mins. (Table 1, Run #12)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Experimental conditions were reactor pressure, 0.3 Torr; total gas flow rate, 65 SCCM; absorbed MW power, 25 Watts; Y, 7.3 cm; Z, 19.9 cm.
substrate occurred with high concentrations of CF in O - 2 Ar plasma, which will be discussed in more detail in section 3.5.

3.2. Etch Rate Parameters

The analysis of the parameters which affect the etch rate of PI downstream of a MW plasma was based on experiments investigating the dependence of the etch rate on total reactor pressure, total gas flow rate, gas flow velocity, absorbed MW power and on substrate temperature. The relative intensities of emission from neutral atomic oxygen and fluorine (using argon actinometry) were measured during these investigations.

3.2.1. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Reactor Pressure

A Veeco throttle valve was used during these experiments to vary the absolute pressure in the system (Figure 4). The dependence of the etch rate, on the reactor pressure is shown in Figure 16. The pressure was varied from 0.25 to 0.50 Torr. The absorbed MW power was 60 Watts. As the pressure in the system increased, the etch rate decreased nearly linearly.

The emission spectral lines IO, IF and IAr from the plasma were also measured during these experiments. The IO/IAr, IF/IAr and IO/IF intensity ratios are shown as a
function of pressure in Figure 17. The intensity ratios IO/IAr, IF/IAr and IO/IF show a significant increase with increasing pressure.

Figure 18 shows the intensity ratios IO/IAr, IF/IAr and IO/IF as a function of the reactor pressure for a lower absorbed MW power of 25W, with all other conditions remaining the same. Lower values of the IO/IAr and IF/IAr ratios, and a higher value for IO/IF are now obtained in Figure 18, compared to the 60W curve (Figure 17). The influence of changing the MW power on the intensity ratios measured in the MW plasma is further discussed in section 3.2.4.

3.2.2. Etching of Polyimide Downstream of a Microwave Plasma as a Function of the Total Gas Flow Rate

The total gas flow rate of the gas mixture O\(^2\), CF\(_4\) and Ar through the system was varied, keeping all other experimental parameters constant. The flow rates were varied from 25-75 SCCM. The etch rate of PI downstream of a MW plasma, and the emission spectra from the discharge were measured during the experiments.

Figure 19 shows the etch rate as a function of the total gas flow rate. An increase in the etch rate was observed as the total gas flow rate was raised. The IO/IAr, IF/IAr and IO/IF intensity ratios are shown as a function of the total gas flow rate in Figure 20.
Figure 18
Figure 19

Polyimide Etch Rate (Å/min) vs. Total Gas Flow Rate (SCCM)
Figure 20
3.2.3. Etching of Polyimide Downstream of a Microwave Plasma as a Function of the Gas Flow Velocity

The parameters discussed in sections 3.2.1. (Reactor Pressure) and in 3.2.2. (Total Gas Flow Rate) can be related to each other in terms of the gas flow velocity. In a tube of radius \( r \), the gas flow velocity, \( v \), varies proportionally with the total gas flow rate (FR) and is reciprocally proportional to the reactor pressure (PR) according to:

\[
v = \text{FR} \times \left( \frac{760}{\text{PR}} \right) \times \left( \frac{T}{273} \right) \times \left( \frac{1}{\pi r^2} \right)
\]

where \( T \) is the temperature of the gases in Kelvin (an average temperature of 298K was taken). With the distance between the MW cavity and the wafer fixed, the active species will take less time to reach the wafer at the higher total gas flow rates, and lower reactor pressures. As a result, at higher total gas flow rates and/or lower reactor pressures, there was less opportunity for the active species to be removed through both surface and gas phase reactions and hence more active species will arrive at the wafer per unit time.

In both cases (increasing the total gas flow rate and/or decreasing the reactor pressure), the etch rate increased with increasing gas flow velocity. This behavior is shown in Figure 21 (derived from the data of Figures 16 and 19). Since the complicated geometry of the
5-way cross does not allow the use of a specific value for \( r \), \( r \) was taken to be 10 cm as a first approximation.

Although oxygen and fluorine atom number densities, and the ratio of these densities vary for each point in Figure 21, the dependence of the etch rate on the gas flow velocity is still evident, suggesting the importance of this parameter.

Experimental conditions given in Table 3, show the dependence of the etch rate on the gas flow velocity. A measured etch rate of 5650A/min was obtained with an absorbed MW power of only 60 Watts (Table 3) and with a distance between the MW cavity and substrate of almost 50 cm, in a geometry which rather reduced the gas flow velocity in the vicinity of the substrate. Later, in section 3.3., when the reactor geometry is optimized, higher etch rates are obtained.

