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Atomic Layer Epitaxy of Silicon, Silicon/Germanium and Silicon Carbide via Extraction/Exchange Processes

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13. ABSTRACT *(Maximum 200 words)*

The primary focus of the research for this grant has been the atomic layer epitaxy (ALE) of Si; however, the ALE of SiC has also received serious consideration. A computer assisted study, based on the free energy minimization of a thermodynamic system undergoing equilibrium reactions has shown that the progressive decomposition of SiH_2Cl_2 (the Si precursor of choice in this study) results in the products of $SiCl_2$, H_2, SiH_2Cl_2, HCl and Si. Moreover, above 600°C, $SiCl_2$ is stable. Thus $SiCl_2$ adsorbed onto the surface will not decompose. It is predicted to react with H_2, forming Si on the surface. The experimental program has primarily involved the design and fabrication of equipment to (1) determine the surface adsorption, desorption and chemical reaction routes necessary to achieve the ALE of Si and SiC and (2) produce Si layers of a desired thickness via ALE processes. The ALE of Si was achieved at 815°C using available chemical vapor deposition equipment and information regarding the chemisorption and decomposition of dichlorosilane on the Si(100) surface in the presence of H_2. Reducing the temperature to 770°C did not result in the deposition of Si under any conditions of flow rate or total pressure.

14. SUBJECT TERMS

atomic layer epitaxy (ALE), silicon, silicon carbide, SiH_2Cl_2, adsorption, desorption

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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, Bedair and Nishizawa showed that GaAs could indeed be deposited by ALE. 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.

Research at North Carolina State University within the period of this grant has primarily focused on the ALE of Si; however, the ALE of SiC has also been given serious consideration during the program. A computer study of the progressive decomposition of dichlorosilane, the initial Si–containing gas of choice, as a function of temperature was conducted in concert with the experimental effort. The latter program has primarily involved the design and construction of equipment to (1) determine the surface adsorption, desorption and chemical reaction routes necessary to achieve the ALE of Si and SiC and (2) produce Si layers of a desired thickness via ALE processes. Because considerable time was required to produce and "debug" this equipment, the ALE of Si was attempted and achieved using available chemical vapor deposition equipment and information regarding the chemisorption and decomposition of dichlorosilane on the Si(100) surface in the presence of H_2. The results of this research are described in the following sections.

II. Computer Analysis of the Decomposition of Dichlorosilane

As noted above and discussed below, dichlorosilane (SiH_2Cl_2) was selected as the initial reactant gas of choice for the study of the ALE of Si. To obtain an understanding of the effect of temperature on the progressive decomposition of this molecule, a computer program entitled SOLGASMIX–PV was used with the restriction of one atmosphere total pressure.

SOLGASMIX-PV is a software package that predicts the chemical products of a hypothetical CVD reactor which operates at a given temperature, pressure, and input gas composition. The answers are based on the free energy minimization of the thermodynamic system which contains all the possible gaseous, liquid and solid reactants and products. The data for this minimization procedure is the program's library of the JANAF Thermochemical Tables. One should note that the results are correct only for equilibrium conditions. For example, SOLGASMIX would predict substantial formation of $SiCl_4$ at 400°C from dichlorosilane. This does not occur because of kinetic limitations; therefore, $SiCl_4$ formation must be disallowed at this temperature.

Using SOLGASMIX-PV to model the SiH_2Cl_2 system (with the above restriction) for temperature from 400°C to 1100°C revealed that there will be five significant products: $SiCl_2$, H_2, SiH_2Cl_2, HCl and Si. These results are shown in graphical form as a function of temperature in Figure 1.

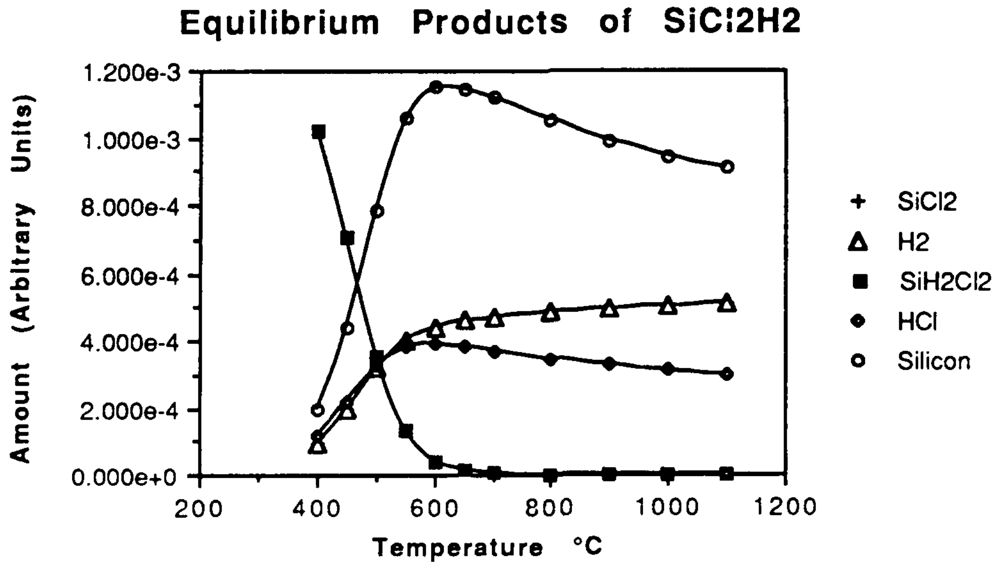


Figure 1. Graph of relative amounts of various product species derived from the decomposition of dichlorosilane as a function of temperature at a total pressure of 1 atm., as predicted by computer-assisted thermodynamic analysis using SOLGASMIX-PV. The Si and H_2 curves overlap and thus are not shown separately.

