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Atomic Layer Epitaxy Group IV Materials: Surface Processes, Thin Films, Devices and Their Characterization

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13. ABSTRACT (Maximum 200 words)
Research concerned with the atomic layer epitaxy (ALE) of silicon carbide (SiC), diamond (c) and cerium dioxide (CeO_2) has been carried out within this reporting period. Equipment for the deposition of each of these materials, as well as experimental procedures for the conduct of the studies are in various stages of design, development and employment. The initial design of the SiC ALE deposition equipment has been tested with the growth of Si on Si(100) using dichlorosilane or disilane coupled with the use of atomic hydrogen produced via cracking of molecular hydrogen over a hot tungsten filament. Microbeam analysis revealed epitaxial single crystal films were obtained above a sample temperature of 400°C. The equipment for the deposition of C from C_2H_4 has also been installed. To achieve the ALE of C, the atomic arrangement during the initial nucleation step has received primary consideration. To achieve two-dimensional growth, organic interlayers will be deposited on the substrate followed by diamond growth. Initial results using linolenic acid as the interlayer and subsequent diamond deposition are encouraging. A system for epitaxial growth of CeO_2 has been designed and is under construction. Operation in early 1992 is anticipated.

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Table of Contents

I.	**Introduction**	1
	References	2
II.	**Atomic Layer Epitaxy of Silicon Carbide**	4
	A. Introduction	4
	B. Experimental Procedure	4
	1. ALE Chemistry for the Deposition of SiC	4
	2. Deposition System	5
	3. Substrate processing	5
	Substrate preparation and loading	5
	Plasma cleaning of the substrates	6
	Film Growth	6
	4. Film Analysis	6
	C. Results	6
	D. Discussion	8
	E. Conclusions	8
	F. Future Research Plans/Goals	9
	G. References	9
III.	**Adsorption and Chemical Reaction Kinetics in Atomic Layer Epitaxy of Silicon Carbide**	10
	A. Introduction	10
	B. Experimental Procedure	10
	1. Sample preparation	10
	2. Equipment design and employment	10
	3. The choice of gases for the deposition of the Si component of SiC	14
	C. Results	14
	D. Discussion	17
	E. Conclusions	18
	F. Future Research Plans/Goals	19
	G. References	19
IV.	**Organic Interlayers for Atomic Layer Nucleation**	20
	A. Introduction	20
	B. Experimental Procedure	20
	1. Diamond Growth	20
	2. Analysis	20
	C. Results	22
	D. Discussion	23
	E. Conclusions	24
	F. Future Research Plans/Goals	24
V.	**Epitaxial Growth of CeO_2 on Si**	25
	A. Introduction	25
	B. Experimental Procedure	25
	1. Thin film deposition	25
	2. Characterization of the thin films	25
	C. Results	25
	D. Discussion	26
	E. Conclusions	27
	F. Future Research Plans/Goals	27
	G. References	27

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I. Introduction

Atomic layer epitaxy (ALE) is the sequential chemisorption of one or more elemental species or complexes within a time period or chemical environment in which only one monolayer of each species is chemisorbed on the surface of the growing film in each period of the sequence. The excess of a given reactant which is in the gas phase or only physisorbed is purged from the substrate surface region before this surface is exposed to a subsequent reactant. This latter reactant chemisorbs and undergoes reaction with the first reactant on the substrate surface resulting in the formation of a solid film. There are essentially two types of ALE which, for convenience, shall be called Type I and Type II.

In its early development in Finland, the Type I growth scenario frequently involved the deposition of more than one monolayer of the given species. However, at that time, ALE was considered possible only in those materials wherein the bond energies between like metal species and like nonmetal species were each less than that of the metal-nonmetal combination. Thus, even if multiple monolayers of a given element were produced, the material in excess of one monolayer could be sublimed by increasing the temperature and/or waiting for a sufficient period of time under vacuum. Under these chemical constraints, materials such as GaAs were initially thought to be improbable since the Ga-Ga bond strength exceeds that of the GaAs bond strength. However, the self-limiting layer-by-layer deposition of this material proved to be an early example of type II ALE wherein the trimethylgallium (TMG) chemisorbed to the growing surface and effectively prevented additional adsorption of the incoming metalorganic molecules. The introduction of As, however caused an exchange with the chemisorbed TMG such that a gaseous side product was removed from the growing surface. Two alternating molecular species are also frequently used such that chemisorption of each species occurs sequentially and is accompanied by extraction, abstraction and exchange reactions to produce self-limiting layer-by-layer growth of an element, solid solution or a compound.

The type II approach has been used primarily for growth of II-VI compounds [1-13]; however, recent studies have shown that it is also applicable for oxides [14-18], nitrides [19], III-V GaAs-based semiconductors [20-33] and silicon [34-36]. The advantages of ALE include monolayer thickness control, growth of abrupt interfaces, growth of uniform and graded solid solutions with controlled composition, reduction in macroscopic defects and uniform coverage over large areas. A commercial application which makes use of the last attribute is large area electroluminescent displays produced from II-VI materials. Two comprehensive reviews [37,6], one limited overview [38] and a book [39] devoted entirely to the subject of ALE have recently been published.

The materials of concern in this program include silicon carbide (SiC), diamond (c) and cerium dioxide (CeO_2). Equipment for the ALE deposition of each of these materials, as well as the experimental procedures for the conduct of these studies are in various stages of design,

development and employment. The following sections introduce each topic, detail the experimental approaches, report the results to date and provide a discussion and a conclusion for each material. Note that each major section is self-contained with its own figures, tables and references.

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II. Atomic Layer Epitaxy of Silicon Carbide

A. Introduction

The extremes in the thermal, mechanical, chemical, and electronic properties of all the common polytypes of SiC allow the types and the numbers of current and conceivable applications of this material to be substantial. From an electronics viewpoint, it possesses a range of wide band gaps [1] at 300 K, e.g., 2.2 eV (3C), 2.86 (6H) and 3.3 eV (2H); as well as high values of saturated electron drift velocity of 2×10^7 cm/s (6H) [2] (a slightly higher value has been predicted [3] for 3C (beta) because of reduced phonon scattering); junction breakdown electric field (5×10^6 V/cm [4] and thermal conductivity (3.5 W/cm°C at 300 K) [5]. As such, the primary driving forces for the current interest in SiC for electronic applications are its capabilities for high-power, -speed, temperature, and light-emitting devices resistant to radiation damage. Discrete devices having these properties have been achieved and characterized in the laboratory.

The high thermal conductivity of SiC also indicates the potential for high density integration of SiC devices. This idea has received considerable impetus with the recent development and scale-up of the seeded-sublimation growth technique for producing commercially viable single crystal α (6H)-SiC boules from which highly thermally conducting wafers are attained. Significant advances have also been made in the growth of monocrystalline beta and alpha (6H) thin films via chemical vapor deposition (CVD) and the incorporation of n- and p-type dopants into these films during deposition or via ion implantation.

The objective of this research is to extend the state-of-the-art regarding SiC thin films via the employment of atomic layer epitaxy to deposit the material on selected substrates and eventually to fabricate devices using this method. The following subsections describe the experimental procedures and discuss the results and conclusions of the research conducted in this reporting period.

B. Experimental Procedure

1. ALE Chemistry for the Deposition of SiC

The chemistry which we believe necessary to achieve the ALE of SiC depicted in Figure 1. Firstly, the bare Si surface (1A) is exposed to a flux of Si_2H_6 (1B). The Si_2H_6 molecule decomposes into SiH_x precursors as it nears the heated substrate, and a monolayer of these precursors adsorbs onto the sample (1C) forming a terminating layer subtended the remaining hydrogen atoms. The presence of the H prevents the deposition of another layer of silicon precursors until these terminating atoms are removed. In the next step, the substrate and its adsorbed layer are rotated into the environment of a hot filament and a flux of C_2H_4 (1D). In

this step, C precursors replace the hydrogen termination, leaving a surface terminated by these C precursors (1E). The cycle is then be repeated (1F).

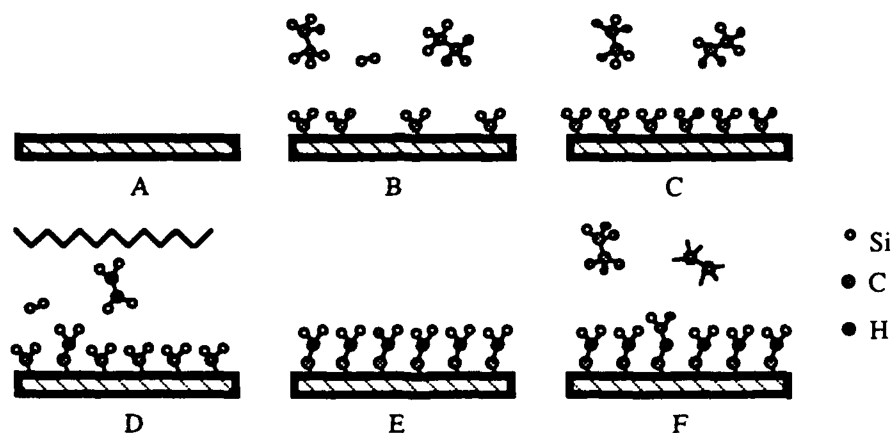

Figure 1. Schematic of the chemistry envisioned for the atomic layer epitaxy of SiC on Si.

