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# PLASMA IMMERSION ION IMPLANTATION (PIII) FOR INTEGRATED CIRCUIT MANUFACTURING; FOURTH QUARTERLY PROGRESS REPORT

by

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and J. Benasso

Memorandum No. UCB/ERL M91/116

18 September 1991 - 17 December 1991

ELECTRONICS RESEARCH LABORATORY

College of Engineering
University of California, Berkeley
94720

**Fourth Quarterly Progress Report**
**18 September 1991 - December 1991**

# PLASMA IMMERSION ION IMPLANTATION (PIII) FOR INTEGRATED CIRCUIT MANUFACTURING


CCTP Contract #C90-071

Applied Materials Inc.



| | |
|---|---|
| Project Managers: | N. W. Cheung, UCB<br>M. A. Lieberman, UCB |
| Product Manager: | W. J. Wriggins, Applied Materials |
| Program Manager: | P. R. Klein, CA Office of Competitive Technology |

# FINANCIAL REVIEW

**CompTech Program**
**Plasma Immersion Ion Implantation for Integrated Circuit Processing**
**Grant No. C90-071**
**Final Quarterly Report**
**September 18, 1991 - December 17, 1991**

| Participant | To Date Planned | To Date Actual | Percent Actual of Planned | This Quarter Planned | This Quarter Actual | Percent Actual of Planned | Next Quarter Planned |
|---|---|---|---|---|---|---|---|
| CompTech | 140,000 | 134,400 | .96 | 35,141 | 5,600 | .15 | 5,600 |
| Applied Materials | | | | | | | |
| Cash | 70,002 | 70,000 | .99 | 27,234 | 0 | 0 | 0 |
| In-kind | 15,000 | 15,000 | 1 | 3,750 | 7,000 | 1.86 | 0 |

The amounts include indirect costs for CompTech, but not for AppMats.

**CompTech Program**
**Plasma Immersion Ion Implantation for Integrated Circuit Processing**
**Grant No. C90-071**
**Matching and Non-Matching Contributions this Quarter**

| Participant | Cash Spent by Grantee | In-Kind | Total Matching | Cash Spent by Grantee | In-Kind | Total Non-Matching Committed |
|---|---|---|---|---|---|---|
| Applied Materials* | 70,000 | 15,000 | 85,000 | 0 | 0 | 0 |
| Total | 70,000 | 15,000 | 85,000 | 0 | 0 | 0 |

*No Cash or Equipment was received from the Participant

**CompTech Program**
**Plasma Immersion Ion Implantation for Integrated Circuit Processing**
**Grant No. C90-071**

| Line Item | CompTech Budget | Expenditures this Quarter | Cumulative Exp. Thru Nov '91 | Committed but Not Billed Dec '91 | Balance of Grant | Expended and Committed |
|---|---|---|---|---|---|---|
| Salaries & Wages | 53,268 | 3,248 | 53,268 | 0 | 0 | 100% |
| Benefits | 5,726 | 420 | 5,726 | 0 | 0 | 100% |
| Travel | 2,000 | 443 | 2,000 | 0 | 0 | 100% |
| Supplies | 29,207 | 1,220 | 29,207 | 0 | 0 | 100% |
| Overhead | 44,199 | 2,465 | 44,199 | 0 | 0 | 100% |
| Audit | 5,600 | 0 | 0 | 5,600 | 5,600 | 0% |
| Total | 140,000 | 7,796 | 134,400 | 5,600 | 5,600 | 96% |

## PERSONNEL

| | | |
|---|---|---|
| N.W. Cheung | Project Manager | UCB |
| M.A. Lieberman | Project Manager | UCB |
| W.J. Wriggins | Product Manager | Applied Materials |
| P.R. Klein | Program Manager | OCT |
| R.A. Stewart | Postdoctoral Research | UCB |
| C.A. Pico | Postdoctoral Research | UCB |
| J. Tao | Visiting Scholar | UCB |
| M.H. Kiang | Graduate Student | UCB |
| C. Yu | Graduate Student | UCB |
| V. Vahedi | Graduate Student | UCB |
| B. Troyanovsky | Undergraduate Student | UCB |
| W. En | Undergraduate Student | UCB |
| E. Jones | Undergraduate Student | UCB |
| J. Benasso | Technician | UCB |

**Collaboration with Other Research Groups**

| | | |
|---|---|---|
| Dr. Ian Brown | Research Scientist | Lawrence Berkeley Lab |
| Dr. Kin-Man Yu | Research Scientist | Lawrence Berkeley Lab |
| Dr. Andy Keenan | Research Manager | Prometrix Inc. |

# PROJECT REVIEW

## I. INTRODUCTION

Ion implantation is an important technique in integrated circuit fabrication. Due to the continuing trend toward smaller, faster and more densely packed circuitry, conventional ion implantation technology faces several challenges. Two major challenges are throughput, which is limited by the available ion current, and the production of very low energy ion beams for shallow implants. Other important concerns include charging, channeling, shadowing and damage.

