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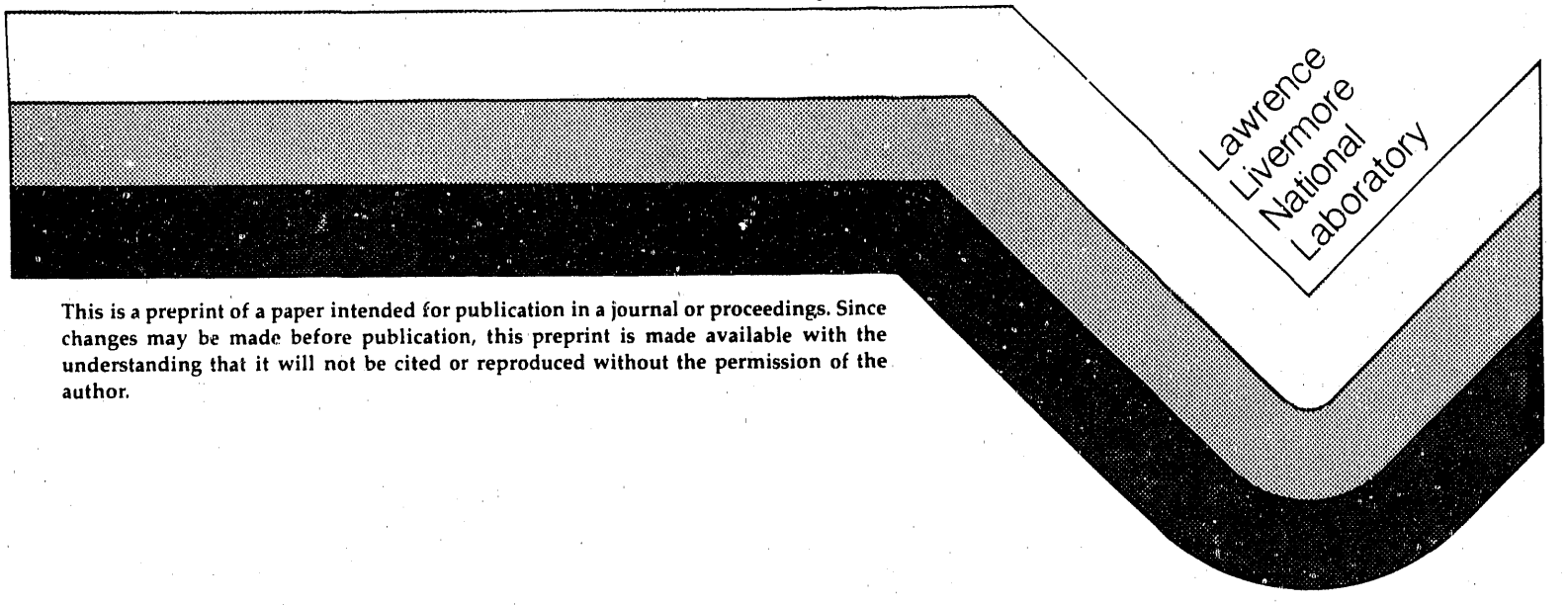

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A High Ternperature, Plasma-Assisted Chemical Vapor Deposition System*

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We have designed and built a high-temperature, plasma-assisted, chemical vapor deposition system to deposit multilayer optical coatings of SiO_2 and doped-SiO_2 on flat substrates. The coater concept and design is an outgrowth of our recent work with Schott Glaswerke demonstrating the use of plasma assisted CVD to prepare very high damage threshold optical coatings. (That work is reported in a companion paper at this Symposium).

The coater is designed to deposit up to several thousand alternating quarterwave layers of SiO_2 and doped SiO_2 on SiO_2 substrates at deposition rates up to several microns per minute. The substrate is resistively heated to about 1000°C during the deposition phase of the process. The plasma is driven by a 13.56 MHz RF unit capable of producing power densities of up to 140 W cm^{-3} in the reaction zone. The coater is designed to be adaptable to microwave generated plasmas, as well as RF. Reactant gas flow rates of up to 10 slm can be achieved at a 10 torr operating pressure. Reactants consist of O_2, $SiCl_4$ and a volatile halogenated dopant (e.g. $GeCl_4$ or CCl_2F_2). These gases react in the plasma volume producing SiO_2 with dopant concentrations (e.g. GeO_2) of up to a few percent. A variable dopant concentration is used to produce index differences (nominally about 0.01) between adjacent optical layers.

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Some of the major technical problems associated with the design and construction of this coater are discussed. These include flow distribution and its effect on deposition uniformity, substrate heater design and operation, choice of RF vs. microwave driven plasma and diagnostics design and placement. To address many of these issues, we have relied heavily on numerical and experimental modeling of the fluid flow, reaction kinetics, and heat transfer within the coater. Furthermore, preliminary experiments carried out on prototype designs were used to guide our development efforts.

1.0 Introduction

High reflectivity (HR) coatings for the next generation laser fusion driver will require laser damage thresholds not less than 40 J/cm^2 at 1.06 μ wavelength[1]. Considering that bulk fused silica possesses a high laser damage threshold and is made by high temperature chemical vapor deposition, an effort has been initiated to apply a high temperature deposition method to the creation of a multilayer HR reflector. This so-called "kilolayer" concept, and its success in a circular tube geometry, is described more fully in another paper in this publication[2]. The key processing issue now is to translate this process to one suitable for flat substrates.