From the data in Figure 1 it may be noted that:

- Throughout the temperature range of the graph, $SiCl_2$ and H_2 are formed in equal amounts.
- At lower temperatures, SiH_2Cl_2 is stable and does not decompose.
- At higher temperatures, $SiCl_2$ is stable, so $SiCl_2$ adsorbed onto the surface will not decompose, but would evaporate intact.
- Since ALE requires the decomposition of adsorbed $SiCl_2$ on the surface, the optimal growth temperature will be between the limiting cases of SiH_2Cl_2 stability, and $SiCl_2$ stability. This allows a range between 400°C and 1000°C.
- Furthermore, the decomposition of adsorbed $SiCl_2$ should follow the reaction:

$$SiCl_2 + H_2 = Si + 2HCl$$

As a result, there should be a high equilibrium concentration of HCl at the optimal growth temperature. From the SOLGASMIX results, the maximum in HCl is predicted to occur at around 620°C. Temperatures above this will not violate the HCl criterion, but since ALE growth will be fairly slow, care must be taken to ensure that the rate of simple thermal deposition of silicon from SiH_2Cl_2 does not reach a significant level compared to the ALE growth rate. For example, with the receiver turning at 30 rpm, and allowing for a complete coverage per cycle, growth would occur at 120 monolayers a minute, or for Si(100) growth this is 163 angstroms per minute. To grow at this rate by thermal CVD would require a temperature of around 700°C. Therefore, for this growth rate, 700°C is considered an upper temperature limit.

III. Design and Construction of a Thermal Desorption System for the Study of the ALE of Silicon and Silicon Carbide

A UHV vacuum system has been designed and assembled for the study of growth kinetics of silicon and silicon carbide by the atomic layer epitaxy method. The system has three chambers: a load lock, a remote hydrogen plasma cleaning chamber, and a desorption chamber equipped with a shielded mass spectrometer. Labeled schematic drawings of the latter two chambers are presented in Figures 2 and 3.