An alternative to conventional ion implantation that may eliminate several of the above problems is *plasma immersion ion implantation* (PIII). We have successfully applied PIII to semiconductor device fabrication for a number of VLSI applications including sub–100 nm p+/n junction formation, conformal implantation for trench doping, and palladium seeding for electroless Cu plating. The PIII process is illustrated in Figs. 1 and 2.

Ions that are created in an electron cyclotron resonance (ECR) plasma source, diffuse into a process chamber where they are extracted directly from the process plasma in which the wafer holder is located (Fig. 1). The substrate holder is biased to a high negative voltage (either pulsed or DC) and the ions are accelerated to the wafer through a high-voltage plasma sheath (Figs. 2a, 2b). Since the ion energy is controlled by the applied voltage, very low energy implants ($\leq$ 1 keV) are possible. In addition, since PIII operates with an ECR plasma discharge, a range of pressures from 0.1–100 mTorr may be used. Thus, the angular distribution of the implanted ions can be adjusted by varying the gas pressure. This feature is very attractive for conformal doping of nonplanar surface topographies such as high-aspect-ratio trenches.

PIII can also operate in a triode (Fig. 2c) mode by introducing a sputtering target near to or within the ECR source chamber. The sputtering rate can be controlled by applying a suitable bias to the target. This technique provides the capacity of implanting any solid material into the substrate as long as the material has reasonable sputtering and ionization rates. In addition, dual ion implantations of both the source and sputtered atomic species can be achieved by varying the target and wafer holder biases.

Several features of PIII make it an attractive alternative to conventional ion implantation. With the high current capability of PIII, the throughput of present integrated circuit steps can be substantially increased. Also, the intermediate step of the ion source and all of its support equipment is completely elim-