The task requires separation into four roughly concurrent efforts; preliminary experimentation with the coating process, examination of heat and mass transport issues, investigation of fundamental plasma characteristics and hardware production and evaluation. With respect to mass transport, Wilcock et al.[3] and Law and Masliyah [4] have successfully used naphthalene sublimation in the analysis of mass transport uniformity. Since, mathematically, naphthalene sublimation (removal) is equivalent to deposition in terms of uniformity, we constructed a test bed to model the mass transport in the proposed reaction chamber geometry. We wished to determine whether the proposed geometry would lead to a uniform deposition and what the critical parameters were that would assure uniform mass transport.

With respect to plasma characteristics, we have demonstrated deposition of up to ≈5000 quarter wave layers inside a 3.0 cm diameter tube[2] using 2.45 GHz radiation to excite the plasma. However, the ability to scale plasma applicators at 2.45 GHz uniformly for large flat substrates, the cost of such scale-up and possible use of other radiation frequencies remain unresolved issues. As an example of frequency dependence, two literature studies concerning a photoresist stripping process can be used to compare RF versus microwave plasmas. The papers by Dzioba et al.[5] and Degenkolb et al.[6,7], describe experimental systems that are nearly identical, with similar reaction volumes, pressures, and oxygen flow rates. However, the study utilizing 2.45 GHz exhibited a more highly-excited oxygen plasma environment, inferred from the optical emission spectrum, and an order-of-magnitude increase in the stripping rate compared to the study which used 13.56 MHz radiation. The extent to which differences such as this would affect our CVD coating apparatus is unknown at this time, but could have a large impact in terms of hardware development and coating performance, particularly laser damage resistance. We have constructed a plasma test bed to investigate the differences between RF and microwave plasmas and to refine plasma diagnostic techniques.

Among the diagnostic techniques being considered for monitoring the coating environment are residual gas analysis for mass balance and impurity monitoring and determination of the electron density (n_e) and electron temperature (T_e) [8] with a Langmuir probe.

2.0 Experimental

Preliminary deposition studies were carried out in a horizontal silica tube reactor, shown schematically in figure 1. The tube was 7.62 cm in diameter (expanded to 12 cm in the reaction zone) and approximately 61 cm long. The tube was contained in a radiantly heated furnace with the heating zone approximately 30 cm long. A thimble containing a fused silica substrate, a graphite susceptor and a boron nitride insulator was inserted into the hot zone of the reaction tube. The graphite served as the absorber in the radiant furnace and as the driven electrode for the application of RF at 13.56 MHz. Gas flows of oxygen, silicon tetrachloride and germanium tetrachloride were established using mass flow controllers. Pressures were monitored with Baratron gauges and controlled by a butterfly valve controller. Typical operating parameter ranges are given in table I.

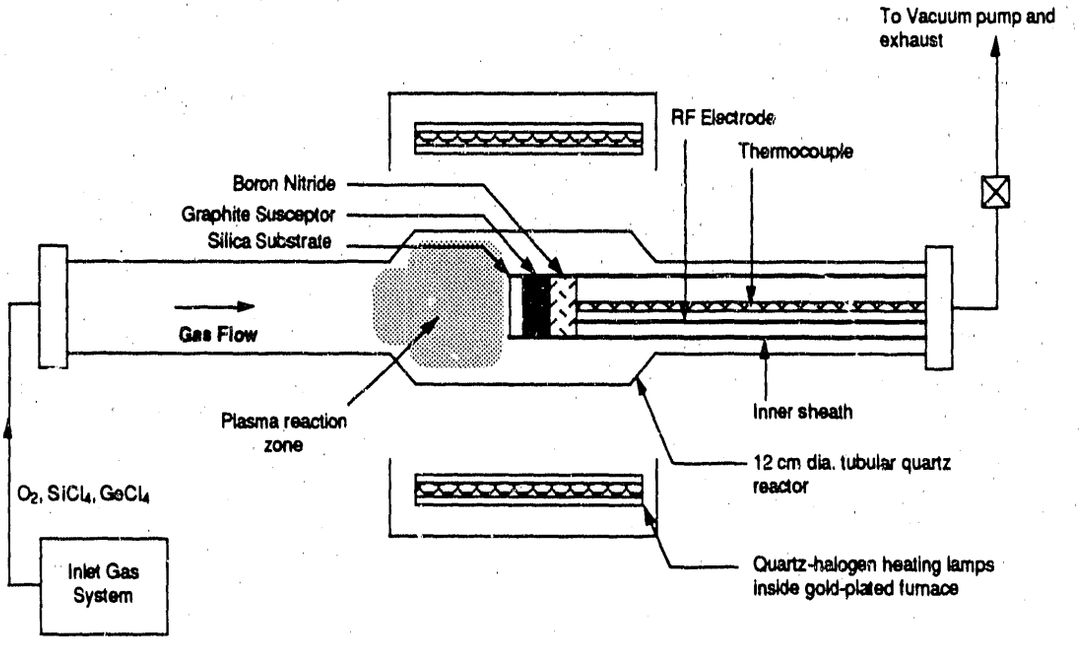

Figure 1. Schematic of radiantly heated plasma CVD reactor.