The retention time, \( T \) in seconds, of the gases in the MW cavity can be found using:

\[
T = \frac{L}{v}
\]  

(3)

where \( L \) is the length of the MW cavity in cm, and \( v \) is the gas flow velocity. The length of the MW cavity was constant (3.45 cm) in all experiments. The retention time of the gases in the MW cavity was therefore proportional to the absolute pressure in the system. With longer retention times, the gases could dissociate more readily, thus increasing the density of the active species in the
Table 3

Dependence of Etch Rate on Gas Flow Velocity

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Total Flow Rate (SCCM)</th>
<th>Total Pressure (Torr)</th>
<th>Gas Flow Velocity (cm/min)</th>
<th>Etch Rate (A/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>263.2</td>
<td>0.77</td>
<td>903</td>
<td>2775</td>
</tr>
<tr>
<td>2</td>
<td>394.8</td>
<td>1.07</td>
<td>974</td>
<td>3917</td>
</tr>
<tr>
<td>3</td>
<td>526.3</td>
<td>1.36</td>
<td>1022</td>
<td>4998</td>
</tr>
<tr>
<td>4</td>
<td>657.9</td>
<td>1.636</td>
<td>1062</td>
<td>5654</td>
</tr>
</tbody>
</table>

Experimental conditions were absorbed MW power, 60 Watts; Y, 26.3 cm; Z, 18 cm; gas feed composition, 76% O2, 19% CF4 and 5% Ar; r, 10 cm.
Figure 17 shows an increase in the IO/IAr, IF/IAr and IO/IF intensity ratios as the pressure was raised. These changes in the spectral line intensity ratios indicates that the processes which influence the decrease in the etch rate, with increasing pressure, must occur downstream of the MW cavity, and not in the plasma. As the total gas flow rate increased, there was a smaller residence time in the cavity. Figure 20 shows that the IO/IAr and IF/IAr intensity ratios decreased, although the IF/IAr ratio decreased more rapidly than the IO/IAr ratio. Therefore, the etch rate increased with increasing total gas flow rates as the IO/IF ratio approached an optimum value in the plasma.

The observed increase in the etch rate with an increase in gas flow velocity (Figure 21) may be due to:

(i) an increase in the number of active species striking the substrate per unit time;

(ii) a decrease in the reaction time of the active species, with other particles, and/or with the walls of the apparatus; and

(iii) a change in the IO/IF ratio with reaction time as the active species are transported through the apparatus.
3.2.4. Etching of Polyimide Downstream of a Microwave Discharge as a Function of Microwave Power

The etch rate of PI downstream of a MW plasma was studied as a function of absorbed MW power (Figure 22). The ratio of the atomic line intensities IO/IAr, IF/IAr and IO/IF were also measured as a function of absorbed MW power (Figure 23). An increase in the absorbed MW power in the MW cavity provided more energy to produce more oxygen and fluorine atoms in the plasma. As the absorbed MW power increased, the IO/IF intensity ratio decreased, indicating that in the plasma, less oxygen atoms were being produced relative to fluorine atoms. The change in the MW power changed the IO/IF ratio, thus altering the etching process of PI.

Figure 24 shows the IO/IAr, IF/IAr and IO/IF intensity ratios as a function of absorbed MW power for a wafer whose PI coating was previously etched away. The results are nearly identical to that reported in Figure 23, indicating that the emission spectrum from the plasma is independent of the nature of the wafer located downstream of the discharge.

3.2.5. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Substrate Temperature

The etching process is an exothermic process since the temperature of the substrate increased a few degrees
Figure 23
Figure 24
during the etching of PI. However, when the substrate was exposed downstream of the MW plasma with a high concentration of CF, a decrease in the temperature of the wafer was always observed.

The etch rate of PI was studied at different temperatures, keeping all other experimental parameters constant. The absorbed MW power was 50 Watts. Figure 25 shows the Arrhenius plot for \( \ln R \) versus 1000/T. The etch rate was measured as a function of substrate temperature between 28°C and 47°C (in separate experiments). An activation energy of 0.14±0.03 eV was found from Figure 25 for the etching of PI downstream of a MW plasma.