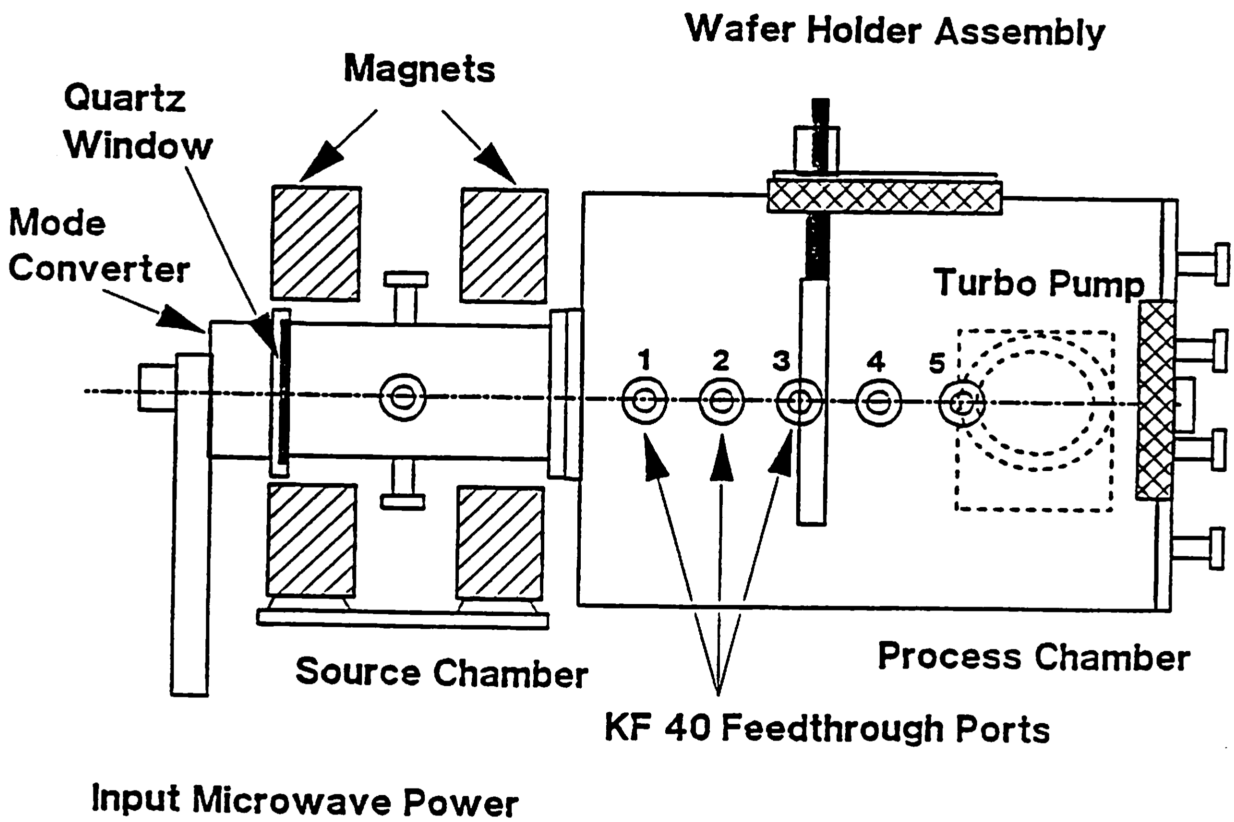
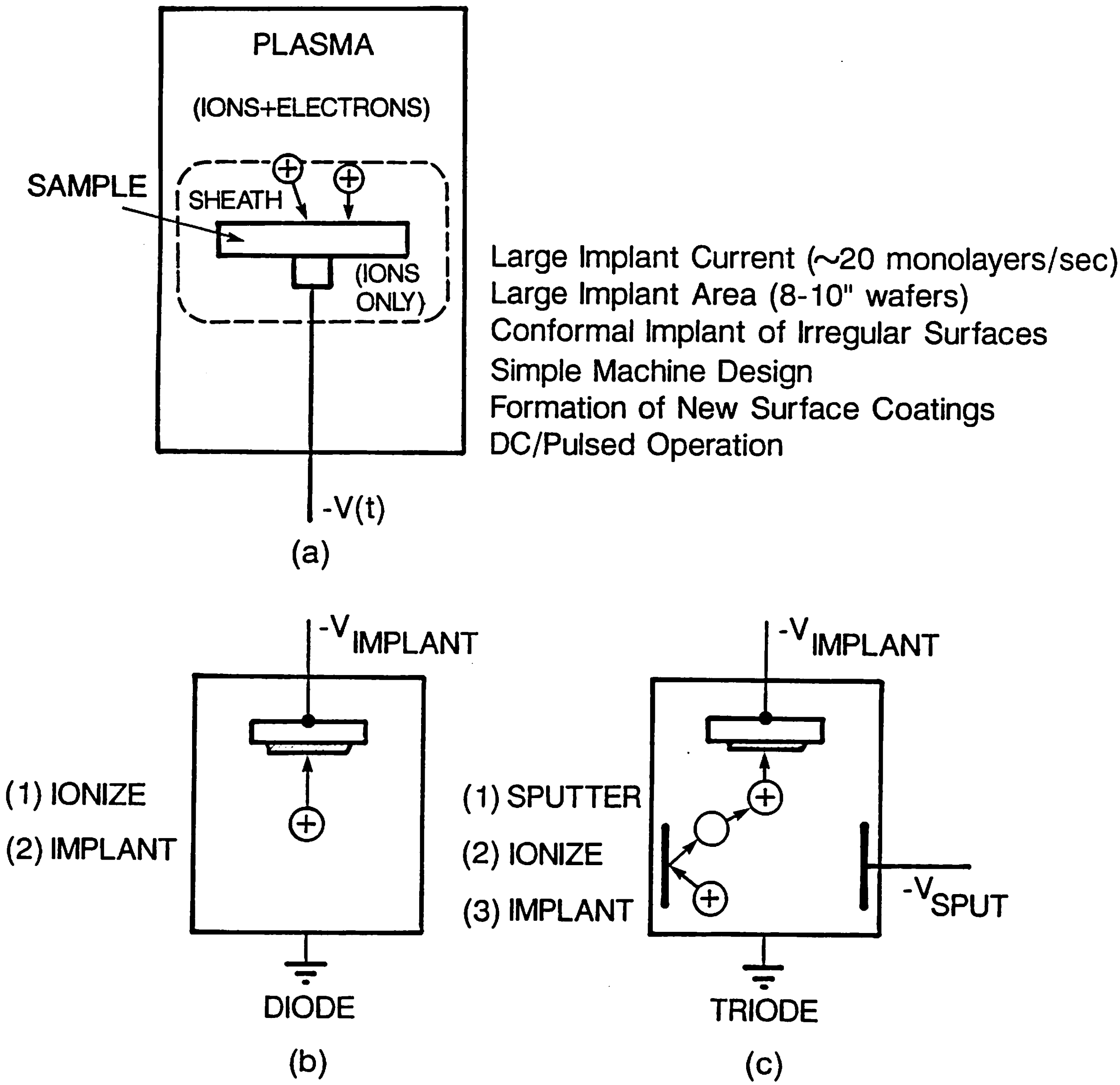



*Fig. 1:* Schematic side view of the PIII Reactor




Figs. 2 (a), (b), (c): Unique Features of PIII inated, leading to a simple reactor design that is compatible with the cluster tool concept.