2. Deposition System

To accomplish the ALE of SiC, a vacuum system has been designed and completed. The system is presently configured to process 1 inch wafers. However, the apparatus may be adapted to handle samples to 2 inches in diameter. The system consists of three chambers: a load lock, a remote hydrogen plasma cleaning chamber, and a growth chamber. The system was fabricated from stainless steel with knife edge seals and is high vacuum capable. Base vacuum in the cleaning and growth chambers is in 10^{-9} torr range. Process gasses are regulated by thermal mass flow controllers, process pumping is handled by a rotary vane pump, and high vacuum is achieved through cryo-trapped diffusion pumps. The substrates are heated using a SiC-coated graphite resistance heater heated immediately below the substrate carrier plate which rotates above the heater. Selected deposition ports contain W filaments located above the substrates which are used for the decomposition of C_2H_3 or H_2.

3. Substrate Processing

Substrate preparation and loading. To date, all thin films have been grown on heavily arsenic doped silicon (100) wafers having a resistivity of <.005 ohm/cm. The as-received wafers are RCA cleaned and then thermally oxidized to grow approximately 750 angstroms of oxide for passivation. Immediately before use, the wafers are placed in 20:1 D.I. H_2O:HF to strip the oxide, quickly loaded into the load lock and transferred to the plasma cleaning chamber. The substrates experience 10^{-7} torr vacuum within 15 minutes.

Plasma cleaning of the substrates. During plasma cleaning, the loaded substrates are heated to 250°C under flowing purified Ar at 0.3 torr. Once at temperature, hydrogen flow is started, and an r.f. plasma is remotely ignited and stabilized at 40 watts. Anthony et al.[6] has found that the optimal surface passivation of silicon by atomic hydrogen occurs at around 150°C. Therefore after cleaning at 250°C for 30 minutes, heater power is turned off, and the samples cool under the remote plasma to a temperature of less then 100°C. Total cleaning time is about 1 hour. Samples are then rapidly transferred to the growth chamber.

Film growth. (The following details a typical growth run to grow Si on Si.) Once installed in the growth chamber, the samples are heated to the growth temperature under a flux of purified hydrogen. Once at growth temperature, the flow of both disilane and the hydrogen purge gas is started and stabilized, and the W filaments are brought to temperature. Flow rates are determined by system geometry, growth pressure, and rotation speed. After flows, temperature, and pressure are stable, the sample rotation is begun. At the end of the run, samples stop and cool under hydrogen.

4. Film Analysis

The system has no in-situ analytical instruments, thus the deposited films are removed for SIMS, SEM, and RHEED analysis. Since the substrates are heavily doped, film thickness can be measured using SIMS depth profiling by looking for arsenic in the spectrum. In addition to measuring film thickness, SIMS data gives information on film contamination and cleanliness of the interface. It has been determined that using heavily doped wafers is unnecessary because interfacial C and O contamination is always detectable by SIMS. The SEM was used to determine surface morphology of the films. RHEED analysis was preceded by a 30 minute flash at 900°C to remove the native oxide on the films to give clearer diffraction patterns.

C. Results

A typical SIMS depth profile of a Si film grown on Si (001) with disilane is shown in Figure 2. This sample was RCA cleaned, oxidized, HF dipped, installed in the system and subsequently plasma cleaned. The data in Figure 2 shows that the concentration of C in the film is lower than the C concentration in the wafer. Furthermore, the C and O peaks at the interface reveal the residual surface contamination noted above. These peaks are present in all SIMS depth profiles and represent typical levels of interfacial C and O.

The amount of C and O incorporated into the growing film increases with growth temperature, as can be seen in Figure 3. Across the range of temperatures shown in Figure 3, disilane readily decomposes to form a film. This pyrolytic decomposition is often used in ALE processes; however, in this research chemically controlled processes are derived. Thus, growth temperatures will be lowered, resulting in reduced film contamination.

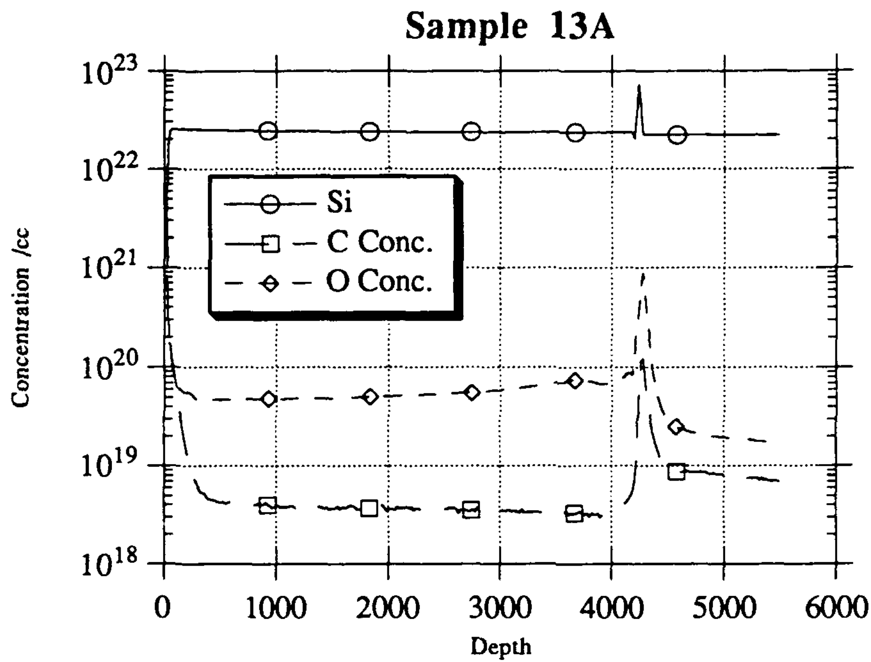

Figure 2. Typical SIMS profile of the Si films deposited on Si(001) by atomic layer epitaxy with disilane.

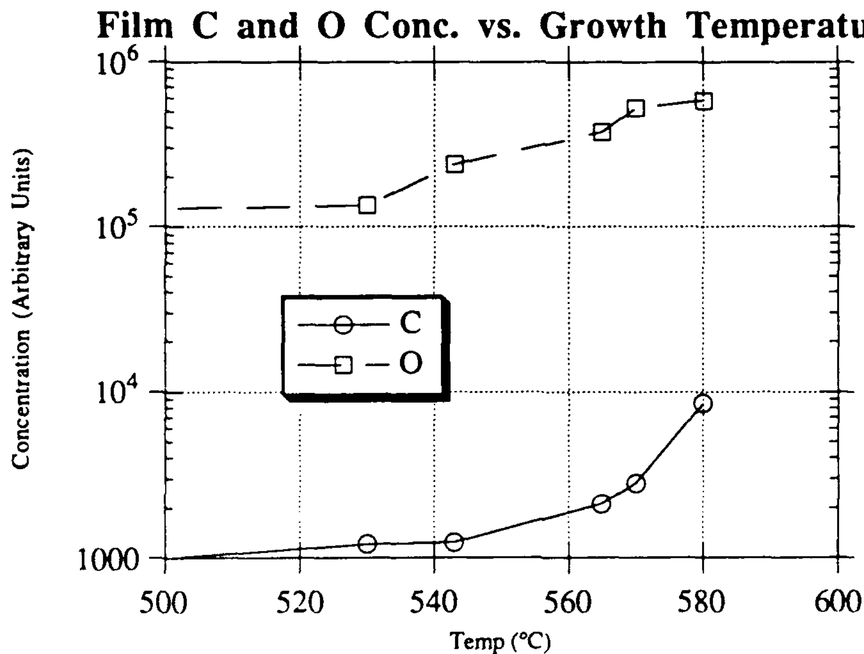

Figure 3. The results of SIMS profiles of C and O found within Si(001) films deposited of Si(001) wafers at the temperatures noted using disilane.

D. Discussion

From the SIMS results, we have concluded that disilane undergoes pyrolytic decomposition on the Si(001) substrates on the samples and on the hoι receiver plate that the samples sit upon. In addition, the films contain significant amounts of C and O. Previous very high temperature (T > 600°C) experiments also resulted in the incorporation of traces of Fe and Cr into the films. To minimize or eliminate all of these problems, we have designed a new vane assembly which is on order. This new piece is shown in perspective in Figure 4. It will be made of TZM, a molybdenum based alloy. Quartz cones through which process gases will flow past hot filaments will be situated on top of the new assembly. The new filaments are larger than the present design. Thus they will be more effective at both cracking the source gas and providing a more uniform temperature rise on the sample surface. Once installed, the new vane assembly will provide a more uniform flow of source gas which will allow better separation of the different species. This upgrade is in progress simultaneously with additional modifications to facilitate improved ALE growth of SiC.