3.2.6. Etching of Polyimide Downstream of a Microwave Plasma as a Function of Reactor Geometry

3.2.6.1. Varying Injector Distance

Changing the distance, \( Z \), between the end of the injector and the substrate (Figure 2) at constant total gas flow rate, reactor pressure and absorbed MW power also affected the etch rate of PI. The dependence of the etch rate as a function of the distance, \( Z \), between the end of the injector tube and the substrate (without changing the position of the substrate) is given in Figure 26. The total gas flow rate was 50 SCCM. The etch rate decreased as the injector was moved further from the substrate. A
Figure 25
greater distance between the injector and the substrate required more time for the active species to reach the PI substrate, thus possibly decreasing their concentration near the substrate by diffusion, by recombination on the walls of the apparatus and/or by chemical reactions occurring in the gas phase. The decrease in the etch rate between the Z distance 3.8 cm and 13.5 cm was about 38%.

In another experiment, the substrate was raised into the upper arm of the apparatus. The distance Z was now 1 cm. All other parameters were kept constant, as before. Using \( r = 5.08 \) cm (radius of the arm), the value of the gas flow velocity was calculated to be 4,230 cm/min, using equation (3). In addition, in this region, atomic concentrations of oxygen and fluorine would almost certainly be greater than at the center of the cross due to a decreased reaction time of active species in the gas phase and on the walls of the reactor chamber.

Under conditions with a higher gas flow velocity (absorbed MW power, 59 Watts; reactor pressure, 1.6 Torr; total gas flow rate, 658 SCCM; 76% O, 19% CF, 5% Ar), the etch rate was 28,100 A/min. When the length of the injector tube (Y in Figure 2) was shortened to 10.2 cm, the same conditions yielded an etch rate of 34,300 A/min. Apparently, the etch rate is strongly influenced by the gas flow velocity (which incorporates the reactor geometry into it) and hence the number and maybe the type of active
species striking the substrate per unit time.

3.2.6.2. Varying Injector Design

In several experiments, the MW cavity was placed in a vertical position (Figure 27), instead of in a horizontal position (Figure 2) as described previously. With the vertical cavity, a direct path of photons from the MW cavity to the substrate was achieved. The sum of the distance parameters X, Y and Z gives the total distance between the center of the MW cavity and the substrate as indicated on the schematic drawing, with the vertical MW cavity (Figure 27).

By employing high total gas flow rates, short distances between the MW cavity and the substrate, by using the vertical injector design and maximizing all other parameters such as reactor pressure, absorbed MW power, gas flow velocity and gas composition (as discussed in the previous sections), with regard to their effect on the etching of PI, high etch rates were obtained. In Table 4, etch rate measurements are given for some of these experiments, using the vertical MW cavity design, and with the substrate raised into the upper arm of the MW apparatus. Etch rates up to 45,000 A/min (Table 4, Run #6) were obtained with an absorbed MW power of 63 Watts.
TABLE 4
Etch Rate Measurements for High Gas Flow Rates and Short Distances
Between the Vertical Cavity and the Substrate

<table>
<thead>
<tr>
<th>Exp.</th>
<th>Pressure,</th>
<th>Flow</th>
<th>Gas</th>
<th>% O₂</th>
<th>% CF₄</th>
<th>% Ar</th>
<th>X,</th>
<th>Y,</th>
<th>Z,</th>
<th>Absorbed</th>
<th>Etch</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>torr</td>
<td>Rate</td>
<td>Flow</td>
<td></td>
<td></td>
<td></td>
<td>cm</td>
<td>cm</td>
<td>cm</td>
<td>Power,</td>
<td>Rate</td>
</tr>
<tr>
<td></td>
<td></td>
<td>sccm</td>
<td>Velocity,</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Watts</td>
<td>µ/min.</td>
</tr>
<tr>
<td>1</td>
<td>4.0</td>
<td>2,148</td>
<td>5,496</td>
<td>81.98</td>
<td>18.02</td>
<td>--</td>
<td>4.0</td>
<td>7.4</td>
<td>2.7</td>
<td>52</td>
<td>17,382</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>2,034</td>
<td>5,203</td>
<td>75.80</td>
<td>24.20</td>
<td>--</td>
<td>4.0</td>
<td>7.4</td>
<td>2.7</td>
<td>51</td>
<td>23,883</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>2,027</td>
<td>5,184</td>
<td>72.60</td>
<td>27.40</td>
<td>--</td>
<td>4.0</td>
<td>7.4</td>
<td>2.7</td>
<td>51</td>
<td>24,694</td>
</tr>
<tr>
<td>4</td>
<td>4.0</td>
<td>2,069</td>
<td>5,292</td>
<td>70.15</td>
<td>29.85</td>
<td>--</td>
<td>4.0</td>
<td>7.4</td>
<td>2.7</td>
<td>51</td>
<td>37,460</td>
</tr>
<tr>
<td>5</td>
<td>4.0</td>
<td>1,987</td>
<td>5,084</td>
<td>66.71</td>
<td>33.29</td>
<td>--</td>
<td>4.0</td>
<td>7.4</td>
<td>2.7</td>
<td>51</td>
<td>27,151</td>
</tr>
<tr>
<td>6</td>
<td>1.6</td>
<td>662</td>
<td>4,236</td>
<td>72.22</td>
<td>20.4</td>
<td>7.38</td>
<td>4.0</td>
<td>7.4</td>
<td>0.5</td>
<td>63</td>
<td>45,000</td>
</tr>
<tr>
<td>7</td>
<td>1.6</td>
<td>662</td>
<td>4,236</td>
<td>72.22</td>
<td>20.4</td>
<td>7.38</td>
<td>4.0</td>
<td>7.4</td>
<td>0.5</td>
<td>58</td>
<td>43,000</td>
</tr>
<tr>
<td>8</td>
<td>3.2</td>
<td>1,152</td>
<td>3,684</td>
<td>69.5</td>
<td>22.95</td>
<td>7.55</td>
<td>4.0</td>
<td>7.4</td>
<td>0.8</td>
<td>52</td>
<td>33,240</td>
</tr>
</tbody>
</table>
3.3. Etch Rate Measurements at Different Locations on the Polyimide Wafer