The PIII program at Berkeley in 1990-91 is supported by a $70,000 cash and $15,000 in-kind grant from Applied Materials, Inc., and a $140,000 contract from the State of California Office of Competitive Technology. The goal of the project is to transfer the PIII process under development at Berkeley to Applied Materials, Inc.

## II. SUMMARY OF PROGRESS

The three critical issues for transfer of the PIII technology to Applied Materials are:

A. Process Demonstration. Demonstrate PIII processes that are more cost effective than conventional ion implantation.

B. Process Integration. Demonstrate PIII process compatibility with conventional IC processes to fabricate a complete integrated circuit.

C. Reactor Demonstration. Demonstrate a reactor that meets the required process uniformity and lack of oxide breakdown over a 200 mm wafer.

To address the first critical issue, three processes are being developed to demonstrate PIII superiority over conventional ion implantation:

(1) We have demonstrated the formation of 800 angstrom thick pn junctions with leakage currents less than 25 nA/cm$^2$ and low interfacial defect densities, comparable to the best commercial pn junction fabrication processes. The process consists of a 10kV $SiF_4$ pre-amorphization PIII implant followed by a 5kV $BF_3$ boron implant, followed by a one second rapid thermal anneal to activate the dopant. However, an obstacle to pn junction fabrication is condensation of $BF_3$ polymer, and/or substrate etching by $BF_3$ dissociation products, which interfere with both the implant and the measurement of implant dose. Safety considerations preclude our using di-borane ($B_2H_6$) or any arsenic or phosphorous-containing gases in our laboratory at Berkeley. Characterization and control of $BF_3$ condensates and etching are described in Sec. III, and are currently one thrust of our work.

(2) The second process being developed is conformal doping of trenches for trench capacitor or trench isolation. We have demonstrated conformal doping of trenches using a high-pressure (~5 mTorr)

$BF_3$ PIII process, with the doping boundary delineated by a crude staining technique . We are refining our staining technique to delineate simultaneously a number of equiconcentration contours. We have also recently obtained theoretical and computer simulation results on the angular distribution of ions hitting the wafer.

(3) The third process being developed is the formation of a metal seed layer for selective, electroless copper plating of oxide trenches. This process is a demonstration of the triode PIII configuration (see Fig. 2c).

To address the second critical issue (Process Integration) and part of the third critical issue (Oxide Breakdown), we have developed a complete PIII processing compatibility test chip to investigate wafer charging as a cause of oxide breakdown and the use of poly-silicon as a $p+$ doping source. The test chip is a PMOS process including inverters and ring oscillators, in which PIII is used for all (two) p+ doping process steps. The complete chip has been designed, simulated and fabricated at Berkeley, and working devices (e.g., inverters) have been obtained.

To address the remainder of the third critical issue (Process Uniformity), we are using analysis, computer simulation, and experiments to model the formation of the PIII process plasma, its injection into the process chamber, and the actual implantation process itself. We have developed a model of the implantation for pulses with finite rise- and fall-times. We have developed and are using a 2D simulation code to model the injection of the source plasma into the process chamber. We have recently extended this model, as described in Sec. VII. We have characteriszed experimentally the plasma uniformity using a multidipole plasma confinement system on the process chamber in argon $CF_4$, and $BF_3$ gases over a range of pressures and ECR source powers. We have achieved a density uniformity over an 8" wafer of ±1%. We have also used optical emission spectrometry to determine the concentrations of particular atomic species in the process chamber.

A key test of uniformity is actual implanted dose. We are developing a distributed-pulser ion implant model for the dose. We have used PIII to implant 4" wafers, having an $n+$ doped surface layer with argon ions. We then determine the implant uniformity by measuring the increase in the resistivity of the layer due to the damage induced by the implanted argon ions. Our preliminary results show that implant uniformities of ±3% can regularly be achieved. Our major limitation to achieving even better implant uniformities appears to be the non-optimized (non-axisymmetric) design of the wafer holder (particularly, the wafer holder clips), and not any limitation arising from the PIII process itself. In cooperation with G. Lecouraf and W. J. Wriggins at Applied Materials, we are performing an implant uniformity study using $BF_3$ for 6" wafers. We are also using a triad of three, 4" wafers to determine implant uniformity over larger (8" and 10" diameter) areas.

The milestones are shown in Table 1. The Month 1 milestone was met ahead of schedule.

The Month 3 milestone was met ahead of schedule. A manuscript describing the excellent low leakage properties of the junctions will appear in *Applied Physics Letters*. The results are at least as good as those achievable using any other commercial process.