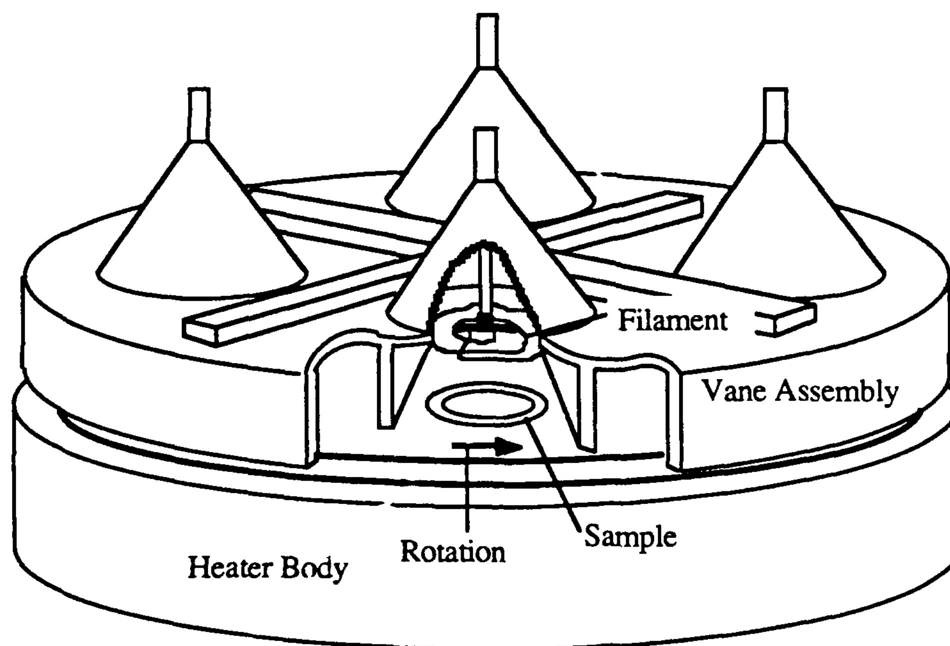

Figure 4. Schematic of new vane assembly and quartz filament holders for the SiC ALE system.

E. Conclusions

Good quality single crystal films of Si on Si (001) have been deposited via pyrolysis of dichlorosilane. However, much better and higher purity films have been grown using disilane at lower temperatures, but with decreased uniformity across the substrate. A cleaner vane

design that more efficiently distributes the source gases has been designed and is being fabricated.

F. Future Research Plans/Goals

The ALE reactor is being modified for more effective growth of SiC. This entails the fabrication and installation of a new vane assembly to more efficiently distribute the gases and the installation of long-life cracking filaments. In addition, substantial plumbing of ultra high purity ethylene and disilane and associated valving, mass flow controllers and regulators is in progress. Once assembled, we will begin work on ALE of SiC at temperatures in the range of 300°C to 500°C, commensurate with our findings of disilane decomposition and the low temperature decomposition of Si-H bonds studied by Crowell [7] with whom we have had several discussions.

G. References

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III. Adsorption and Chemical Reaction Kinetics in Atomic Layer Epitaxy of Silicon Carbide

A. Introduction

The objective of this portion of the ALE program is the study of the surface adsorption and chemical reaction kinetics of the ALE process for depositing SiC layers. An ultra-high vacuum (UHV) system has been designed and constructed for this purpose. The vacuum system consists of three chambers: a load lock, a plasma cleaning chamber and a desorption chamber equipped with a shielded mass spectrometer. Analytical capabilities include temperature programmed desorption and measurements of kinetic uptake. The system is 100% operational.

B. Experimental Procedure

1. Sample preparation

The substrates are one inch, As doped <100> silicon wafers. They are initially cleaned using a modified RCA method. The steps used in this cleaning process include 5 minutes in 60°C H_2SO_4, D.I. water rinse, 5 minutes in 60°C $NH_4OH+H_2O_2$, D.I. water rinse, 5 minutes in BOE etchant, and D.I. water rinse. Each substrate is subsequently placed into the load lock and transferred to the plasma cleaning chamber.

The top flange of the cleaning chamber (Figure 1) is equipped with a nominal one inch quartz tube on which is wound a several turn coil of 0.125 inch copper tubing which is connected to a radio-frequency (RF) source. The electric field produced within the quartz tube by the energized coil causes the rapid movement of any free electrons such that their collision with argon molecules introduced into the tube causes ionization which cascades and results in the generation of a plasma. This argon plasma is be used to excite a hydrogen plasma from the H_2 gas introduced downstream from the plasma. The sample to be cleaned is not immersed in the plasma, thus plasma- induced surface damage is minimized. This cleaning method also does not require high temperatures, as most other methods, thus the substrate surface and the interior doped regions will maintain their initial character. However, prior to processing, the sample must be heated to ~1000°C to desorb the hydrogen passivation layer. [1]

2. Equipment design and employment

The mass spectrometer is encased in an apertured chamber (Figure 2), which has been configured specially for thermal desorption studies. The mass spectrometer chamber is contained in the main chamber of the desorption system (Figures 3 and 4). The spectrometer, manufactured by Hiden Analytical Ltd.. is able to monitor the partial pressure of sixteen different species as a function of both temperature and time. It is equipped with a spectral library of over 70 common gases, and it allows the user to subtract out the known library

spectra of common gases from an experimentally obtained spectrum. This feature allows the species of interest to be isolated in the obtained spectra.

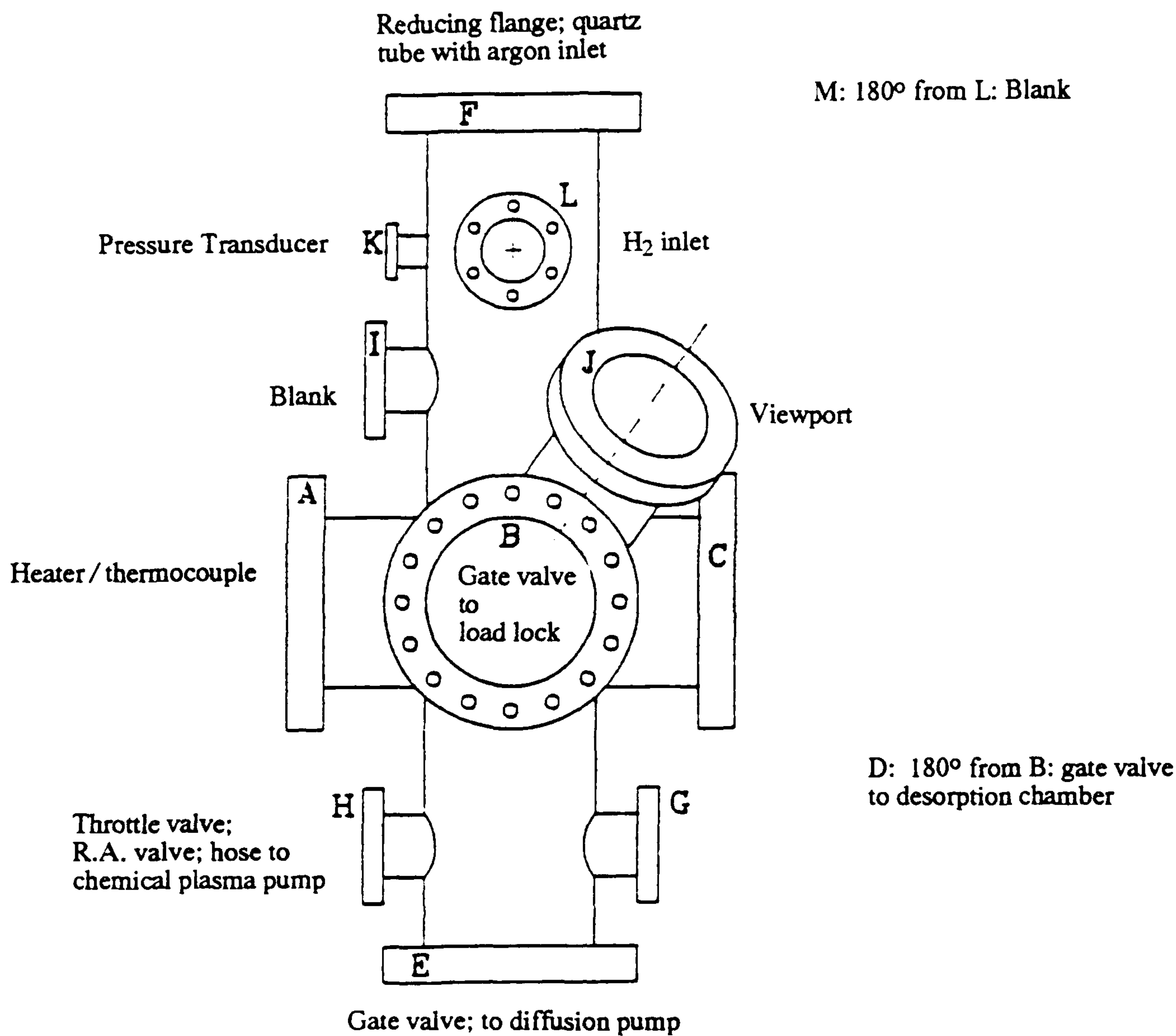

Figure 1. Schematic of hydrogen plasma cleaning chamber for removing oxide and free carbon from substrate surfaces prior to loading into thermal desorption chamber.