Upon removal of an etched wafer from the system, the center of the wafer appeared to have no PI on the surface. However, a ring of PI was observed around the outer diameter of the silicon wafer. Experiments were therefore carried out to determine whether the etch rate was uniform.

A single wafer was used for this experiment. The total gas flow rate was 50 SCCM, absorbed MW power was 19 Watts and the distance Z was 13.5 cm. Without changing the parameters of the experiment, the laser beam was moved, striking various parts of the PI wafer.

Figure 28 shows the locations where the etch rates were measured on the wafer. These positions were obtained from visual estimates of the laser beam on the wafer. A statistical treatment of the data is given in Table 5.

Measuring the etch rate at different locations on the substrate have, indeed, shown a rather homogeneous etch rate distribution. The appearance of nonhomogeneity on the surface of the wafer after etching may be caused by an uneven coating of the PI initially. A description of the substrate preparation was given in Appendix I.

3.4. The Induction Effect

Etching of a PI wafer that was not previously
Table 5

Statistical Treatment of Data for Etch Rate Measurements at Different Locations on a Polyimide Wafer

<table>
<thead>
<tr>
<th>Exp. #</th>
<th>Etch Rate (Å/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>400</td>
</tr>
<tr>
<td>2</td>
<td>410.7</td>
</tr>
<tr>
<td>3</td>
<td>403</td>
</tr>
<tr>
<td>4</td>
<td>425</td>
</tr>
<tr>
<td>5</td>
<td>428</td>
</tr>
<tr>
<td>6</td>
<td>416.2</td>
</tr>
</tbody>
</table>

Mean Value, $X = 413.8$

Average Deviation, $\bar{d} = \frac{\sum_{i=1}^{n} [X_i - \bar{X}]}{n} = 9.25$

Relative Average Deviation $= \frac{\bar{d}}{X} = 2.2\%$

Standard Deviation $= \sqrt{\frac{\sum_{i=1}^{n} [X_i - \bar{X}]^2}{n-1}} = 11.4$

Relative Standard Deviation $= 2.75\%$

* See Figure 27 for locations.
exposed to the plasma showed an initial increase (induction period) in the etch rate and wafer temperature with time. After the induction period, the etch rate levelled off and remained relatively constant with time. This induction or saturation effect has been investigated.

Figure 29 shows the gradual rise in the temperature and the etch rate over a period of time, when a new wafer was exposed downstream of the MW plasma. The absorbed MW power was 25 Watts.

With a new wafer in the system, the experiment was repeated under the same conditions. An old wafer was placed on top of the new wafer initially for two hours with the plasma on. The top wafer was attached to a glass tube (passing through the right side of the MW apparatus in Figure 2), with a piece of copper wire. After the initial two hours, the top wafer was removed while still under vacuum and with the plasma on. The temperature and etch rate were measured over a period of time once the top wafer was removed. In comparison to Figure 29, Figure 30 shows only a slight increase in the etch rate and temperature observed over a period of 48 minutes.