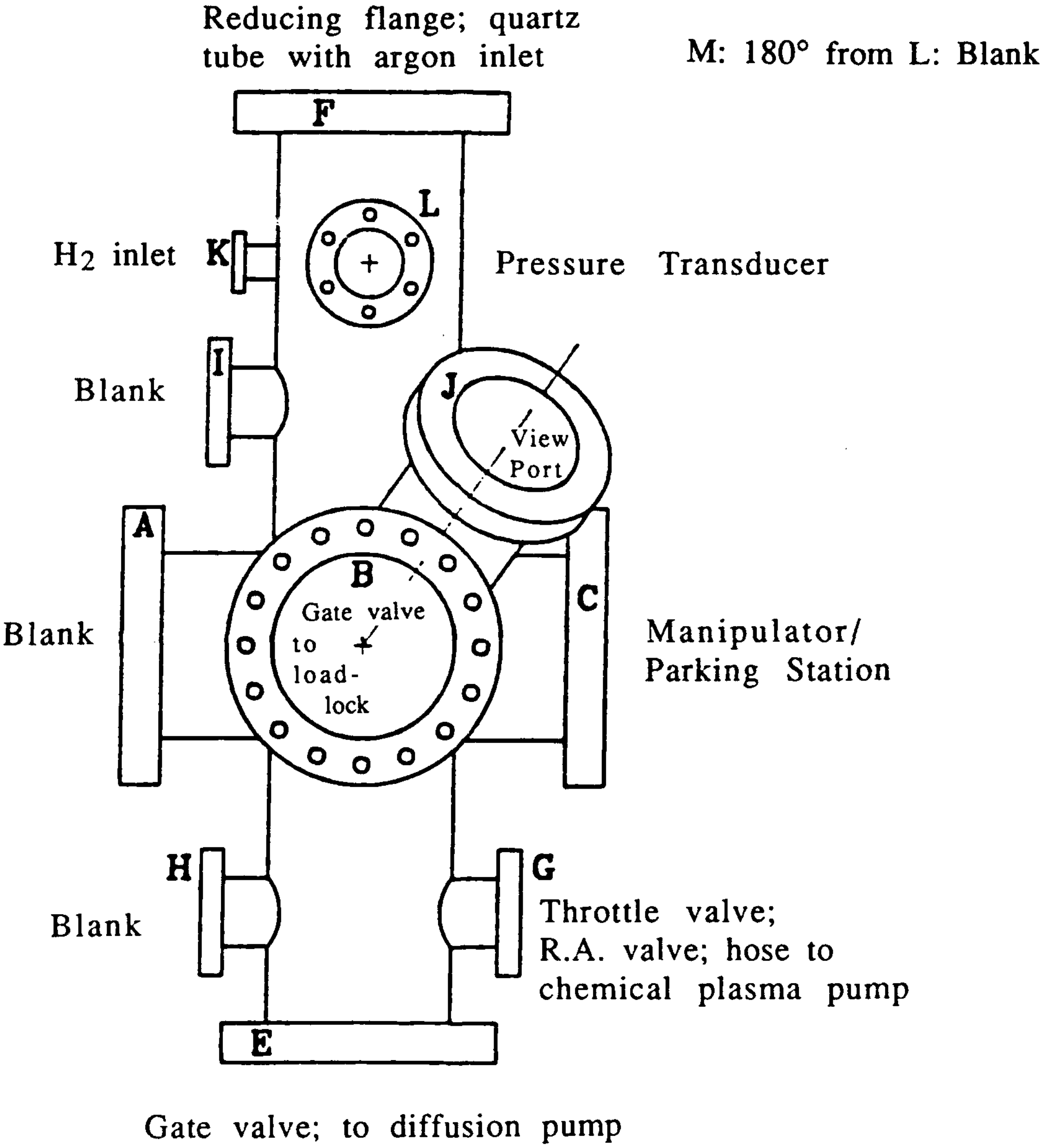


Figure 2. Schematic of hydrogen plasma chamber for removing oxide and free carbon from substrate surfaces prior to loading into thermal desorption chamber.

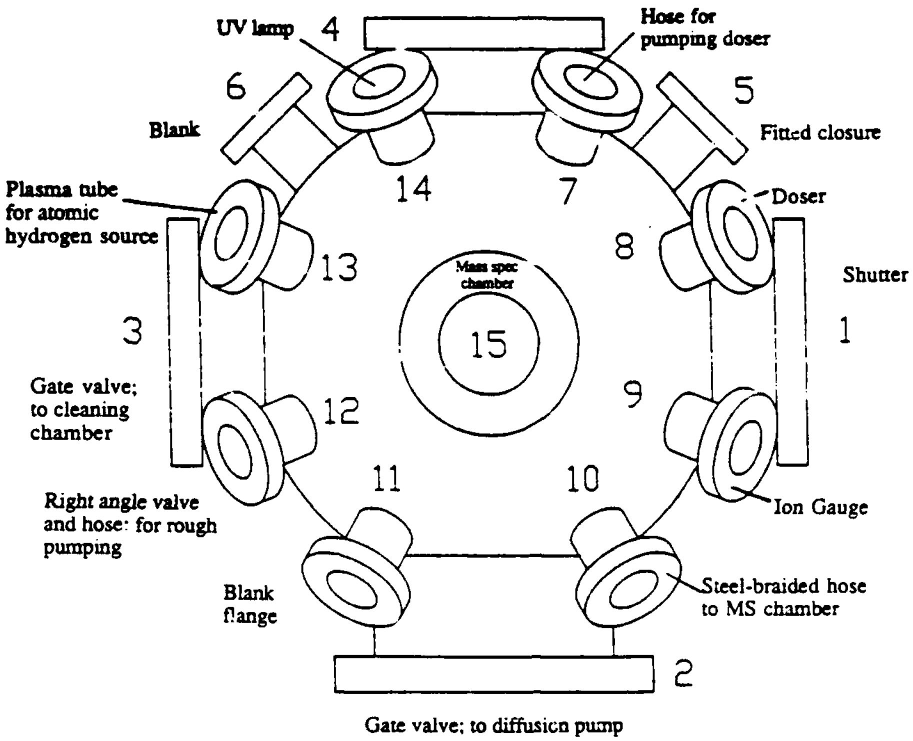


Figure 3a. Schematic of the front of the thermal desorption chamber showing the placement or entry ports for each equipment part.