Mass transfer experiments were performed in a 1:1 scale model of the proposed coater (fig. 2) with a reaction volume of approximately 800 cm^3 [9]. The substrate-to-injection plate spacing could be adjusted with appropriately sized spacers. A Duo Seal 1398 vacuum pump allowed pumping rates as high as 5 slm through the reactor at reaction chamber pressures from 200 to 2000 Pa. A gas distribution plate consisting of a square array of 237 holes of 0.0635 cm diameter on 1 cm centers or 72 holes of 0.229 cm diameter on 1 cm centers was studied. Substrates were prepared by hot pressing naphthalene at approximately 78°C and 68 MPa pressure into aluminum molds. The substrates were weighed before and after the sublimation experiment to determine the mass of naphthalene that sublimed and from this an average rate of removal was calculated. The substrate surface was also profiled before and after a run on a Moore profilometer (resolution 3 X 10^{-4} cm) to determine uniformity of sublimation.

Table 1. Summary of typical operating conditions used in our preliminary radiant heating plasma CVD experiments

Pressure	0.3-3.0 torr
Flow rate oxygen	100-500 sccm
Flow rate $SiCl_4$	20-90 sccm
Flow rate $GeCl_4$	0-10 sccm
RF power (CW exp.)	300 Watts
RF power (peak)	57-94 Watts
RF power (average)	8.5-15 Watts
Pulse width	10-15 X 10^{-3} sec
Pulse Repetition Frequency	10-30 Hz
Temperature	1050-1250°C
Reaction time	60 min.
Number of experimental runs	16

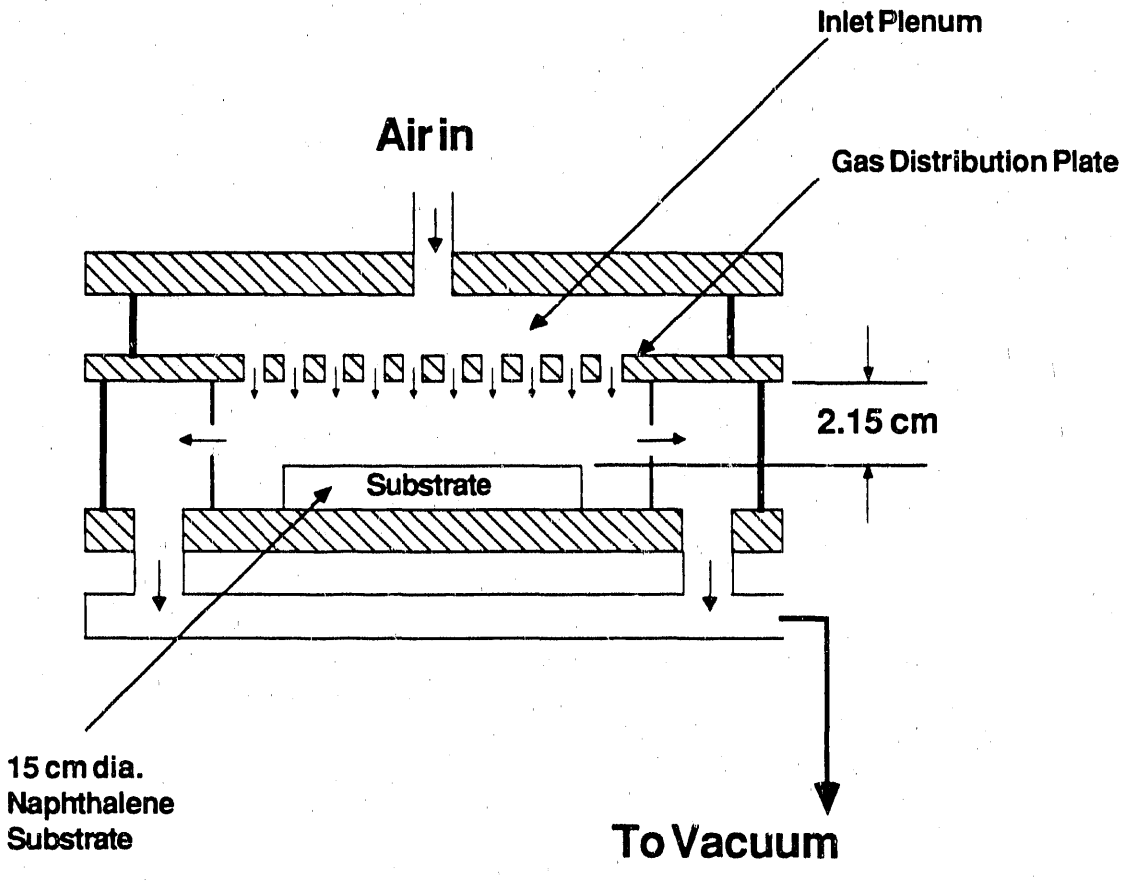

Figure 2. Schematic of the mass-transfer test system

Initial experiments on plasma characteristics were carried out in a silica reactor. Langmuir probe experiments were done in a horizontal fused silica tube of 15 cm diameter in the reaction zone and an overall length of 90 cm, as shown in figure 3. The plasma was excited by RF at 13.56 MHz using 2.5 cm wide strips of metal as electrodes that were attached to the outside of the reactor tube in a clam-shell arrangement. The Langmuir double probe was constructed as described by Chen [10] and placed as close to the electrodes as possible and extended into the plasma region approximately 5 cm. Presently, diagnostics experiments are conducted in a full scale mock-up of the proposed PCVD coater geometry as shown in figure 4, with a diameter of 15 cm and a height adjustable from 1 to 7 cm. The plasma is excited by either a parallel plate RF electrode arrangement, with the driven electrode at the bottom of the chamber, or with a waveguide applicator for 2.45 GHz radiation. A residual gas analysis system using an Inficon Quadrex 100 Residual Gas Analyzer (RGA) was attached to the exhaust port of the test chamber.