These experiments tend to indicate that the observed induction period may be due to surface reactions of the active species in the apparatus. When the surface of the apparatus was conditioned for two hours, only a small induction period was observed. Studies were done to
Figure 29
investigate how the parameters of an experiment affected the induction period of a new wafer.

With the same experimental conditions as above, the saturation of unexposed PI wafers were studied for various absorbed MW powers. High absorbed MW power was found to significantly lower the time needed for a new wafer to reach a constant etch rate.

When a new wafer was exposed downstream of a MW plasma with 25 Watts of absorbed MW power and the above conditions, a saturation effect was seen as in Figure 31. Figure 31 shows a maximum etch rate of about 1550 A/min after 18 minutes. A higher maximum etch rate of 2100 A/min was achieved for a previously unexposed wafer in Figure 32 when an absorbed MW power of 42 Watts was used to saturate the wafer. The time of saturation in Figure 32 was about 15 minutes after exposing the new wafer downstream of a MW plasma.

With a further increase in the absorbed MW power during saturation, higher etch rates were achieved after shorter time periods. An absorbed MW power of 62 Watts was used to obtain a maximum etch rate of 2400 A/min in Figure 33 after exposing the new wafer for 10 minutes. A temperature rise from 27.2°C to 28.6°C occurred while the etch rate was increasing.

The total flow rate in the system can also affect the saturation time for a new wafer to reach the maximum etch...
Figure 32
rate. With the same parameters as above and with 62 Watts of absorbed MW power, the total gas flow rate was increased to 75 SCCM. In comparison to Figure 33, the maximum etch rate increased to 2900 A/min in Figure 34. It was noted earlier (section 3.2.2.) that an increase in the total gas flow rate raised the etch rate of PI. The time for saturation with a new wafer has decreased in Figure 34, to approximately 8 minutes, with a corresponding temperature rise from 20.6°C to 24.3°C.

The emission spectra were measured during the saturation of the PI wafer for different times of exposure. The etch rate as a function of time during saturation of the new wafer is presented in Figure 31. The intensities of the spectral lines were measured after two, fifteen and twenty-five minutes of exposing the substrate downstream of the MW plasma. The results in Table 6 show consistent IO/IAr, IF/IAr and IO/IF intensity ratios in contrast to a rising etch rate during the saturation seen in Figure 31. This indicates that the induction or the saturation effect is not connected with the processes in the plasma, but are associated with processes on the reactor walls and/or on the surface of the substrate.
Figure 34
Table 6

Emission Spectroscopy Results for Varying Exposure Times of a New Wafer

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>IO/IAr rel.</th>
<th>IF/IAr rel.</th>
<th>IO/IF rel.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>.278</td>
<td>.221</td>
<td>1.26</td>
</tr>
<tr>
<td>15</td>
<td>.280</td>
<td>.217</td>
<td>1.29</td>
</tr>
<tr>
<td>25</td>
<td>.278</td>
<td>.225</td>
<td>1.24</td>
</tr>
</tbody>
</table>

Experimental conditions were reactor pressure, 0.3 Torr; total gas flow rate, 65 SCCM; absorbed MW power, 25 W; Y, 26.3 cm; Z, 15.3 cm; and gas composition, Table 1, Run #4.
3.5. Passivation of Polyimide

Exposing the substrate downstream of a MW plasma with a high concentration of CF in O$_2$ - Ar resulted in a passivation of the surface of the PI to etching (an effect described for RF plasmas in reference 7).

3.5.1. XPS Studies

XPS analysis at different stages of etching, passivation, removal of passivation and resumption of etching of PI downstream of a MW plasma, gave a detailed view of the surface composition during these different stages. Samples were prepared at RIT, Rochester in the Plasma Science Laboratory and XPS analysis were done at IBM Laboratories, Endicott.

Etch rates and substrate temperatures, during the stages of etching, passivation, removal of passivation and resumption of etching are shown in Figure 35. The etch rate in Figure 35 initially increased and does not immediately level off and reach a saturation value. The temperature also rose during the initial increase in the etch rate. During the passivation and removal of passivation stages (Figure 35), the etch rate was immeasurably small (<20 A/min), while the temperature dropped, levelled off and began to rise again with time.

The resumption of measurable etching occurred after
about 34 minutes after the removal of passivation stage (Figure 35). The resumption of a measurable etch rate was again followed simultaneously by an increase in the temperature. The temperature continued to increase while the PI substrate etched at its saturated value.