The Month 5 milestone and the Month 8 milestone, which is a follow-on- to the Month 5 milestone, were not met. Hence we are behind schedule on the trench sidewall doping project.

The Month 9 milestone has been met. We have designed and fabricated a PMOS test chip, and have obtained working devices.

The Month 10 milestone was met. We have demonstrated planarization of copper interconnects with good adhesion to oxide, and few structural defects.

The Month 12 milestone deals with collisional modeling of the PIII implantation process and with the two-dimensional modeling and computer simulation of plasma and implant radial profiles. At the request of Dr. W. J. Wriggins, Product Manager from Applied, we have given the work on plasma and implant uniformity a high priority during the previous quarter, and have achieved favorable results, as described in Section III. We are now confident that we have a process with adequate uniformity, as demonstrated by both experimental measurements and modeling results.

## III. DETAILED DESCRIPTION OF PROGRESS

### A. $BF_3$ Deposition and Reproducibility (C. A. Pico)

For the past year we have been struggling with reproducibility and on again/off again deposition of $BF_3$ during *p-n* junction implant fabrication. We have since determined some key factors behind our reproducibility problem. This enabled us to finally determine the parameter space of operation which leads

## Table 1

## Milestones

**Month 1**

Start characterization of 8" wafer Engineering PIII Reactor.

**Month 3**

Demonstrate low leakage current sub-100nm $p^+$n junctions with current density less than 25 nA/$cm^2$ at a reverse bias of -5V.

**Month 5**

Demonstrate trench sidewall doping uniformity to ± 50% for 7:1 aspect-ratio trenches. Junction uniformity will be measured by staining methods and spreading resistance measurements.

**Month 8**

Demonstrate electrical characteristics of doped trenches showing no surface state inversion and adequate oxide breakdown strengths using C-V and breakdown measurements.

**Month 9**

Completion of a testing integrated circuit using PIII for sub-100nm junction formation to show compatibility with conventional process flow. The testing circuit will be a ring oscillator or an inverter.

**Month 10**

Demonstrate planarization of Cu interconnects using PIII seeding for 2:1 aspect-ratio oxide trenches. Verify electromigration reliability and adequate adhesion to oxide, and examine microstructural defects using cross sectional scanning electron microscopy.

**Month 12**

Complete collisional modeling of PIII and first-order 2-D PIII model. Includes analytical model of ion energy and angular distribution along with particle-in-cell computer simulation verification, ion current versus time for realistic PIII pulse shapes, and analytical and static 2D simulation of plasma density distribution in magnetic bucket process chamber geometry and ion implant radial profiles.

**Month 12**

Analysis of Phase I process development progress. Fine tuning for process optimization.

to $BF_3$ deposition. At the same time, we determined that, instead of deposition, we could etch Si in a $BF_3$ plasma under the proper conditions.

With our ability to attain repeatable conditions, we began a systematic study to characterize the plasma properties. This included measuring ion density as a function of system parameter and correlating it with implant dose per pulse for Ar and $BF_3$.

Below, we report on our progress in $BF_3$ for implant and plasma characterization.

1. Deposition

In order to circumvent $BF_3$ deposition, various diluting gases were added to suppress the deposition. Gases tried were $H_2$, $CH_4$, Ar, and He. None were successful in suppressing $BF_3$ deposition.

Later it was found that background $H_2O$ from a previous experiment was the catalyst leading to $BF_3$ deposition. It was learned that, when $BF_3$ did not deposit, the Si substrates were etched by the $BF_3$ plasma. Having then determined that $BF_3$ deposition and Si wafer etching could be controlled, a pseudo-phase diagram consisting of $BF_3$ condensation and $BF_3$ etching of Si was determined as a function of microwave power and $BF_3$ pressure. In addition, the etch rate of Si by the $BF_3$ plasma was determined as a function of gas pressure and microwave power.

Together, these results have led to our finally achieving reproducible implants of $BF_3$ into Si. We routinely achieve implant uniformity of 3-8% across a 4" wafer. These results are not for optimal implant conditions. Hence, we anticipate achieving better uniformity in the future. Regardless, we have met the 5% uniformity bell weather mark set at the start of this project.

2. Reinterpretation of Past Data

In an earlier quarterly we reported that a logarithmic plot of the inverse sheet resistance of $BF_3$ implanted wafers as a function of the log of the implant dose resulted in a slope of $\sim 0.8$. That is to say, the inverse sheet resistance of activated $BF_3$ implanted Si is proportional to (dose) to the power 0.8. It was expected to be proportional to the 1.0 power. This discrepancy was used to show that we had deposition problems. It has been recently learned that conventional ion beam implanters find the inverse sheet resistance to be proportional to (dose) to the 0.75 power. We now believe that our wafer response to implanted dose is as expected and shows that PIII is a reliable method for implanting boron in Si.