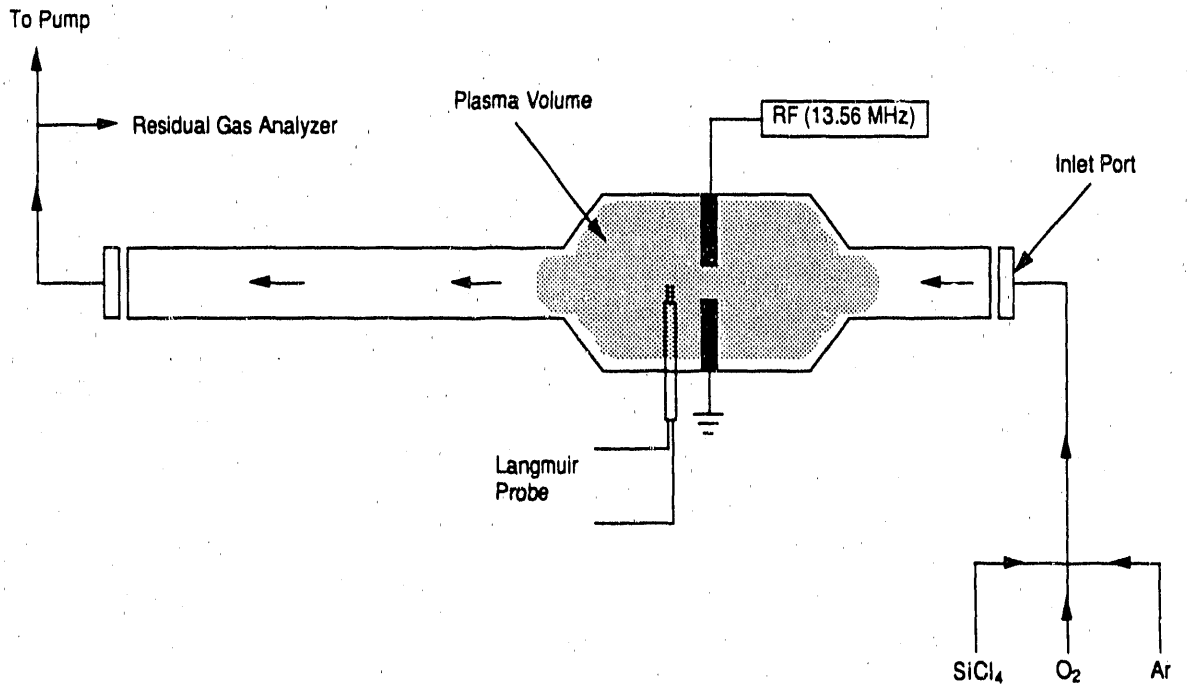

Figure 3. Schematic of tubular plasma test bed

3.0 Results and Discussion

3.1 Preliminary Deposition Experiments

Preliminary deposition experiments using 13.56 MHz RF to drive the reactive plasma in the horizontal, radiantly heated furnace pointed out several significant problem areas. First, the substrate temperature was difficult to determine. The thermocouple monitor could only read the back of the susceptor and was influenced by the driving RF electric field. Second, the deposited layers were uneven and contained particulates. The existence of cold walls in contact with the process caused generation of particulate silica, which found its way onto the growing film. Also, there was considerable leakage of the plasma into undesirable areas of the reactor, such as directly behind the susceptor and along the walls of the thimble. This leakage significantly reduced the plasma power density available in the reaction volume. In addition, the total RF power available was only 1 kW.