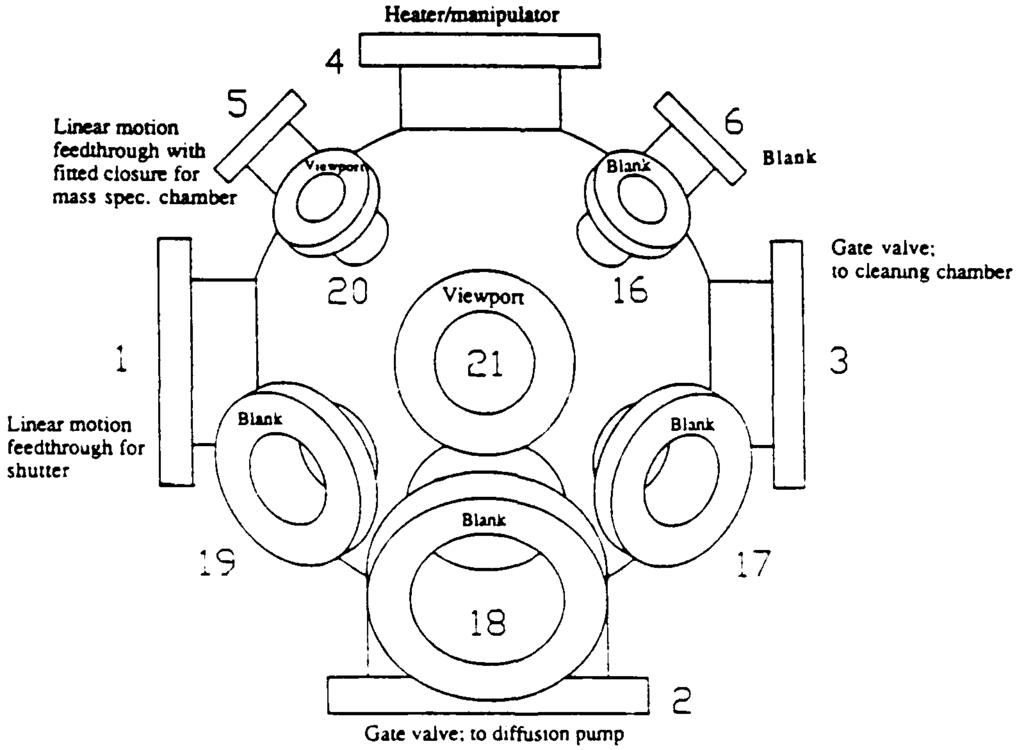


Figure 3b. Schematic of the rear of the thermal desorption chamber showing the placement or entry ports for each equipment part.

The top flange of the cleaning chamber (Fig. 2) 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 electrical field produced within the quartz tube by the energized coil causes the rapid movement of any free electrons such that their collision with Ar molecules introduced into the tube causes ionization which cascades and results in the generation of a plasma. This plasma will, in turn, be used to excite a hydrogen plasma from the H_2 introduced downstream from the Ar. The sample to be cleaned is **not** immersed in the plasma, thus plasma-induced surface damage is minimized. This 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.

The mass spectrometer (Fig. 4) has been configured specially for thermal desorption studies. It is contained in the main chamber of the desorption system (Fig. 3). This particular spectrometer 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, thus the species of interest can be isolated in the obtained spectra. For example, 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 as a function of the temperature using our mass spectrometer.

The desorption chamber also has additional features that will allow us to use the mass spectrometer in two ways. First, 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 (or its decomposition product) and all possible other decomposition products, the temperature at which the adsorbed molecule 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.

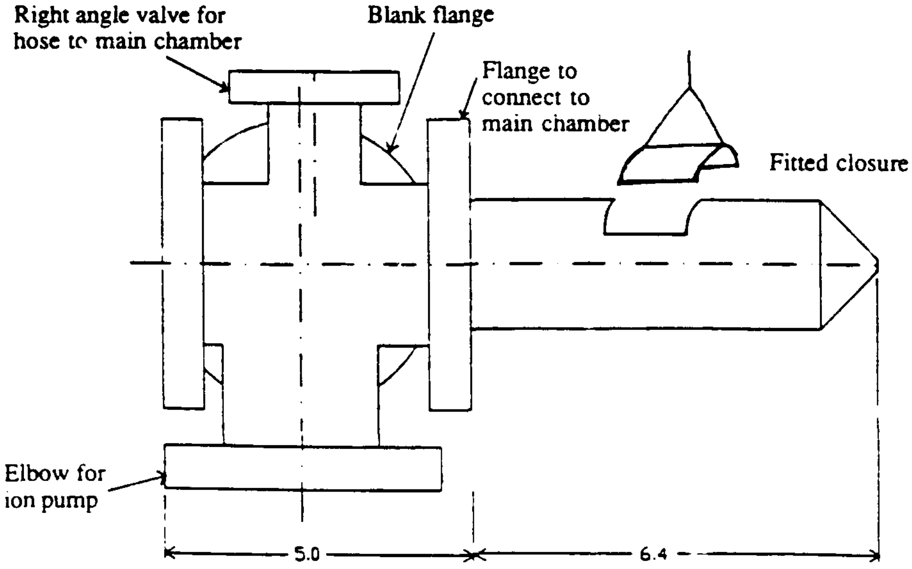


Figure 4. Schematic of mass spectrometer chamber (left side) and mass spectrometer tube (right side) for thermal desorption system.

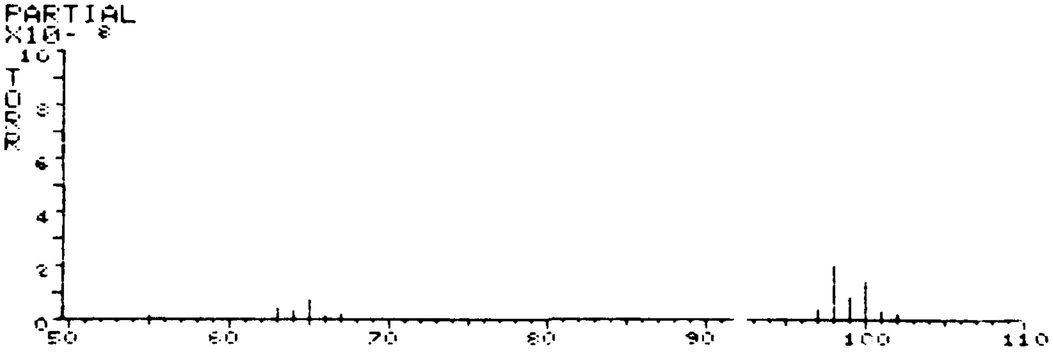


Figure 5. Decomposition spectra of dichlorosilane. See Table I for correlation of gas species with mass number.