The relative atomic concentrations for carbon, oxygen and fluorine (from XPS analysis) during the various stages of etching, passivation, removal of passivation and resumption of etching are presented in Figure 36. Relative atomic fluorine concentration on the PI surface is significantly higher after passivation and several minutes into the removal of the passivation (Figure 36). This is in agreement with the XPS analysis of passivated PI surfaces in RF plasmas [9].

The ratios C/O, F/O and F/C are given in Figure 37. The C/O ratio (Figure 37) after the first 4 minutes of etching, was approximately constant up to the end of the experiment, probably because there was only a short period for passivation.

In the papers [9,10] the 01s peaks of XPS results for an unetched substrate, and a substrate exposed to a pure O2 RF plasma were analyzed and compared. A possible formation of polycarbonate ( > C = O) and peroxy (C - O - O - C) groups in the samples treated with an oxygen RF plasma was discussed.
Figures 36 and 37 indicated that during the removal of passivation (and during the etching), relative fluorine concentration (and also F/O and F/C ratio) initially increased and then decreased. These results need to be further studied.

3.5.2. Deposition During Passivation

At high concentrations of CF in an O - Ar plasma, a white material was observed to be present on the walls of the apparatus. The detection of nitrogen via XPS analysis of PI films treated in these plasmas implies that if deposition were occurring at the PI surface, it is noncontinuous. In addition, analysis of glass surfaces exposed to the CF rich plasma, showed that carbon and fluorine were present, however, there was no indication of fluorocarbon type bonding as was observed on passivated surfaces [7].

A sample of the white precipitate from the reactor walls was analyzed using an infrared spectrophotometer. The sample was prepared following the procedure in Appendix II. By comparing the IR spectrum of the deposited material in Figure 38 with the reference spectrum in Figure 39 (a-c) from the literature [36], we may conclude that polymerization, forming a teflon-like polymer, occurred in the downstream of the MW plasma during passivation of the PI. The melting point of the
Fig. 42B.
POLYTETRAFLUOROETHYLENE
KBr Wafer
Source: Harwick Standard Chemical Company, LNP Engineering Plastics Division

Fig. 42C.
POLYTETRAFLUOROETHYLENE
KBr Wafer
Source: Whitford Chemical Corporation
sample was found to be greater than 400°C. A sample of teflon was also scanned (Figure 40) and is in agreement with the literature spectra [37].

So, in discussion, an excess of fluorine atoms in the system probably competes with oxygen atoms for the active sites during passivation, changing the structure of the PI, resulting in a small measurable etch rate (<20 A/min). Besides changing the structure of PI during passivation, an inert teflon-like polymer may be coating the PI substrate.

3.5.3. Depth Profile of a Passivated Polyimide Substrate

In all experiments, prior to passivating the substrate, the PI was etched downstream of a MW plasma, until a saturation of etching was reached. Passivation of the PI substrate was accomplished by exposing the substrate downstream of a MW plasma with a high concentration of CF. The passivation was removed, after some time, by exposing the substrate downstream of a MW plasma with a lower CF concentration. During this last step, very slow etching occurred initially (removal of passivation) before saturated etch rates were measured again (resumption of etching).

Substrates were passivated for different lengths of time, and the time to remove the passivation was measured. An absorbed MW power of 49 Watts and a total gas flow rate
of 52 SCCM was used. Experiments were done with the MW cavity in the horizontal position (Figure 2) and with the substrates placed closer to the plasma (18.1 cm) in the upper arm of the cross.

A linear dependence of the time of the removal of passivation with the time of passivation was observed. However, the measured dependence of the time of the removal of passivation on the time of passivation does not allow conclusions about the distribution of fluorine in the PI. The fluorination of a small surface layer may result in a very small etch rate during the removal of passivation and therefore a long time is required for the removal. Similarly, the fluorination of deeper layers, with the same total fluorine concentration, would have relatively faster etch rates, but possibly the same time for the removal of passivation.

The passivation of PI occurs due to a high degree of fluorination of the polymer and it may be proposed that the removal of passivation was actually the removal of the fluorinated layers due to a slow etching process. In several cases, during the experiments, it was possible to measure the small etch rate during the removal of passivation stage. The measured etch rates during the removal of passivation were taken to be reciprocally proportional to the fluorine concentration in different
layers of the PI, describing the fluorine depth profile.

The fluorine depth profile was investigated for passivated PI substrates. A detailed description of the preparation for the PI film is in Appendix I. During these experiments, after passivating longer than 20.4 minutes, the PI was etched completely away during the removal of passivation step. Increasing etch rates were measured during the removal of passivation step, indicating a fluorine depth profile for the passivated PI substrate.