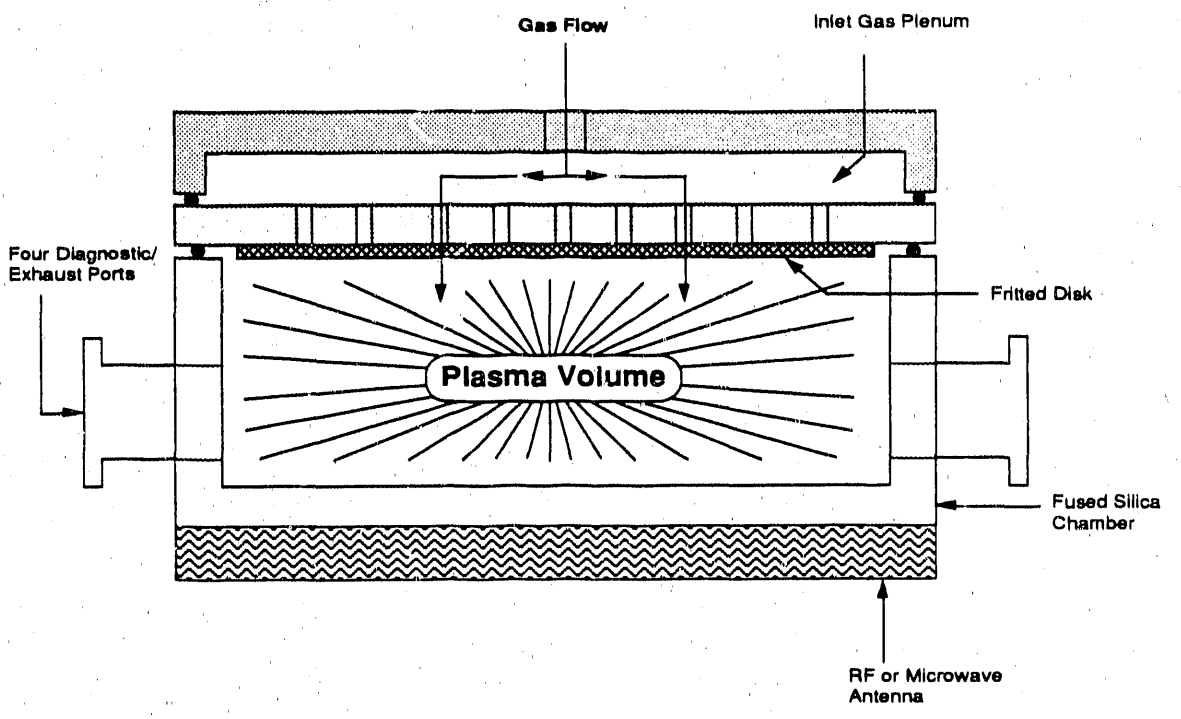

Figure 4. Schematic of parallel-plate plasma test bed.

3.2 Mass Transport

Figure 5 shows the surface profile of a naphthalene disk before and after a sublimation run where the disk was exposed to 2 slm flow for 5 hours to remove approximately 50% of the naphthalene material. The increased surface roughness following sublimation is attributed to the crystalline nature of the naphthalene causing preferential removal based on grain orientation. The mass removal rate was greater at the outer edge of the disk than at the center due to edge effects associated with a finite disk size. An analysis of the radial removal rate versus total amount of material removed, neglecting the outer 1.5 cm edge, shows the uniformity to be ±5%. Figure 6 compares the dimensionless mass transfer rate versus Reynolds number (Re) for experiment with that predicted by stagnation flow theory assuming uniform gas injection through the top plate. Here we define the Reynolds number as,

$$R_e = \frac{HV}{\eta} \tag{1}$$

where H is the distance separating the gas injection plate and substrate (cm), V is the superficial axial injection velocity (cm/sec) and η is the kinematic gas viscosity (cm^2/sec). The mass transfer rate is made dimensionless by,

$$y' = \left(\frac{W}{tA}\right)\left(\frac{P}{P_{sat}}\right)\left(\frac{H}{\mathcal{D}\rho M}\right) \tag{2}$$

where:

W = Mass loss (gm)
t = time (s)
A = Naphthalene surface area (cm^2)
P = Pressure (torr)
P_{sat} = Naphthalene vapor pressure (torr)
H = Reactor height (cm)
$\mathcal{D}$ = Naphthalene diffusivity in air (cm^2/s)
ρ = Gas density (g/cm^3)
M = Molecular weight naphthalene (gm)

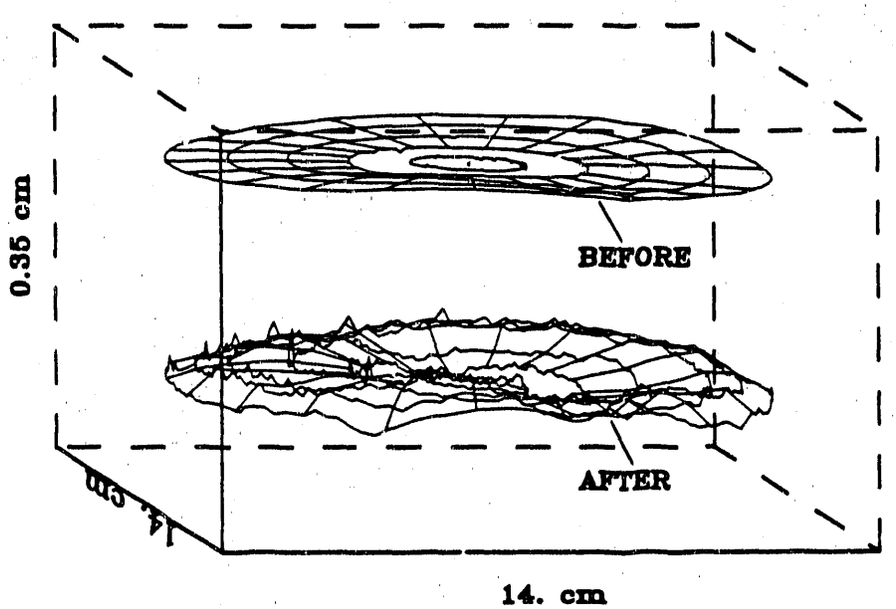

Figure 5. Plot of the naphthalene disk surface contour before and after evaporation.

For low Reynolds numbers, the mass transfer rate agrees with the stagnation flow theory [11] and the removal of naphthalene is uniform. Above a Reynolds number of about 3 the mass removal rate increases sharply due to jet impingement as shown in figure 7. Here, jet impingement has caused locally high mass removal directly under the inlet orifices, causing a dimpling of the naphthalene surface. These studies have defined flow rate ranges, for a given reactor and gas distribution geometry, that lead to radially uniform mass transfer in the reactor; further details of this work are given in ref. 9.