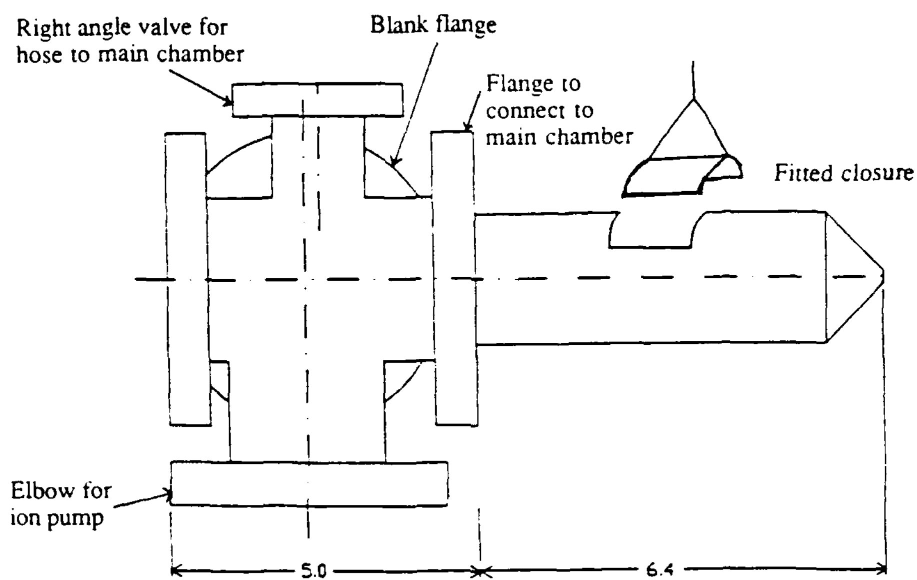

Figure 2. Schematic diagram of mass spectrometer chamber.

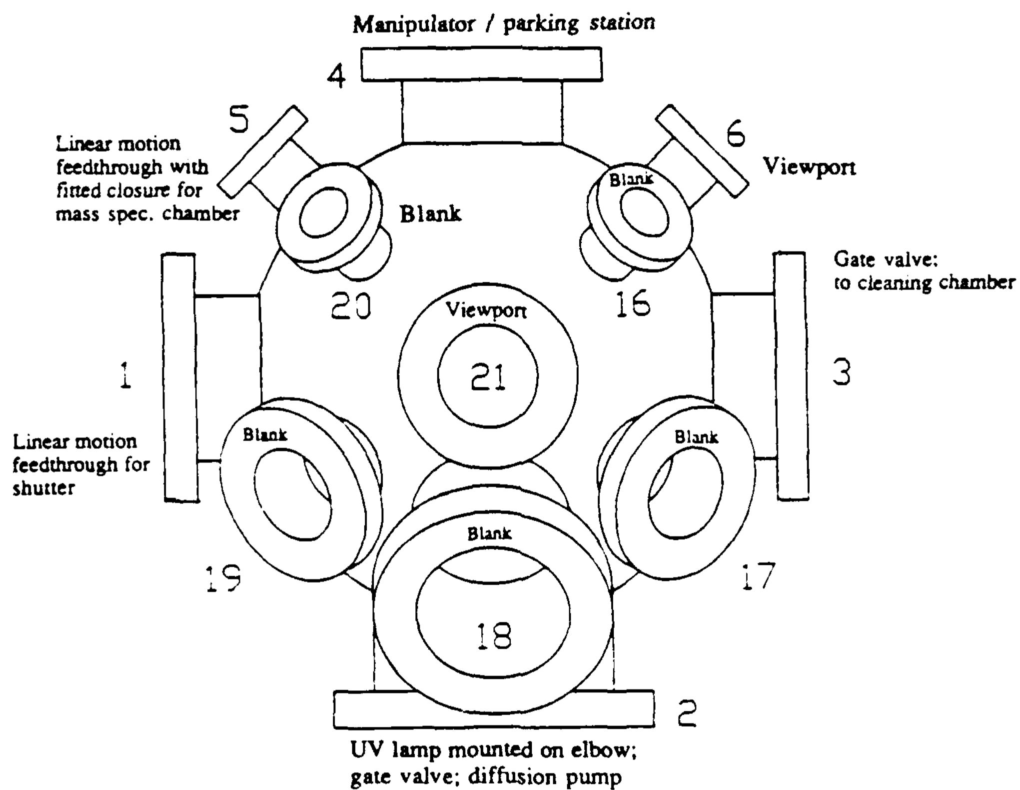

Figure 3. Schematic of desorption chamber for ALE studies.

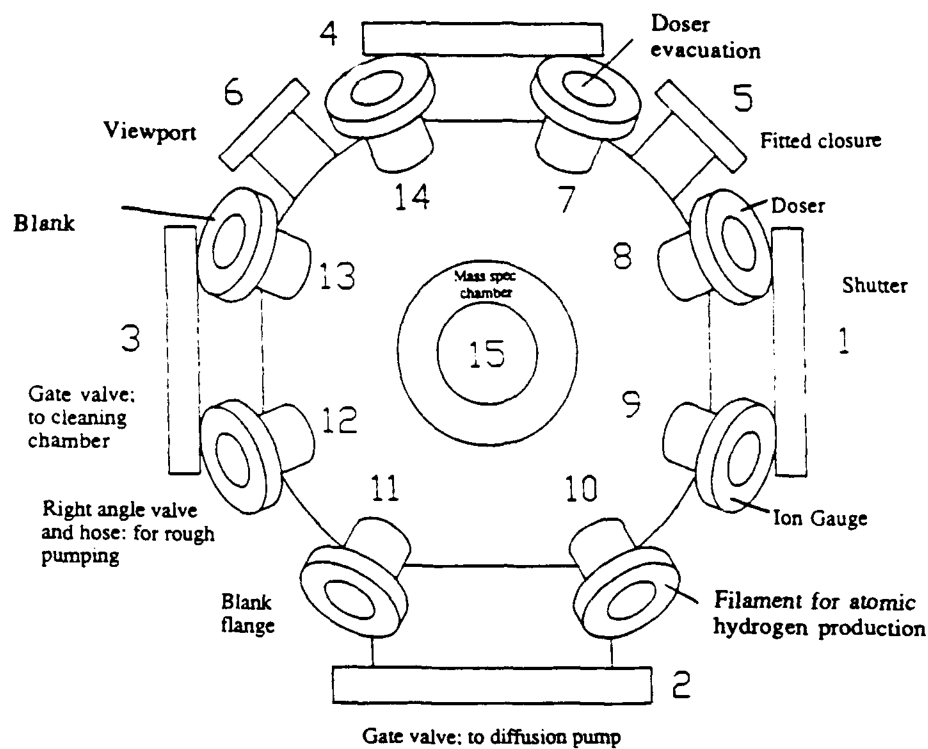

Figure 4. Schematic of desorption chamber showing mass spectrometer location.

The desorption chamber also has additional features that allow one to use the mass spectrometer in two different ways. Firstly, the mass spectrometer chamber has an aperture in direct line of sight with the sample. By increasing the temperature of the sample and monitoring the pressures of the adsorbed molecule and its possible decomposition products, the temperature at which the adsorbate desorbs and/or further decomposes can be identified. This data yields the activation energy necessary for desorption of the major species and subspecies. By analyzing the shape of the desorption curve for conditions of low coverage, a plot of the desorption rate versus temperature can be obtained .[2,3]

For the second type of measurements, the mass spectrometer chamber has been equipped with a fitted closure that can be easily raised and lowered for sampling the random flux of a particular species in the system. This feature, coupled with a shutter placed between the doser and the sample, allows one to extract quantitative kinetic adsorption information. Before the introduction of the gas, a spectrum is taken to obtain a baseline measurement of the species of interest. Then, with the shutter covering the sample and the fitted closure closed, the gas is turned on and a measurement of the background pressure of the introduced species is taken.

The shutter is subsequently moved away from the sample. The measurement of the decrease in the background signal tells one how much gas has been adsorbed. When the pressure reaches the original background level, the gas introduction is terminated. This data yields the adsorption rate and sticking probability versus the absolute coverage.[2,3]

3. The choice of gases for the deposition of the Si component of SiC

An important aspect of ALE growth is its self-limiting nature. After studying all commercially available silicon-containing species, dichlorosilane was first chosen as the initial candidate for study for atomic layer growth of silicon, primarily because of the halogen chemistry. The first decomposition product is hydrogen, and this reaction has an enthalpy of 152 kJ/mol. The remaining chlorines will not be removed by molecular hydrogen or by other silicon atoms. The result will be the adsorption of one layer of silicon, terminated by chlorines. The presence of the chlorines will prevent further adsorption of the silicon species at that site. Once full coverage is achieved, the chlorines can be removed by the introduction of atomic hydrogen. This reaction has an enthalpy of -452 kJ/mol. The final result is the growth of one atomic layer of silicon.

Infrared spectroscopy has shown that for a germanium substrate, the Si-Si bond in disilane is the weakest. At temperatures beginning at 110K, the molecule dissociatively absorbs as SiH_3. [4] The adsorption rates, thermal desorption kinetics, and processing capabilities of dichlorosilane and disilane are being compared to determine the best candidate for ALE, as discussed in the next subsection.

Once the work on the thermal desorption kinetics of dichlorosilane and disilane is completed, the research will be extended to include a source for depositing carbon via the ALE method. After examining the results of previous research by and extended discussions with Prof. John T. Yates at the University of Pittsburgh (with whom we are collaborating on this program) regarding the adsorption kinetics of various carbon-containing gases, acetylene has been chosen as the source for carbon. Professor Yates has fully characterized the adsorption kinetics of various hydrocarbon species, including acetylene, ethylene, propylene, propane, and methane. It was determined that a double (or triple) bond between carbons in the source gas was necessary for adsorption on a silicon surface. The second (or third) bond degenerates to provide the mechanism for bonding to the surface. Acetylene was chosen over the other gases because it had the lowest adsorption temperature.[5,6]

C. Results

The library spectra of dichlorosilane that was experimentally obtained is shown in Figure 5 and presented in Table I. Figure 6 also shows the partial pressures of the dichlorosilane

decomposition products obtained in this research as a function of temperature using our mass spectrometer.