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

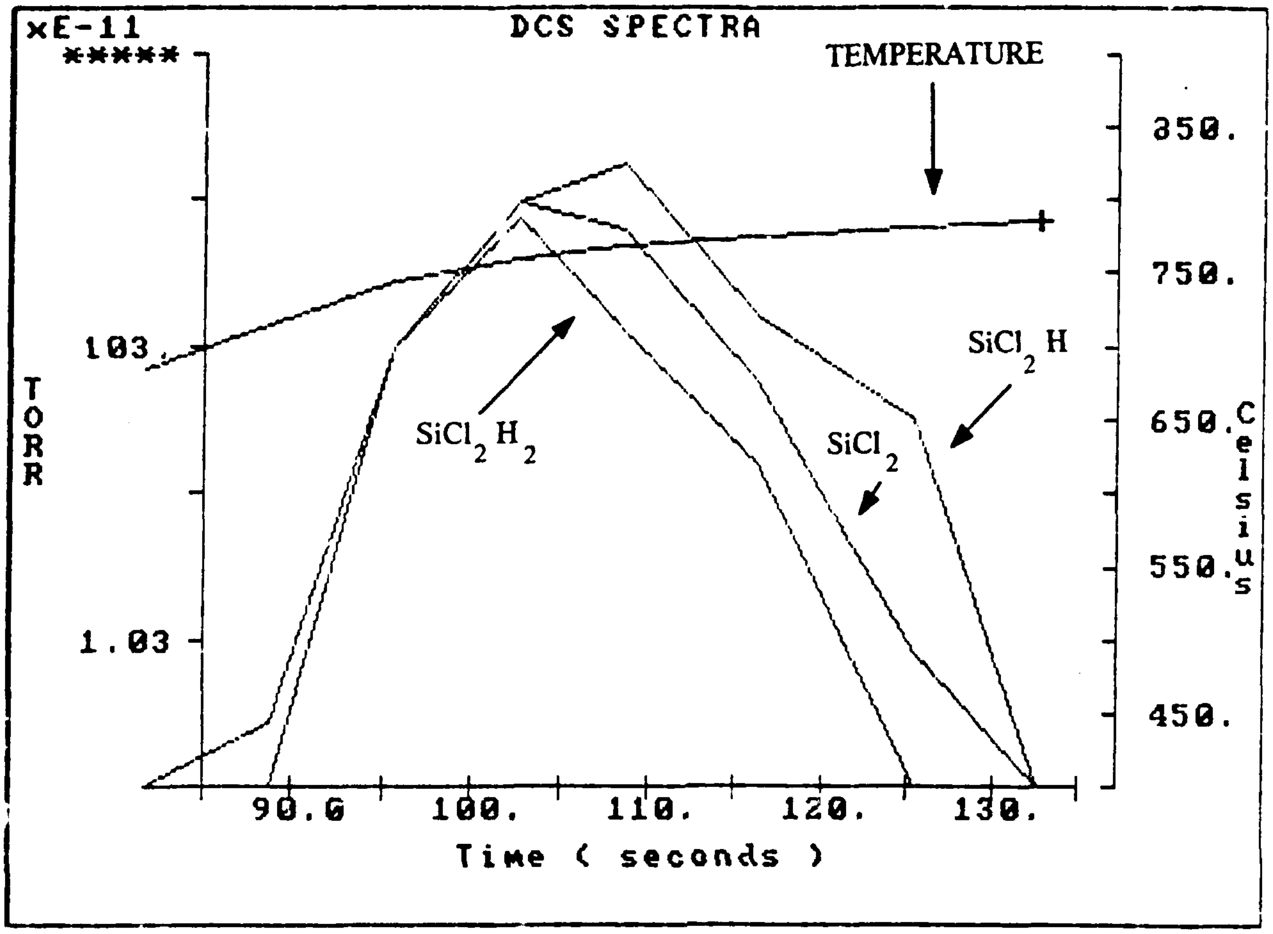


Figure 6. Partial pressures of the SiH_2Cl_2 decomposition products shown in the spectra of Figure 5 and Table I.

For the second type of measurements, the mass spectrometer chamber has been equipped with a fitted closure (see Figure 4) 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 for the sample, allows us 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 then reaches the original background level, the gas introduction is terminated. This data yields the adsorption rate and sticking probability versus the absolute coverage.

The first process to be characterized using the above system will be the epitaxial deposition of silicon onto a silicon(100) substrate by atomic layer methods. This method is of great interest for maintaining uniform coverage over a device structure. An important aspect of ALE growth is its self-limiting nature. After studying all commercially available silicon-containing species, dichlorosilane was chosen as the best candidate for atomic layer growth 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.

Once the work on the thermal desorption kinetics of dichlorosilane is completed, the research will be extended to include a source for depositing carbon via the ALE method. After examining previous research by Prof. John T. Yates at the University of Pittsburgh on the adsorption kinetics of various carbon-containing gases, acetylene has been chosen as the source for carbon. Professor Yates has fully characterized the kinetics of thermal desorption of various hydrocarbon species such as ethylene, acetylene, propane, and propylene. 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 temperature of desorption.

Future equipment development plans include the incorporation of a liquid nitrogen cooled sample holder. This will allow us to extend the kinetic measurements to temperatures less than 300K. We wish to be able to cool the sample without sacrificing the ability to transfer in fresh samples via the load lock.