3. Plasma Characterization

Ion density measurements were done for both Ar and $BF_3$ as a function of microwave input power and gas pressure. We find that the Ar ion density rises monotonically with pressure until it peaks near 15 to 20 mTorr. Thereafter it decreases relatively slowly. For $BF_3$, the ion density peaks at $\sim 2$ mTorr and falls quickly. No attempt has yet been made to explain the different behaviors of these two gases. It has been found that the ion density rises nearly linearly with input microwave power for each gas.

Under plasma immersion ion implantation processing, the dose per pulse of Ar was measured as a function of microwave input power, gas pressure, and implant voltage. Aron was chosen because of its ideal behavior and monatomic properties. The dose per pulse was found to rise linearly with microwave power for -5kV pulses. When pressure was varied, the dose per pulse rose nearly proportional to pressure for pressures between 0.25 mTorr and 1 mTorr. Above 1 mTorr the dose per pulse remained nearly constant. We do not understand why the dose per pulse does not mirror the ion density behavior at this time. The dose per pulse was measured as a function of pulse duration for pulse times of 0.4 to 2.4 μsec. A plot of these results appears linear (dose per pulse versus pulse width) regardless of whether it is plotted versus pulse width to the 1, 1/2, or 1/3 power. However, the most reasonable fit is to a 1/2 power. In this way, the y intercept is at a value that is read when pulsing is done but not connected to the sample holder. Finally, the dose per pulse was measured as a function of pulse voltage. The dose per pulse rose linearly with increasing voltage up to 7 kV. Above that the pulse shape became irregular due to the impedence mismatch of the pulse network and the plasma impedence. This resulted in a significant reflected component of the input voltage pulse. Pulse echos and pulse ringing were observed. This caused the dose per pulse to become sublinear with increasing pulse voltage.

Similar experiments are now underway for $BF_3$ gas. Initial results show that the dose per pulse follows the ion density, unlike the Ar counterpart.

**B. Optical Emission Spectrometry and Actinometry Studies** (I-Chun Liu and R. A. Stewart)

An optical emission study of various processing plasmas including $BF_3$, $SF_6$, and $CF_4$ has been initiated. The emission spectrum is measured ex-situ with a spectrometer that is controlled by a PC to sweep through a specified range of optical frequencies at a particular sampling rate. The intensity of the sampled optical signal is amplified by a photomultiplier tube and recorded by the PC.

Actinometry provides a quantitative measure of the density of a particular atomic species in a plasma. Consider the measurement of F atom concentration in $BF_3$. Actinometry is performed by introducing a small, known amount of a nonreactive trace gas such as Ar into the $BF_3$ plasma. The *intensity* of a known argon line is measured and the concentration of the F atoms can then be determined from the partial pressure of Ar and the relative cross sections for particular excitations of Ar and F.

The purpose of this study is to determine what atomic and (hence) ionized species exist in various plasmas over a wide range of processing conditions, and when possible to quantify the concentrations of these species. A knowledge of the species of ions that exist in the plasma is important to PIII for several reasons. One reason is for the estimation of the range of implanted ions, a quantity that depends on the ion mass. Another reason is the dependence of ion mass on collisionality in the sheath. For example, a directional implant requires $s/\lambda \ll 1$, where $\lambda$ is the mean free path of a particular ionic species and $s$ is the sheath width.

Knowledge of the concentration of a particular atomic species is important for relating the concentration to the rate of a particular chemical or physical process. We have found that $BF_3$ acts as an etchant for certain process conditions. To understand the mechanism causing the etching, we intend to first measure the F atom concentration with actinometry and then see whether it correlates well to the etch rate.

Our initial efforts have consisted of setting up the experiment and determining whether any previous optical studies of $BF_3$ have been made. Figure 3 shows an emission spectrum of $BF_3$ that we recently measured. Thus far we have not found any reported optical studies of $BF_3$ in the literature. Our plan of attack is thus to first perform actinometry using $CF_4$ /Ar which will allow for comparison of widely reported results. When we are confident that our technique is correct we will proceed to study $BF_3$ in detail.