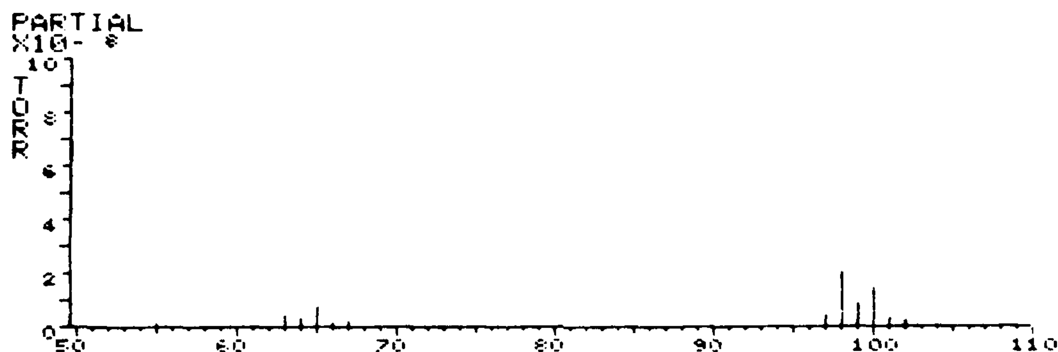

Figure 5. Decomposition spectra of dichlorosilane. See Table I for correlation of gas species with mass number.

Table I. Correlation of mass numbers determined for the spectra of Figure 5 with actual species determined via thermal decomposition studies of SiH_2Cl_2.

SPECIES	MASS (amu)
SiH_2Cl_2	101
$SiCl_2H$	100
$SiCl_2$	99
SiCl	63.5

Adsorption studies of dichlorosilane at various temperatures (at or above 300K) showed nominal or no adsorption of $SiCl_2$ or $SiCl_2H_2$. The adsorption spectrum at 550°C in Figure 7 shows only a slight dip in the signal of $SiCl_2$ when the shutter was removed at the 830 second mark.

A baseline measurement of the cracking pattern of the mass spectrometer was also obtained for disilane. For this set of data, there was no sample in the chamber and no heaters were on. By monitoring the relative partial pressures of all the possible by-products of disilane, a qualitative estimate of the weakest bonds in the molecule can be determined. Also, this will provide a baseline for comparison with a spectrum when there is a sample present. From Figure 8, it can be seen that Si_2H_4 and SiH_3 are the primary decomposition products.

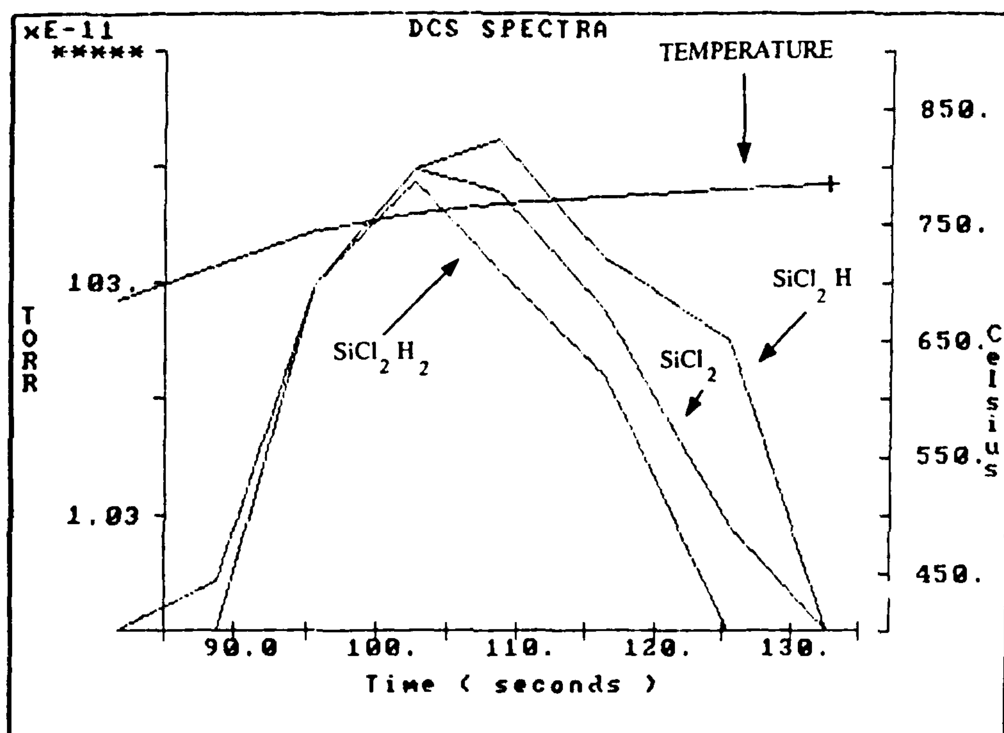

Figure 6. Partial pressures of the SiH_2Cl_2 decomposition products shown in the spectra of Figure 5 and Table I.

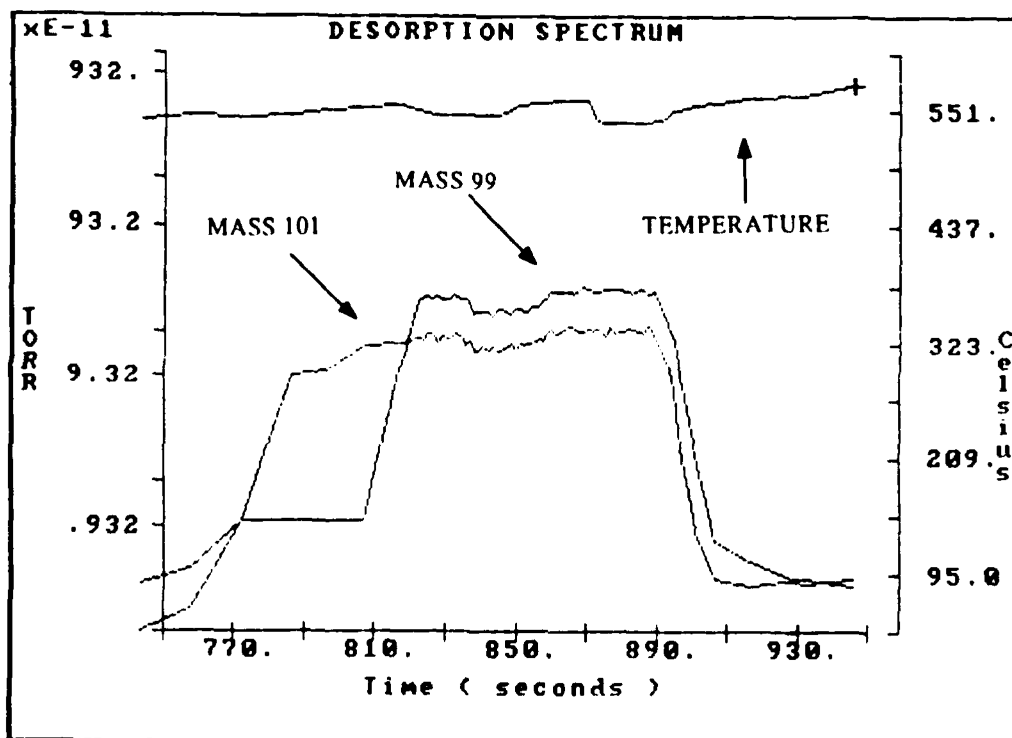

Figure 7. Adsorption spectrum of dichlorosilane at 550° C.

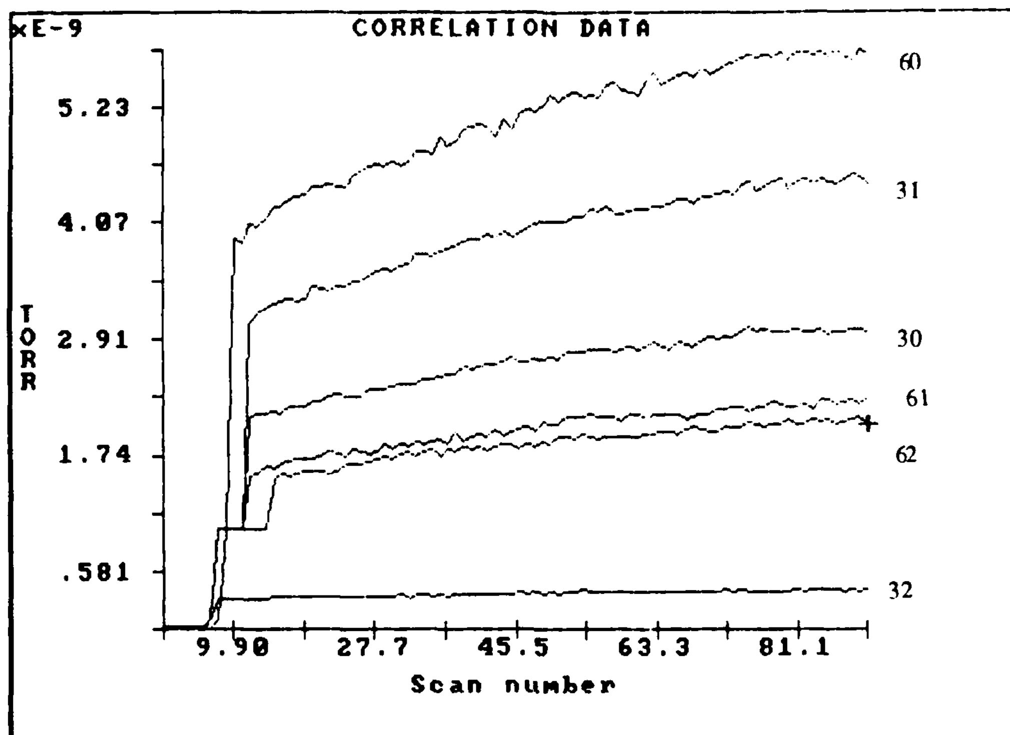

Figure 8. Cracking pattern of disilane showing the partial pressures of the decomposition products.