IV. Design and Fabrication of Equipment for the Deposition of Si and SiC Films via ALE

A. Overview

In this program, two different approaches were taken by the Bedair and Davis groups for the purpose of depositing Si alone (Bedair) or Si and C to reach the ultimate objective of SiC (Davis). In both groups, the *initial* objective was the ALE of Si films. The design philosophies. resulting equipment and the suggested experimental approaches and precautions derived from these two investigations are described in the following two subsections.

B. Equipment Design and Development for the Near Atmospheric Pressure Deposition of Si (Bedair Group)

Overview. The design and construction of the equipment (figure 7) for Si ALE have been completed and the system is near operational condition. The vacuum integrity of the system is currently being tested thoroughly prior to connection of the reactant gases. After this is finished the system will be ready for full operation following a final check of the pressure, temperature, and flow controls. The main objectives in the equipment design were high speed deposition, good system integrity for processing control and minimization of background impurities, and high purity source gases for near atmospheric silicon

Design Philosophy and System Operation. For high speed ALE growth the stage design depicted in Figure 8 is being used. The reactant gases are dichlorosilane (DCS) and hydrogen. The rotating sample (see Figure 9) is exposed to only one gas at a time. The DCS adsorption and decomposition is expected to result in one monolayer of $SiCl_2$ being chemisorbed, as noted in the previous section. The introduction of *molecular* hydrogen results

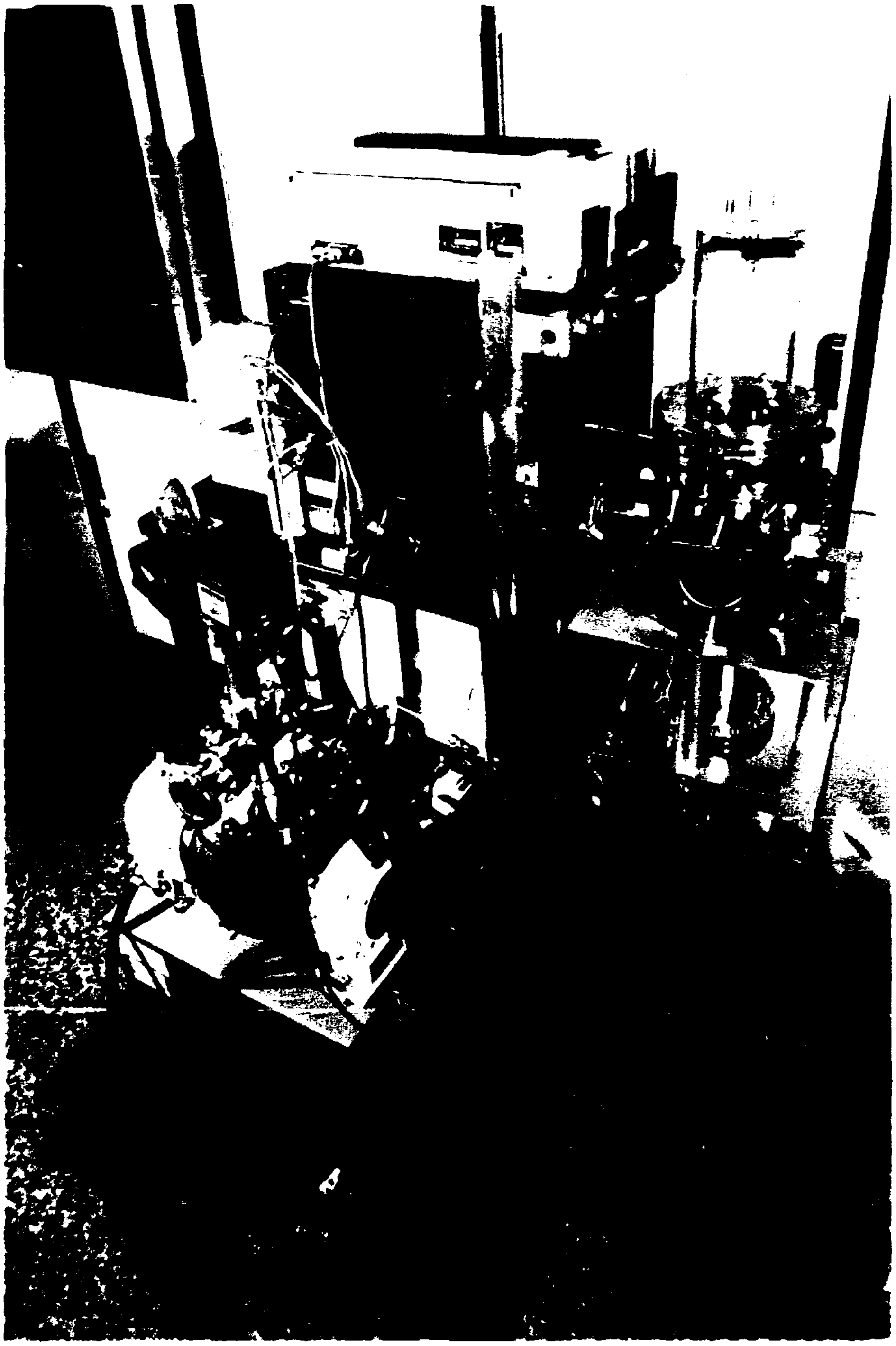


Figure 7. Photograph showing Bedair's system (without glove box) for ALE of Si and Si/Ge alloys and device structures.