In Figure 41, 1/R values for the PI substrates passivated for different time intervals, as a function of the time of the removal of passivation are shown. In Figure 42, 1/R values as a function of the thickness of (highly) fluorinated layers are depicted. Figures 41 and Figure 42 indicate that an increase in the fluorine concentration in the fluorinated layers of passivated PI increased with the time of passivation, and the depth of fluorination increased with longer passivation times.

For a more detailed description of the fluorine depth profile into PI, additional measurements with XPS analysis are necessary. Still, it seems rather convincing that the fluorine can penetrate into PI a depth of 5,000 to 6,000 Å, and probably even more.
Figure 42
3.5.4. Transition Period Between the Removal of Passivation Stage and the Resumption of Etching Stage

The end of the removal of passivation stage and the beginning of the resumption of etching stage was characterized by a significant decrease in the reflected laser beam. To measure the etch rates in the resumption of etching stage, it was necessary to increase the sensitivity of the recording laser beam system (diode and recorder, Figure 1). A copy of an interferogram for this transition period between these two stages is given in Figure 43.

A physical change in the appearance of the PI could be seen with the naked eye when the substrate reached the resumption of etching stage, compared to substrates in all previous periods (etching, passivation and removal of passivation). The substrate became opaque when the resumption of etching stage was reached.

SEM photographs of the PI surface were obtained for different stages of experiments. The surface of the PI was much more "rough" in the resumption of etching stage as compared to previous stages. SEM photographs for PI substrates represented the removal of passivation stage (Figure 44) and the resumption of etching stage (Figure 45), obtained with a magnification of 5000X. In stages previous to the resumption of etching, the surface was
Figure 45
rather smooth, although some craters could be seen on the surface.

XPS analysis of the PI during the resumption of etching stage (Figure 36), shows that the surface atomic composition approached the same composition as in the first stage of the etching experiment. This indicates that probably the chemistry of the substrate in the resumption stage was similar to that found in the first stage of etching.

In an experiment, the resumption of etching stage was prolonged for an additional 16.8 minutes. During this time interval, a layer of 70,500 A (etch rate was 4200 A/min) was removed. The intensity of the reflected laser beam remained very small and the substrate still looked opaque when removed from the system. This might indicate that the roughness of the surface, once created, can "survive" a longer etching process. Such a behaviour could be expected with the isotropy of the etching of PI downstream of a MW plasma.

4.0. Conclusion

Investigations on the etching of PI in the absence of ions and UV photons has been greatly enhanced by the construction of a MW discharge apparatus which permits the etching downstream of a MW plasma.

The etching process was found to depend on the amount
of atomic oxygen and atomic fluorine striking the substrate per unit time, and on the IO/IF spectral line ratio. Although the etch rate of organic materials are dependent on the absolute concentrations of atomic oxygen and fluorine at the surface, for a given concentration of atomic oxygen, there was an optimum concentration of fluorine atoms for which a maximum etch rate was achieved. In a MW plasma, the atomic concentrations of oxygen and fluorine could be inferred using the ratios of the atomic spectral line intensities OI 845/ArI 750 and FI 704/ArI 750 nm. The oxygen to fluorine atomic concentration ratio in the plasma is directly proportional to the ratio of the intensities of emission spectral lines OI 845 nm to FI 704 nm.

The addition of small amounts of CF to an oxygen-argon MW plasma greatly enhanced the etch rate of PI. The maximum etch rate in the MW system occurred at an O -CF composition that was nearly identical to that found 2 4 in the RF system. Passivation of PI to etching occurred when the substrate was exposed downstream of a MW plasma with a high concentration of CF in the gas feed. The passivation was removed, after some time, by exposing the substrate downstream of a MW plasma with lower concentrations of CF. The fluorine depth profile was estimated by measuring the small etch rates during the removal of passivation stage.
The density of active species arriving at the substrate downstream of a MW plasma depended on the geometry of the reactor, the gas flow velocity (which itself depended on the experimental parameters of total reactor pressure, total gas flow rate and, again, on the geometry of the apparatus), and the absorbed MW power.

The induction effect characterized with unexposed substrates was found to be due to surface reactions of the active species with the reactor chamber. Conditioning the reactor walls previous to etch rate measurements is important for reproducibility in the experimental data.

The activation energy for the etching of PI downstream of a MW plasma was found by varying the substrate temperature and measuring the etch rate. The etching of PI is an exothermic process.