D. Discussion

From Figure 6, it can be seen that dichlorosilane begins to thermally decompose around 770°C. No desorption peaks have been seen, which is supported by the small adsorption curves. Also, the performance of the mechanical pump on the system was seriously degraded after pumping dichlorosilane. Even with frequent oil changes, the performance of the pump continued to decline.

The samples are radiatively heated by a tungsten filament. If the sample was heated to a temperature above 500°C for an appreciable amount of time, hydrogen would begin to desorb from the walls of the chamber. Not only did this phenomenon interfere with the flash desorption of hydrogen from the just-cleaned surface, but the large pressure rise made it impossible to monitor hydrogen in any scan. The mass spectrometer has overpressure trips that prevent damage to the unit, and these trips would be activated by the large increase in hydrogen. Figure 9 shows the steep increase in hydrogen pressure as a function of temperature when there is no sample present.

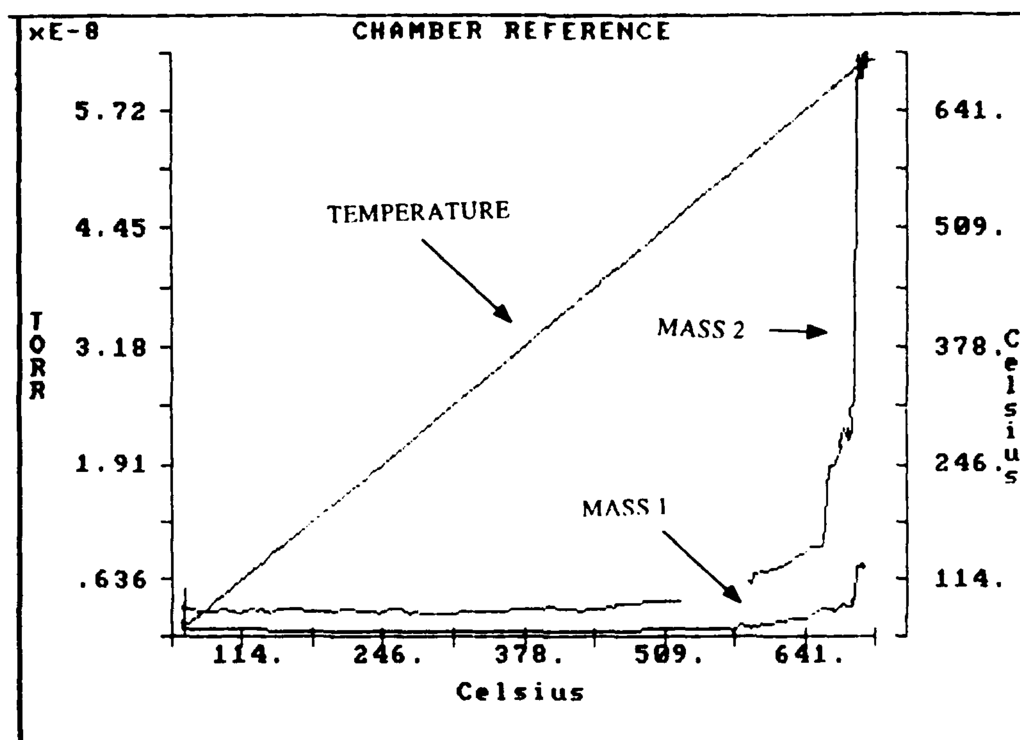

Figure 9. Desorption of hydrogen from chamber walls.

Bakeouts at 300°C for 2-3 days lowered the base pressure, but hydrogen was still a problem. To circumvent this, 1\4" copper tubing was wound around the desorption chamber and connected to a line from a water chiller. The tubing is attached to the chamber by a series of clamps that blanket the chamber. A large filament, other than the one used for heating the sample, is used to radiatively heat the inside of the chamber for a bakeout. The new heating and cooling system is working well.

E. Conclusions

Dichlorosilane has shown to be inadequate for ALE due to its poor adsorption in the absence of hydrogen gas. The simultaneous introduction of hydrogen does not lead to self-limiting growth. In preliminary studies, disilane has shown promise for adsorption at low temperatures, but the overpressure trips mentioned earlier deleted data from the computer file. For the carbon source for ALE of SiC, it has been shown by other researchers that acetylene saturates at monolayer coverage of Si (100) dimer sites.[5]

F. Future Research Plans/Goals

Future research plans include continued studies of disilane as a candidate for ALE of silicon. The adsorption rates and desorption kinetics are being studied for temperatures at and above 300K. The Si-Si bond is the weakest in the molecule, so the deposition scheme would be the adsorption of SiH_3, followed by flash desorption to remove the hydrogen terminating layer.

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IV. Organic Interlayers for Atomic Layer Nucleation

A. Introduction

A primary problem with achieving heteroepitaxy with diamond is the high interfacial energy. Thus, after nucleating, diamond would prefer to grow vertically instead of horizontally, making two-dimensional growth extremely difficult. The investigation of various routes for atomic layer nucleation (ALN) will allow the important aspects governing subsequent growth to be investigated and the tendency towards three-dimensional growth to be surmounted. To provide a pathway for layer-by-layer growth, organic interlayers will be initially deposited on the substrate, followed by diamond growth. The choice of organic layers will be such that they already have carbon bonded in tetrahedral arrays. This should provide excellent sites for the nucleation of diamond. Recent results (for example, see the preprint entitled "Substrate Effects on Bias Enhanced Diamond Nucleation; polycrystalline Cu vs Si(100)" contained in the 1991 Annual Letter Report for contract N00014-90-J-1604) indicate that the carbon surface plays a critical role in this nucleation stage.

B. Experimental Procedure

1. Diamond Growth

Variations in the normal growth procedures will be used to achieve ALN of diamond. A water cooled stage will be fabricated and placed into the present HFCVD system such that lower substrate temperatures may be utilized. This will decrease interlayer desorption and orientation damage. It is expected that growth must occur at temperatures below 500°C for the effective use of such organic interlayers. Thus, initial experiments have been conducted to achieve diamond growth at lower temperatures. However conclusive results have not yet been obtained. Several preliminary experiments were also conducted with an organic compound of interest, linolenic acid. The primary purpose of these experiments was not to yield an ordered organic layer, but rather to simply determine if the organic presence of the enhanced nucleation density. Si wafers with a thin surface oxide were utilized as the substrates. The oxide possesses a polar surface, thereby enhancing the sticking and ordering of the organic interlayer. The samples have been analyzed via scanning electron microscopy.

2. Analysis

Electron-Stimulated Desorption–Ion Energy Distribution (ESDIED) and X-ray Photoelectron Spectroscopy (XPS) will be the first *in vacuo* analytical techniques utilized in this integrated system (see Figure 1) for evaluating the organic layers and the subsequent films. These techniques will be employed by periodically stopping growth, returning the substrate into the analytical chambers, studying the sample, and then returning the sample for further