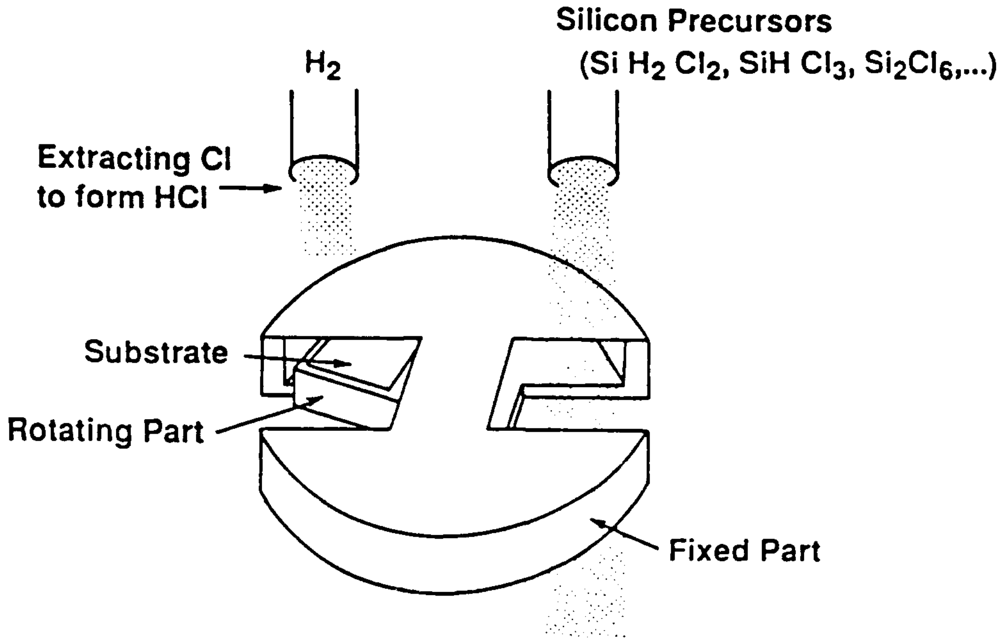


Figure 8. Experimental setup for ALE of Si.

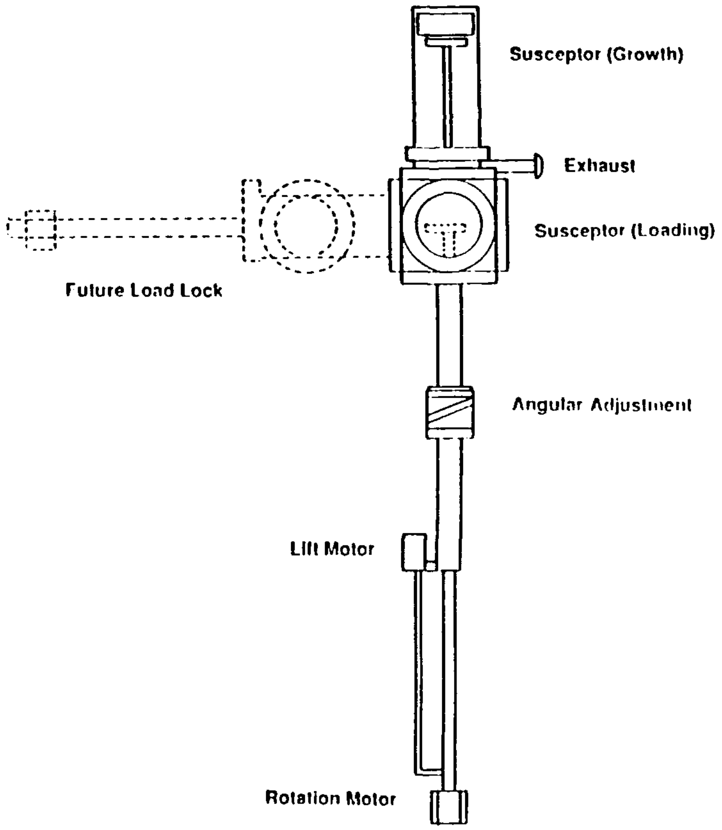


Figure 9. Si ALE reaction chamber design.

in HCl evolution and a pure Si monolayer left on the substrate surface. Therefore, one monolayer is deposited per sample revolution.

The chemical system we are using has been explored recently by Nishizawa [35], though with a different experimental setup. He exposed the substrate to DCS, pumped out and purged the chamber, and then flowed in the second reactant, hydrogen, to complete the reaction. The experimental conditions were from about 800 to 900 C at pressures below 1 mTorr. For good surface morphology crystals he was able to obtain growth rates of about 0.03 microns per hour. We are able to operate over the same temperature ranges by using RF coils to heat the rotating substrate holder, but our technique is better designed for high speed growth. Since the rotating sample is exposed to only one gas at a time, no purge is needed between doses which would slow the growth rate. Under optimum growth conditions, the growth rate is expected to be about 0.2 microns per hour, assuming 2 to 4 seconds per cycle. To further insure separation of the DCS and hydrogen, inert argon is flowed into the system to act as a buffer layer between the reactant gas streams. Since there is no need to evacuate the system between doses, we can also operate at higher pressures. At higher pressures the flux rate of reactant molecules striking the surface in increased, therefore the exposure time necessary for one monolayer formation is reduced and the growth rate is again increased. The pressure in our reaction chamber is controlled by a butterfly valve installed in the systems exhaust line. This valve is coupled with a pressure gauge to set the system pressure at any desired level in the 1 torr to atmospheric pressure range.