3.3 Plasma Characterization

Figure 8 shows some preliminary data taken from Residual Gas Analysis of a mixture of O_2 and $SiCl_4$ exposed to an RF plasma. A very low baseline of oxygen gas is compared with a mixture of O_2 and $SiCl_4$ without plasma, which reveals the fragmentation pattern of silicon tetrachloride. Upon striking the plasma, the fragmentation pattern indicates a dramatic increase in the signal at mass 70, attributed to Cl_2

parent ion, with corresponding decreases in the masses of the lower silicon halides. Residual gas analysis will be useful in characterizing the stable volatile reaction products as well as monitoring the presence of impurities in the gas streams. The major improvement here will be the calibration of the instrument to provide a mass balance for the reactants and products and to increase the mass range such that all fragments of $SiCl_4$ and dopants can be monitored routinely.

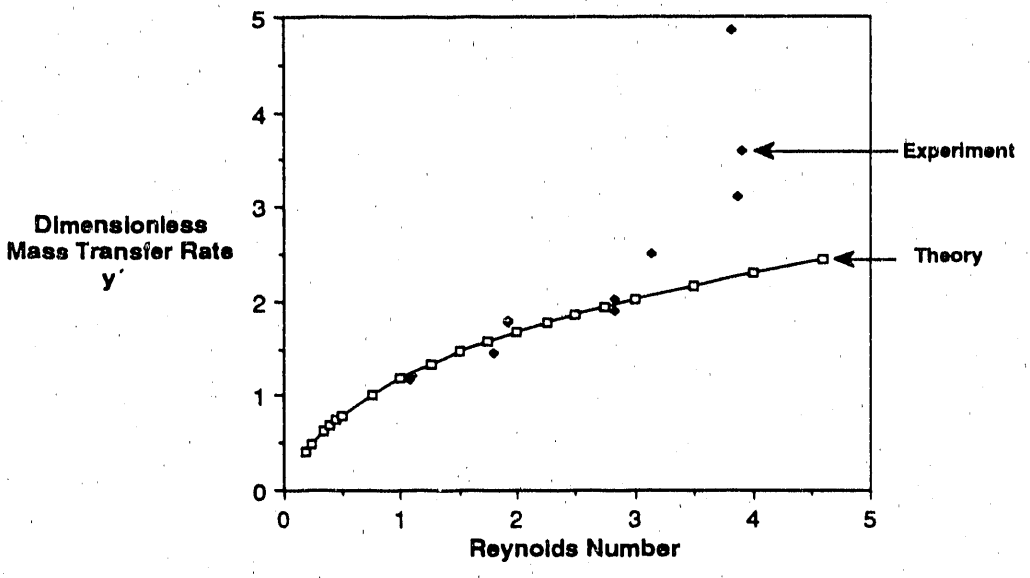

Figure 6. Dimensionless mass transfer rate versus Reynolds number

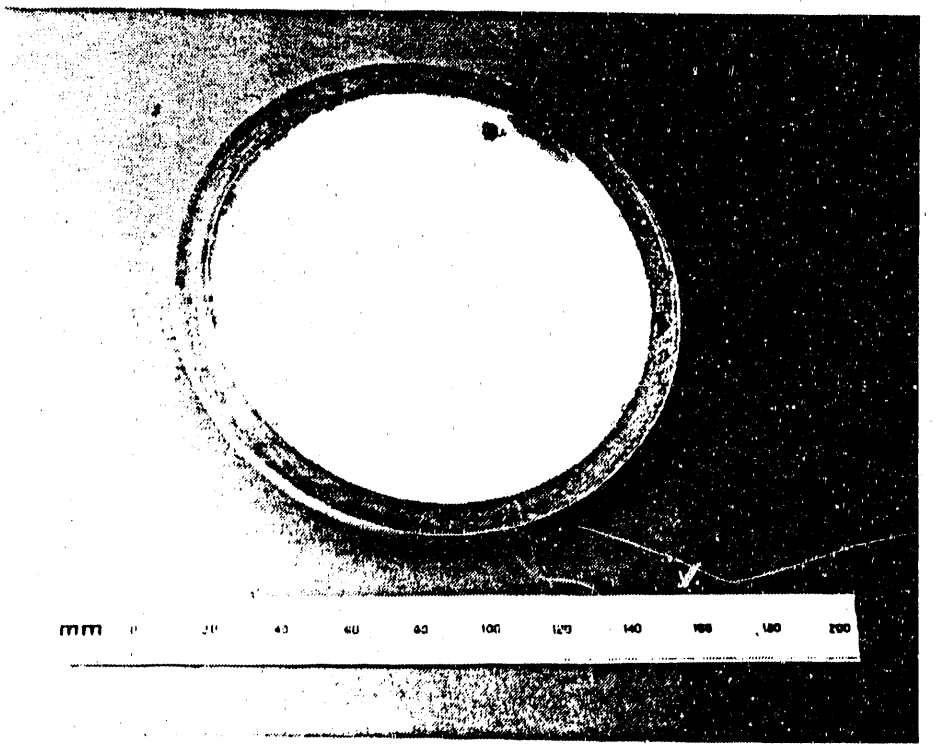

Figure 7. Photo of jet impingement on a naphthalene disk.