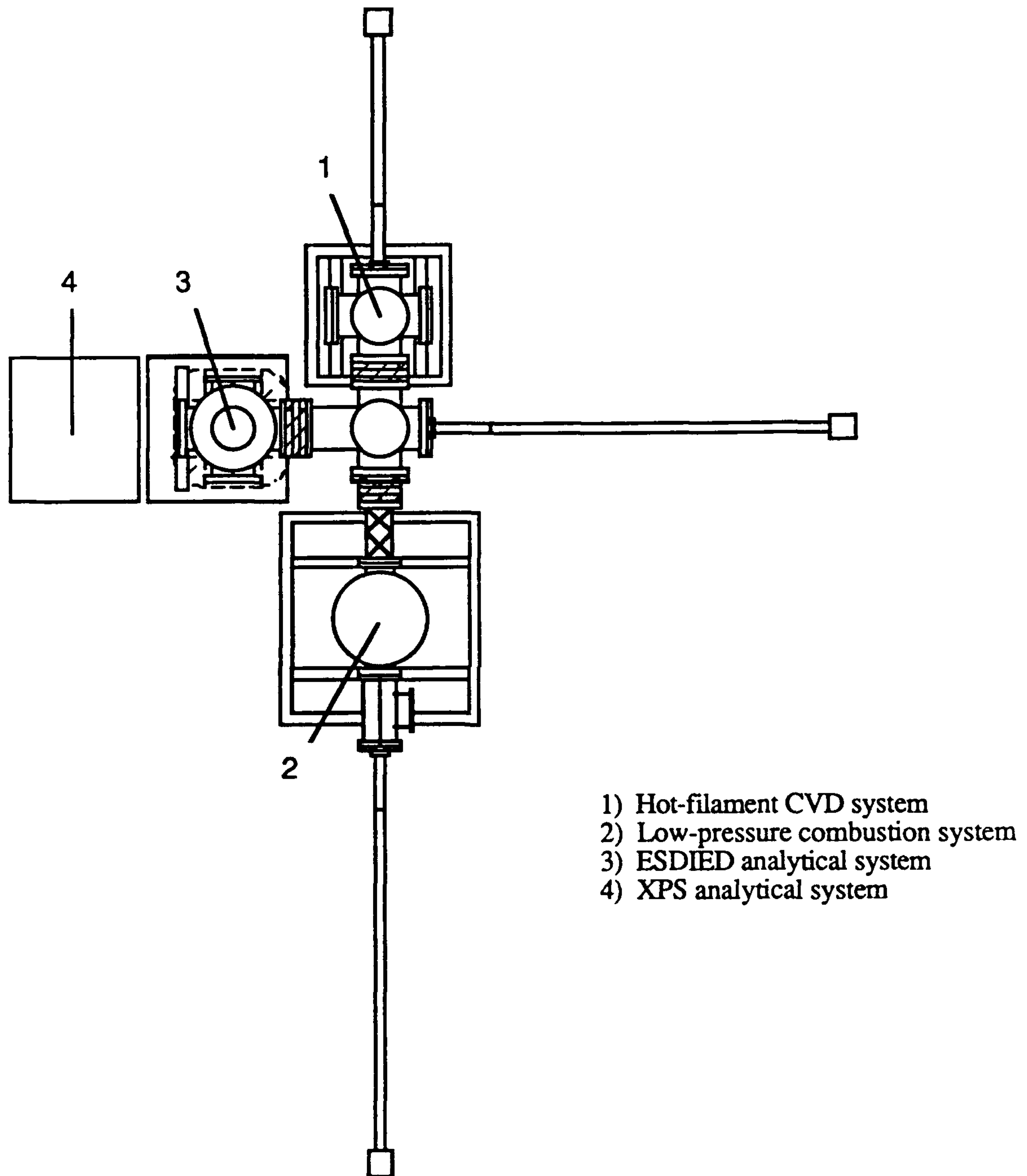


Figure 1. Growth and surface characterization systems to be employed for the research concerning the ALE of diamond.

growth and another cycle. The XPS will allow the chemical composition of the organic layers to be determined. It will also yield some information about the nature of the bonding in these layers. XPS–EELS will enable the investigators to determine the diamond content of the deposited film. The ESD/ESDIED system will be used in both the microwave plasma and the hot filament CVD growth systems. It will be tested first as a separate unit. After the operating parameters and characteristics have been determined, it will be employed to determine the desorption energies of the organic layers which will be a critical parameter when considering the interlayer lifetime in the growth environment. This is accomplished via "threshold" measurements in which the e-beam is ramped from low to high energies and the desorbed ion flux is monitored with the quadrapole mass spectrometer. The mass of the desorbed species will also be determined as well as their energy distribution. This should allow a determination of their identity and yield additional information about the nature of their bonding to the substrate. Progress on the implementation of this technique will be discussed in the Results section.

Another technique to be utilized in this study, but which needs additional investigation, is attenuated total reflectance (infrared) spectroscopy (ATR). Given the proper substrate configuration, this technique allows one to observe thin surface organic layers via infrared absorption. This will enable C–H bonding types to be evaluated as well as the functional sidegroups. Preliminary experiments have been conducted with this technique and will be discussed the Results section.

C. Results

The results to date for the aspects of the project described herein involve primarily system design and construction and some preliminary experiments. The electron stimulated desorption chamber has been designed and the bids received from the vendor. Although the system will be used on its own until the completion of trouble shooting, this chamber is compatible with the X-ray photoelectron spectroscopy chamber and the two growth systems. Manipulators and transfer rods which are necessary for the system have also been ordered. Similarly, the X-ray photoelectron spectroscopy chamber has been designed and ordered along with the electron analyzer. It is expected that the necessary components will be at NCSU in mid-January. The designs have allowed for future expansion with such techniques as Auger Electron Spectroscopy which will also be useful for the analysis of atomic layer nucleation discussed herein. Regarding the electron analyzer, a CLAM II VG instrument was chosen for a variety of reasons. Firstly, XPS will be one of the primary techniques for which this analyzer is used. This is because (1) the X-ray damage to the interlayers will be minimal and (2) the chemical binding information is necessary for determination of the bonding structures within the interlayers after heating. A CLAM II allows higher energy resolution than most analyzers in its

price range, and thus, is ideally suited for this purpose. Additionally, valence band spectra which also yields chemical bonding information are readily obtained with this analyzer at reasonably good signal-to-noise ratios. To insure this, diamond samples were sent to the top analyzer manufacturers, and the data was compared. This allowed the most objective choice of the appropriate analyzer.

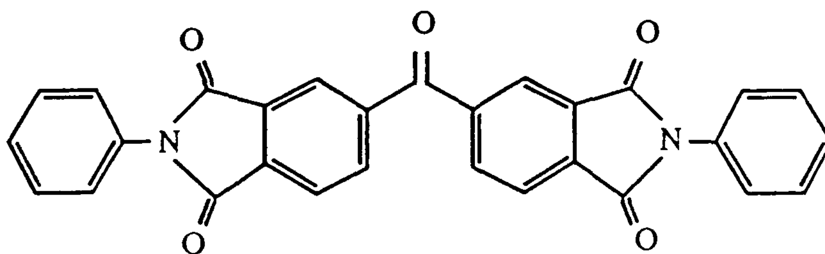
Preliminary attempts at attenuated total reflectance infrared spectroscopy have also been conducted. This technique involves the use of multiple reflections at an interface to enhance the signal from very thin layers. A prism with the proper entrance and exit angles for the spectrometer is used and the film is either held against this prism or deposited directly on the prism. A prism was purchased and used in the initial experiments, but it was found that the geometry was not suitable for the sample mounts available. The authors are currently awaiting the arrival a new infrared spectrometer in the department prior to again attempting the measurements. Preliminary results are expected before the next quarterly report.

Finally, preliminary growth experiments were completed utilizing linolenic acid as an organic precursor. Diamond particles were observed via SEM in streaked patterns. These patterns correlated with streaking that is believed to have occurred during the introduction of the organic onto the silicon substrate.

D. Discussion

Organic interlayers are an exciting method for overcoming the high interfacial energy between diamond and non-diamond substrates. Obviously, these organics will already have carbon in tetrahedral orientations, providing excellent nucleation sites for diamond. By creating oriented interlayers, heteroepitaxy is believed to be feasible and is the goal of this research. Because these techniques are not especially substrate sensitive, this process may also be ideal for growing on steels and other metals on which diamond nucleation is found to be difficult.

Polyimides are one class of polymers which are being considered as a substrate for diamond growth. An example of a typical polyimide is depicted below.



This particular polymer may be well suited as a substrate because it has a glass transition temperature around 500°C and does not decompose until even higher temperatures. The extreme stiffness of the molecular chain backbone gives the molecule a rigid rod nature. The molecular conformation is that of a helix, thus the molecules may be stacked to give a three dimensional ordering sequence. Although the structure is not crystalline, it may be considered an anisotropic liquid that may aid in the nucleation of diamond.

E. Conclusions

The efficacy of organic interlayers was determined by dipping a substrate in linolenic acid and using normal growth conditions in the HFCVD system. Some diamond growth was observed. It is believed that oriented organic interlayers will provide an excellent mechanism for heteroepitaxial growth of diamond.

F. Future Work

The future work for this aspect of the program has been discussed throughout this text. In summary, construction of the X-ray photoelectron spectroscopy/electron stimulated desorption system will continue, and these systems will be connected through an UHV tube to a hot filament deposition system. Testing and characterization of the electron stimulated desorption system will be one of the primary objectives after the systems have been assembled. In addition, various organic interlayers will be studied to determine which will be the most promising. Subsequently, preliminary growth experiments will be conducted.

V. Epitaxial Growth of CeO_2 on Si

A. Introduction

The growth of epitaxial ceramic thin films on silicon is of interest for applications to high quality silicon-on-insulator (SOI) layers and stable capacitor devices. CeO_2 is an excellent candidate for such an insulator, having the cubic fluorite structure, with the lattice misfit factor $\Delta a/a$ for CeO_2 to Si being 0.35%.[1] Also, CeO_2 has a dielectric constant of ~26, which could potentially allow it to be used in stable capacitor devices of small dimensions.[1]

B. Experimental Procedure

1. Thin film deposition

It has been shown that crystalline layers of CeO_2 may be grown on a Si substrate by means of laser ablation.[2,3] This process can be accomplished by irradiating a solid CeO_2 target with a high energy pulse from an excimer laser under ultra-high vacuum (UHV) conditions. This produces a "plume" of CeO_2 molecules which are free to move in UHV and which form epitaxial layers on the Si substrate. By controlling the frequency and the length of the pulses of the laser, one hopes to achieve layer-by-layer growth of the oxide.