### C. A Distributed Pulser-Ion Implant Model (R. A. Stewart)

A model was developed previously for PIII that predicts the temporal variation in implanted current $i(t)$, as well as the energy distribution and total dose/pulse for an applied rectangular pulse [1]. The effect

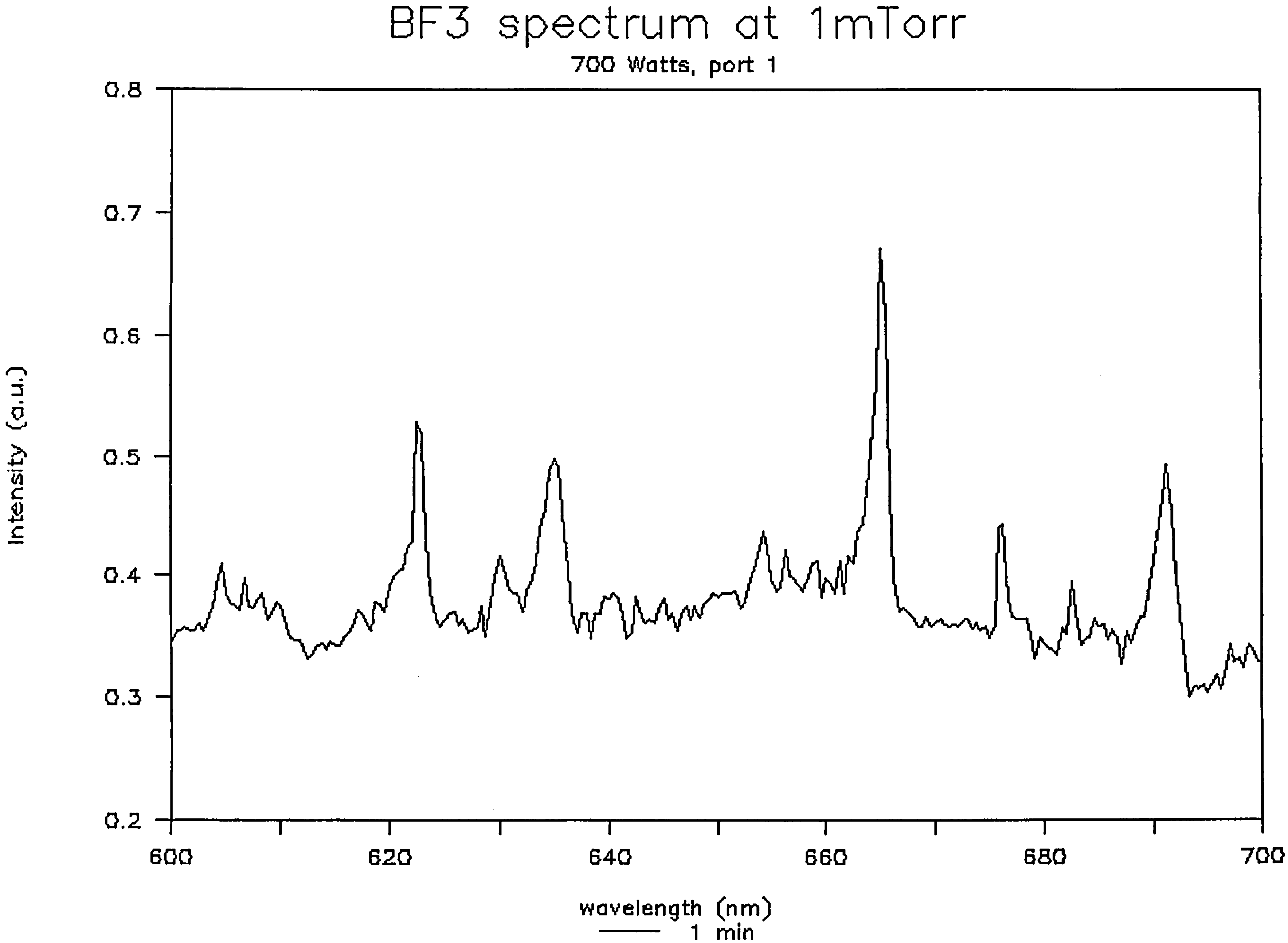



Fig. 3. Partial spectrum of $BF_3$ plasma measured by OES at 700 w microwave power and a pressure of 1 mTorr.

of finite rise and fall times of short ( ~ 1 μs) pulses has also been predicted with both an analytical model and a fluid simulation program [9]. All of the above models neglect some potentially important practical considerations. Foremost of these considerations (at least for some plasma conditions) is impedance mismatch between the pulsed voltage source and the plasma load. Some amount of mismatch is inevitable since the impedance of the non-linear plasma load varies significantly during the application of the voltage pulse.

We have developed a model that treats our thyratron based pulse-line pulser as an ideal voltage source followed by a length of transmission line as shown in Fig. 4. The low impedance voltage source models the thyratron (or any similar tube), assuming that the thyratron does not discharge a significant portion of its voltage during each pulse. The length of transmission line models the pulse-line which is fully charged up before the plasma load is switched into the circuit at the beginning of each cycle. A distributed transmission model is required since the transit time across the line for a pulse can be a significant fraction of the total pulse time. Generally, the transit time across a pulse line is given by $\tau = N\sqrt{LC}$, where $L$ and $C$ are the characteric inductance and capacitance for a section of the line, and $N$ is the number of sections.