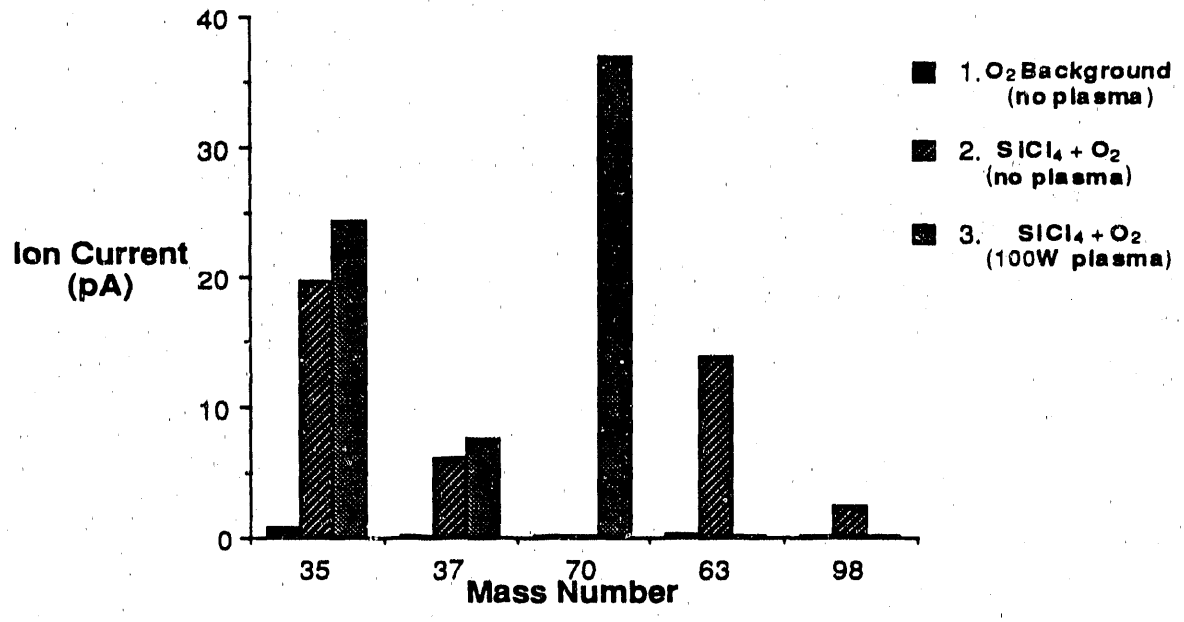

Figure 8. Residual Gas Analysis of coater effluent with and without plasma.

Current-voltage data were taken with a Langmuir double probe in oxygen at 1 torr pressure at several 13.56 MHz RF power levels. Figure 9 shows that with increasing RF power, the electron temperature increases from about 4 eV at 50 watts to approximately 6 eV at 150 watts. Similarly, the electron density increases from about 6.0 X 10^9 cm^{-3} at 50 watts to 1.3 X 10^{10} cm^{-3} at 150 watts. These data are in qualitative agreement with data from Heidenreich et al. [12] investigating oxygen microwave afterglows and Yamagishi et al. [13] investigating air-helium plasmas excited by several methods. The key developments in Langmuir probe measurements will be to extend their operation at high power densities and in the electronegative plasmas anticipated in the coater environment.

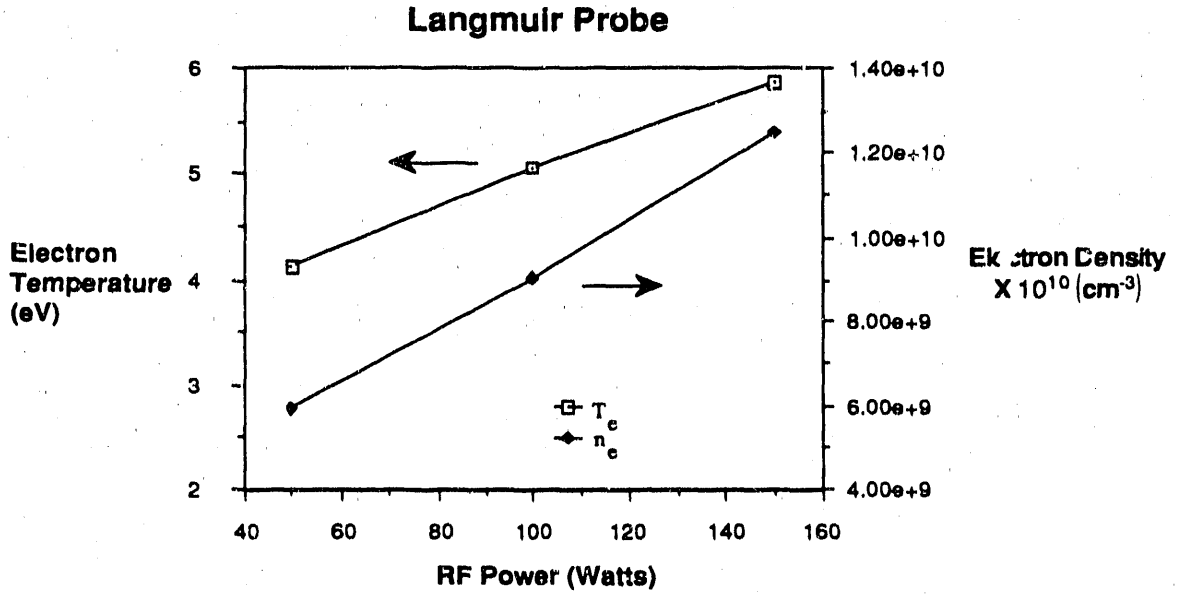

Figure 9. Plot of electron temperature and electron density versus RF power for oxygen gas in a 1 Torr pressure plasma as determined by Langmuir probe.