Varying the absorbed MW power effects the dissociation of the gas species in the MW cavity. An increase in the active species which strikes the substrate per unit time will increase the etch rate.
Films of polyimide were applied to 57.15 mm diameter silicon wafers using a Model Number 1-EC101D-R485 photo-resist spinner. The spinning speed was adjustable from 50 to 10,000 RPM with a controller. A digital tachometer indicated the spinner speed directly. The spin cycle was automatically controlled by an adjustable electronic timer. At the end of the spin cycle, automatic dynamic braking stopped the spinner quickly.

The preparation polyimide film could only be described qualitatively. To apply the polyimide, the substrate was centered onto the vacuum chuck on the spinner. Vacuum was automatically applied to the chuck when the "start" switch was depressed on the unit. With the spinner off and the substrate on the chuck, polyimide was applied to the center of the wafer, covering approximately half the surface. With the spinning speed set low (50 to 150 RPM), the polyimide was allowed to spread across the wafer in a uniform dispersion. If the spinning speed was too high, and the wafer was off center on the chuck, then the polyimide would be thrown more to one side of the wafer, resulting in an uneven coating on the silicon wafer.

For a thin film of polyimide, the spinning speed was increased to approximately 3500 RPM for 5 to 10 seconds.
The substrate was removed from the spinner for the curing process. For a thick film of polyimide, the wafer was spun at a slower speed and for a shorter time.

The curing process involved placing the wafers spun with polyimide into a Type 1500 Thermolyne furnace. The substrates were initially heated at 85°C for 15 minutes in air at atmospheric pressure. With a nitrogen purge at atmospheric pressure, the furnace was then ramped manually to 360°C over a 2-hour period. Once at 360°C, the temperature was kept constant for an additional 30 minutes, before removing the cured substrates from the furnace.
INSTRUCTIONS FOR OPERATION & MAINTENANCE
of the KBr PELLET PRESS & HOLDER

I. Description and Preparation of the Cell

The Mini-Press consists of four parts, one barrel which serves as the pellet holder, two polished stainless steel bolts and one cell slide.

Upon receipt of the Mini-Press Kit, thoroughly wash the barrel and bolts with 1,1,1-trichloroethylene or some other suitable cleaning solvent to remove any traces of machining oil, and prevent subsequent contamination of the sample pellet.

Dry the barrel and bolts under forced air at 105°C and store in a desiccator until further use. NOTE: To prolong the life of the Mini-Press take care not to scratch the polished faces of the bolts. Avoid direct contact of these two faces in the barrel. The cell should be assembled only when a sample will separate the faces of the polished bolts.

II. Sample Preparation and Techniques

Conventionally dried spectroquality potassium bromide (KBr) is used as the matrix. However, for special
applications, other materials such as potassium chloride or cesium bromide may be used.

High quality KBr pellets can be formed with 50 to 100 mg. of material. The minimal amount of matrix required to form a good pellet is 25 mg.

Thoroughly grind approximately 0.5 to 1.0 mg. of solid sample with a mortar and pestle, or use a Wig-L-Bug. Add approximately 100 mg. of KBr and regrind to uniformly mix the matrix with the sample. With friable materials, grinding in a small glass vial with a stainless steel spatula, and thoroughly mixing with KBr, is suitable to form a good pellet.

III. Forming the Pellet

Place one bolt in the barrel and advance five full turns. Deposit 50 to 100 mg. of matrix on the surface of the bolt inside of the barrel. Tap the unit gently to spread the sample uniformly over the lower bolt. Insert second bolt and advance till finger tight. Using two 9/16" open end (box) wrenches or adjustable crescent, gradually exert pressure on each bolt. To operate more easily, the lower bolt may be placed in a bench vise and the top tightened with a wrench. Apply pressure for about
one minute, then remove bolts. If one bolt holds tight in the barrel use a 1" x 6" wrench on the flats of the barrel with a 9/16" x 6" wrench on the bolt.

IV. Determination of Spectrum

Place the cell slide in the space provided in the sample beam of the spectrometer. Mount the barrel containing the pellet on the cell slide so that the flat surfaces of the barrel are in a vertical position. (If the flats lie on the "vee", the barrel will not be centered on the cell slide).

V. Cleanup

The pellet can be removed from the barrel by punching out with a pointed instrument or dissolving with water. NOTE: Do not attempt to drive the pellet out with one of the bolts, this may cause damage to the polished die surface. If water is used, dry the barrel completely and then store the barrel and the bolts in a desiccator.
REFERENCES