In Fig. 4, a resistor R is in parallel with the plasma load, $Z_{plasma}$. The purpose of this resistor, which we include in our experimental setup, is to minimize the sensitivity of the total load seen by the source to the variations in the plasma impedance. This is achieved by choosing R such that $R \gg Z_{plasma}$.

The solution to the model described here will be performed in the time-domain, following a standard technique found in elementary electromagnetics texts, but generalized to account for the non-linear, time-varying plasma load. This complication requires the solution for the load voltage, $v_l$, and load current $i_l$ to be found through solving a non-linear equation for each increment dt in time. The plasma is modeled as a resistive load with resistance $v_l/i_l$, where $i_l = kAv_l^{3/2}/s^2$, corresponding to a quasi-static Child law. Current continuity at the sheath edge requires $i_l = enA ds/dt$, hence equating the two current expressions leads to a differential equation for the sheath width, s(t). The differential equation is integrated for an increment dt to obtain the new sheath width at the new time.

The completion of this model should provide helpful information about the effect of impedance mismatch in our system. In addition, insights may be gained that will aid in the future design of a new pulser.

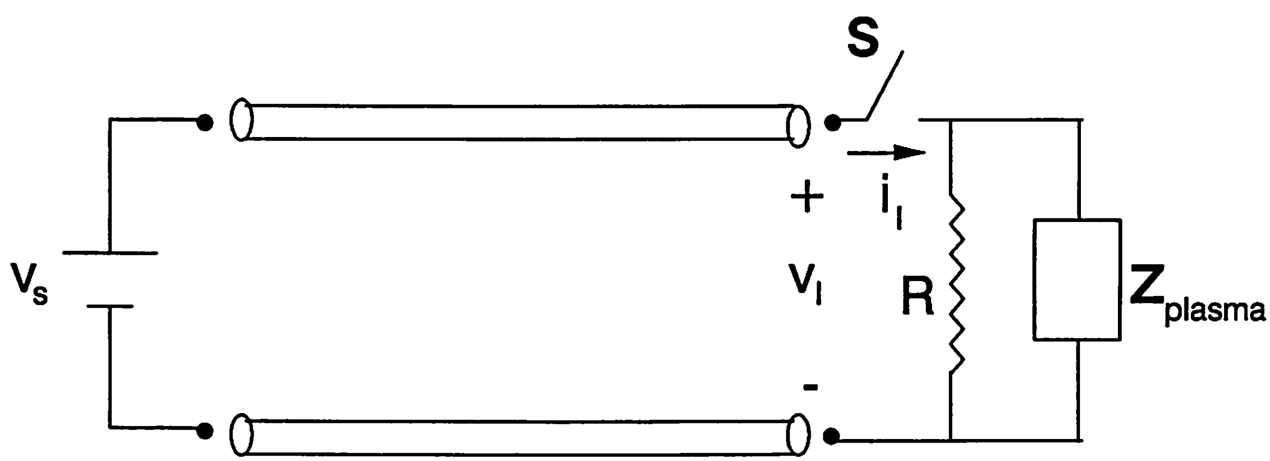



Fig. 4. Distributed circuit model of pulser and plasma load for PIII.

### D. Trench Sidewall Doping (C. Yu)

We have been able to reproducibly produce a contour corresponding to $6 \times 10^{16} cm^{-3}$ boron on high dose high energy B implanted (blanket) samples. We are acquiring more samples with different energy to verify the stain. The difficulty lies in the fact that the contours need to be separated by ~ 1 μm to be observable by our SEM, and high dose ($\sim 1 \times 10^{16} cm^{-2}$) samples at these energies (>1 MeV) are hard to come by. We have corresponded with Eaton Corporation to have them supply some samples for us to use.

A first set of four trench samples have been implanted. The aspect ratios of the trenches are 1:1, 1:5, 1:10. They have been implanted at 5 mTorr with 0, 2 kV, 5 kV, and 10 kV bias at a nominal dose of $1 \times 10^{15} cm^{-2}$. We expect the actual dose to be less than this by up to a factor of 2 or 3 due to etching effects. We plan to first reproduce our initial results [5] by *pn* junction staining of these samples. We intend to verify whether previous reports of conformal doping are actually due to implanted dopants or deposited and diffused impurities. Then we plan to determine the effects of varying pressure, substrate bias, and aspect ratio on conformal doping.

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