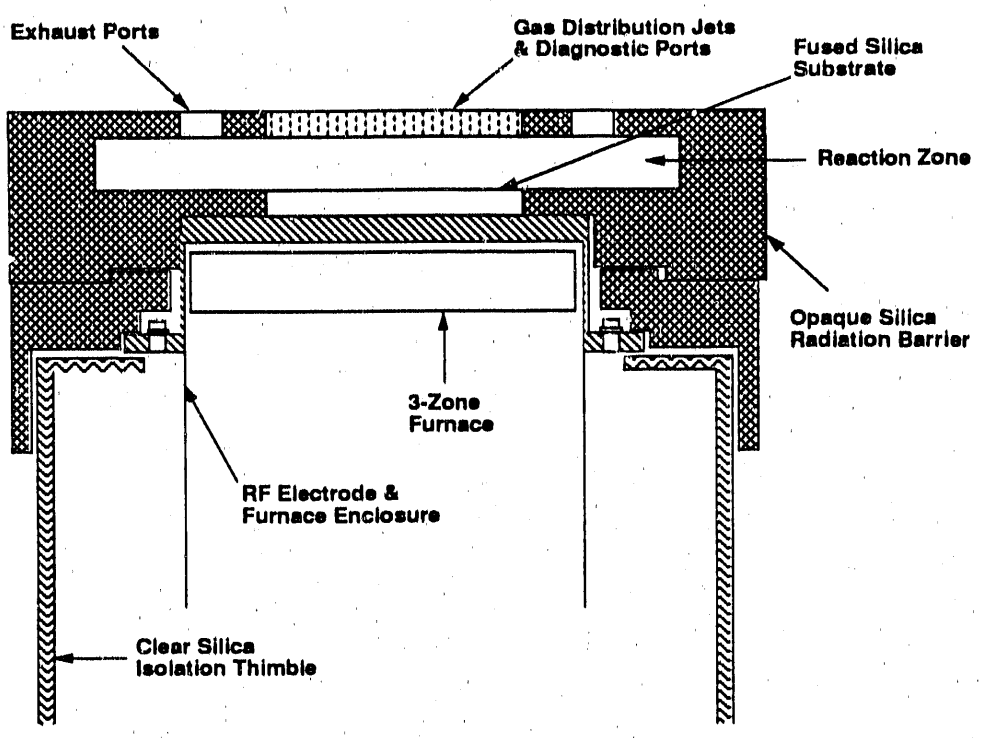

Figure 10. Schematic drawing of PCVD coater reaction chamber.

3.4 Hardware Development

Building on the results of the preliminary investigations, a coating system was specified by LLNL and designed and built by Prototech Research Inc. A schematic of the coating chamber is shown in figure 10. It is capable of handling fused silica substrates up to 15 cm in diameter and 1 cm thick. The furnace is a 3-zone back-heating system designed to heat the substrates to about 1000°C. Some details regarding the reaction environment are described in table 2. The "hot wall" reactor is formed by using closed-cell porous silica glass to enclose the reaction volume and absorb radiant energy from the furnace. Gas is injected through a top plate via an array of gas injection ports and exhausted out the top at the periphery of the substrate. The containment vessel for the furnace acts as an electrode for a 24 kW 13.56 MHz RF generator. Plasma confinement is achieved by isolating the walls of the electrode with a silica thimble which is evacuated to less than 10^{-4} torr. The absorbing silica provides dielectric insulation to suppress plasma breakdown outside of the reaction chamber. The coating apparatus is located in a clean box to prevent particulate contamination. This coater is designed to be as flexible as possible to allow for design changes to meet coating process demands.

Table 2. Summary of designed operating characteristics of the high temperature, plasma CVD coating system

Substrate Size	15 cm dia. X 1 cm thick
Oxygen Flow Rate	0-8 slm
$SiCl_4$ Flow Rate	0-2 slm
$GeCl_4$ Flow Rate	0-500 sccm
RF Power	24 kW maximum
Substrate Temperature	1000°C nominal, 1200°C max.

4.0 Conclusions

We have recently shown that very high damage threshold dielectric coatings can be made using plasma CVD at high temperatures (≈1000°C) [2]. In this paper we discussed our efforts at scaling this process to large, flat substrates (> 10 to 50 cm diameter). There are four main technical issues that must be solved to successfully implement this coating process:

1. Uniform deposition over a large area (± 1-5%)
2. High deposition rates (1-4 $\mu m\ min^{-1}$)
3. Uniform substrate heating at temperatures up to about 1000°C
4. Minimal dopant diffusion

To address these technical issues we have designed, built and operated a series of test bed reactors to look at mass transport, plasma chemistry, and substrate heating issues. We have identified a flow regime that provides uniform radial mass transfer and hence should give uniform deposition. In this work we have used mathematical models to guide and interpret the experiments. In addition, work is in progress to look at the effects of RF versus microwave driven plasmas on the deposition process and we have begun to identify and refine plasma characterization techniques. Based on these results we have built a large coating system designed to coat substrates up to about 15 cm in diameter with several thousand quarter-wave layers of alternating doped and undoped SiO_2. Details of the coater design specifications have been formulated and given. The system is expected to be fully operational by mid-1990.

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