In order to maintain the stoichiometry of the CeO_2 in UHV, some researchers believe it is necessary to flow oxygen at low pressure (10^{-7} - 10^{-8} torr) during growth.[1,2] Ce, however, has a high oxygen affinity and the x in CeO_{2-x} has been reported to be less than 0.01 at 1000° C under 7.6×10^{-9} torr oxygen, indicating that oxygen flow may be unnecessary.[3,4]

2. Characterization of the thin films

In order to observe the quality, crystallinity, orientation, and the growth rate of CeO_2 on Si, *in situ* reflection high energy electron diffraction (RHEED) will be used. A quadrapole mass spectrometer (QMS) will be used to detect residual gases and observe the oxidation state of the ablated CeO_{2-x}. Base pressure in the reaction chamber will be measured by an ion gauge.

C. Results

A design has been developed for a system suitable for growing epitaxial CeO_2 on Si via laser ablation. This system will be self-contained in that it will not share its components with other systems. It will consist of 3 chambers: a load-lock entry chamber equipped with a multi-stage sorption pump, an intermediate chamber with a de-gas station, pumped by a 220 l/s ion pump, and the main chamber for oxide deposition using a 400 l/s ion pump. A 300 l/s turbomolecular pump may be added later, if oxygen flow is deemed necessary, or for another experiment. The three chambers will be linked in such a way that the growth chamber is never open to a chamber that is exposed to atmosphere. In this fashion the strict requirement of

ultra-high vacuum will be achieved. Figure 1 shows a top view of the system arrangement. The laser to be used is a Lamda Physik excimer laser, currently available in the laboratory.

The substrate holder and transport mechanisms will have a 2" diameter substrate capacity. The internal manipulator will provide 360° continuous rotation. For this design the substrate platen will be facing down, and the sample held in place by clips. Also, heating to 1000° C will be provided by an oxygen-resistant quartz lamp within the manipulator. The manipulator will have 2" of vertical motion to allow the target-to-substrate distance to vary.

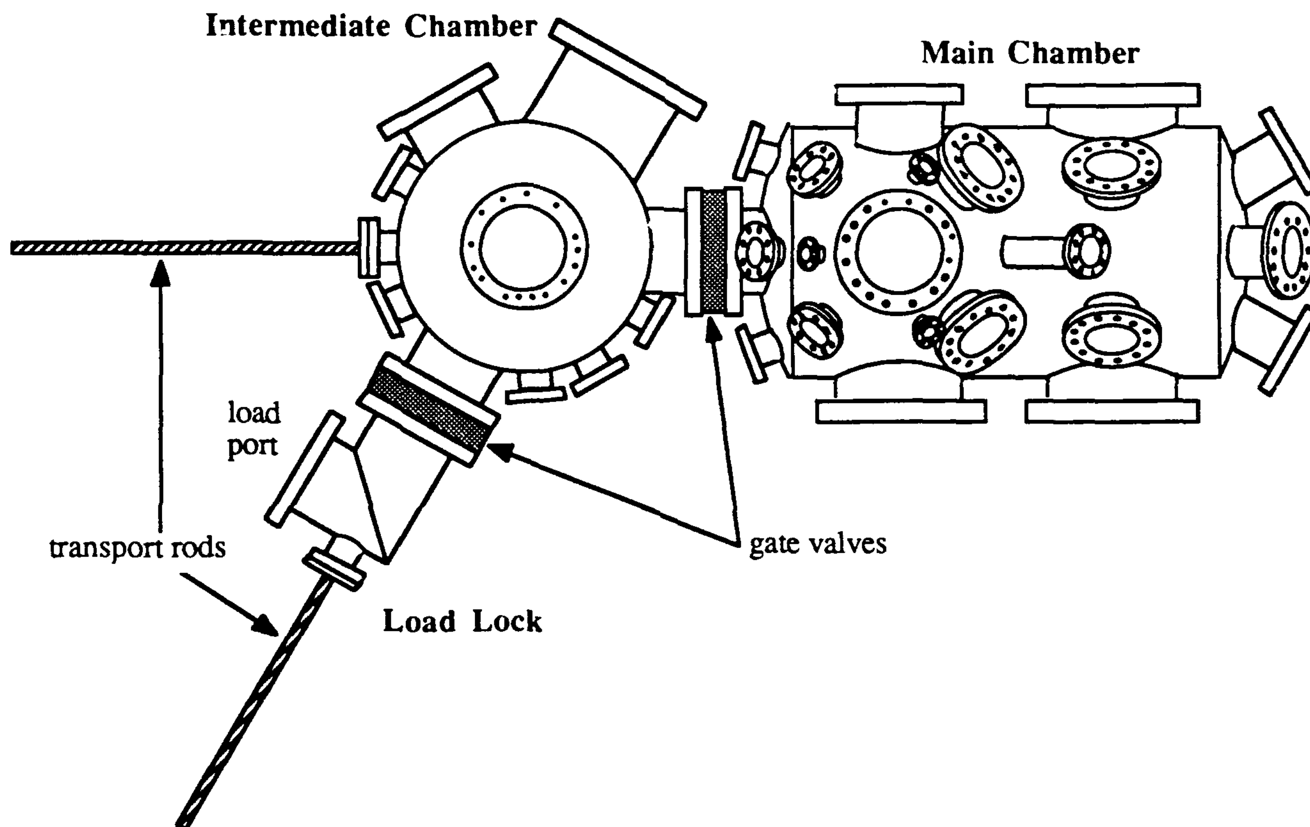


Figure 1. Top view of vacuum chambers for growth of CeO_2.

D. Discussion

A major obstacle in designing a UHV system compatible with oxygen lies in choosing proper materials. For example, typical UHV manipulators are made of molybdenum and are therefore unsuitable for high temperature applications in an oxygen atmosphere. In this design all heated internal parts will be constructed of a Haynes alloy. This is a nickel-based superalloy that is extremely resistant to oxidation at high temperatures. The substrate platen and clips will be made of graphite.

The design of the deposition chamber is of critical importance. In order for growth and characterization techniques to be employed, the positioning of flanges on the chamber must be

carefully planned. Figure 2 shows a side view of the deposition chamber, which is currently under construction.

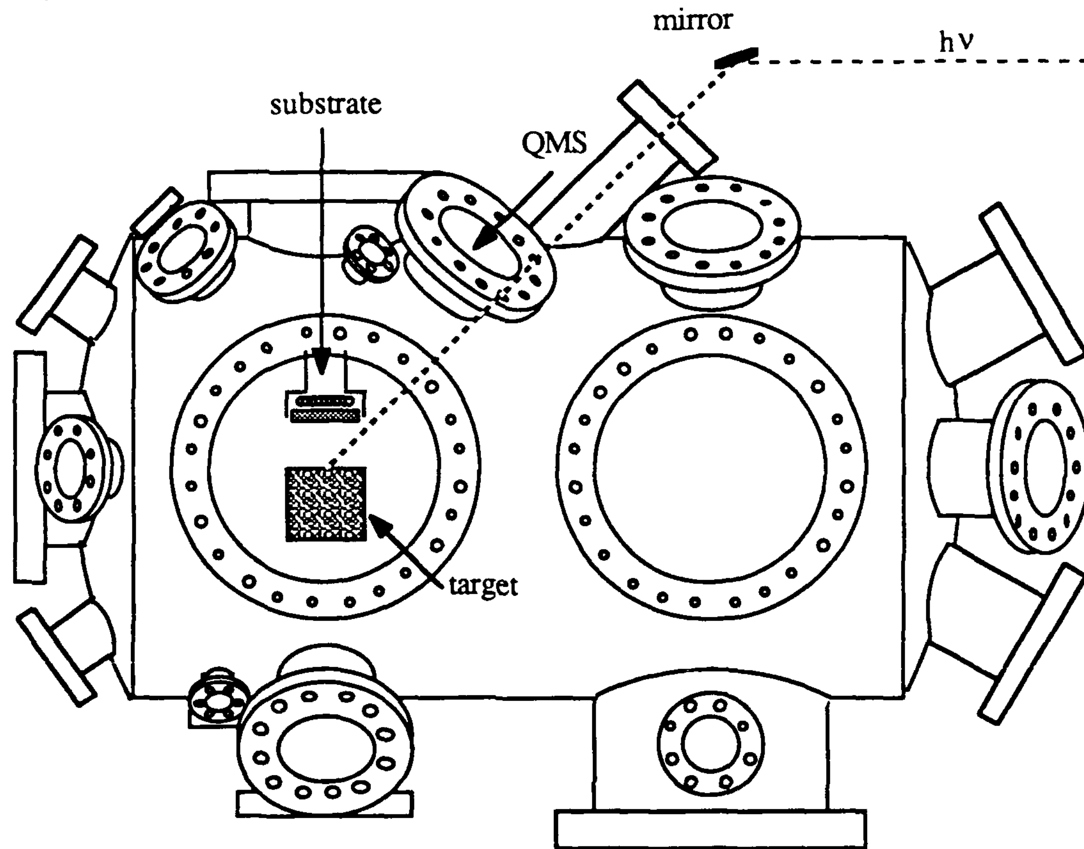


Figure 2. Side view of CeO_2 deposition chamber.

E. Conclusions

The system for epitaxial growth of cerium oxide is currently under construction. The system will be functional by 1992.

F. Plans for Future Work

Immediate plans include fabricating the system and depositing CeO_2.

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