The exposure time of the substrate to the reactants is controlled by a stepper motor, mass flow controllers, and needle valves. The stepper motor is easily programmed to rotate the sample at a resolution of over 20000 steps per cycle at speeds up to about 40 cycles per second. The rotational speed may be programmed over each segment of the cycle to individually control the exposure times of the silicon sample to DCS and hydrogen. Separate metal seal mass flow controllers have been installed to regulate the total flow of DCS, hydrogen, and argon into the system, as shown in Figure 10. The maximum flow rates for

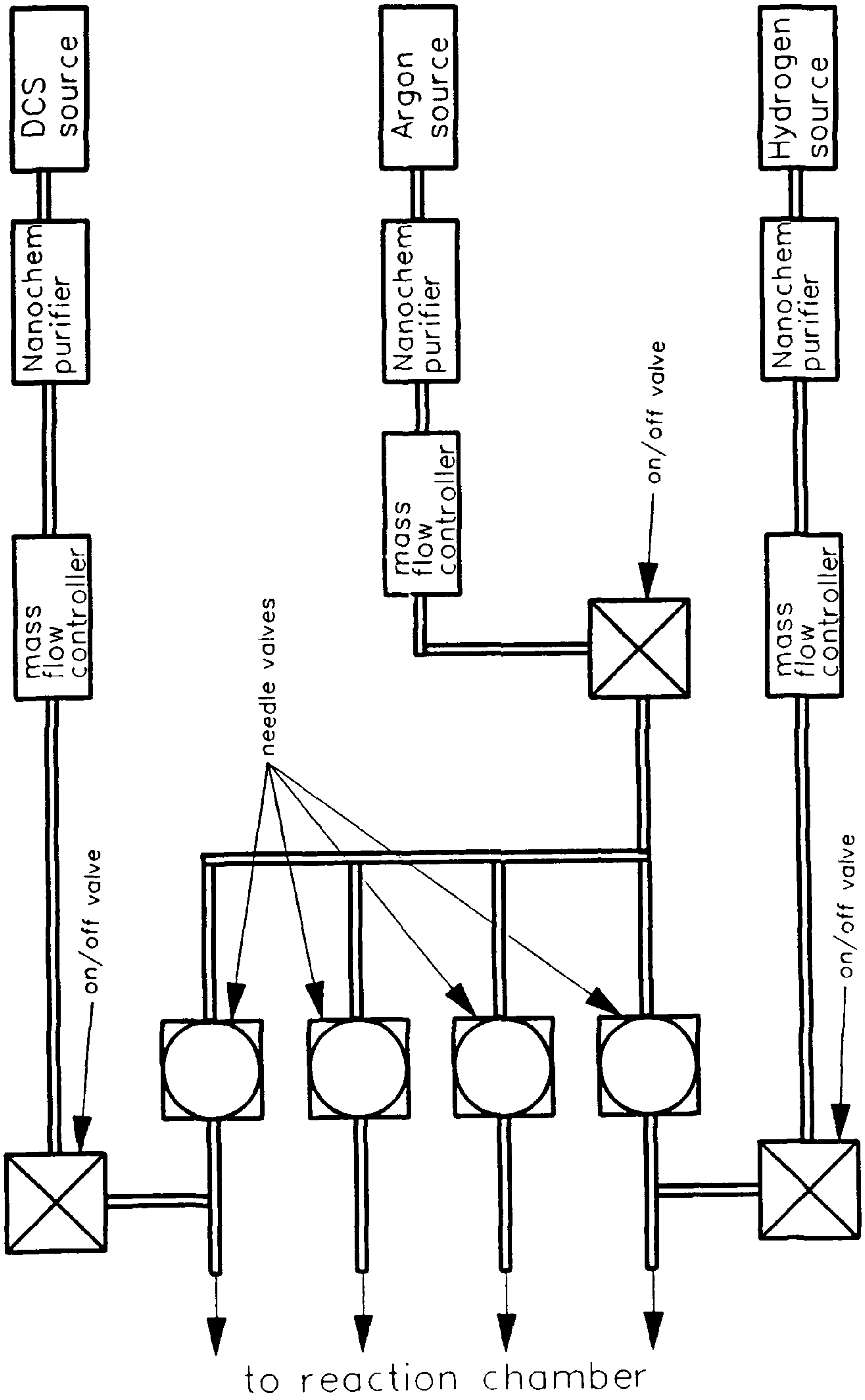


Figure 10. Si ALE gas manifold and purifier system.

these controllers are 200 sccm, 200 sccm, and 5000 for DCS, hydrogen, and argon respectively. Needle valves control the dilution of the DCS and hydrogen streams by Ar as well as the Ar flow rate used to separate the reactant gases. This manifold design is shown in Figure 10. By adjusting the needle valves and mass flow controllers the total flow rate of the reactant gas streams may be kept constant while changing the concentrations of the reactants in the stream. This is desirable to achieve uniform flow profiles across the substrate surface and still regulate the DCS and hydrogen concentrations. Especially at high sample rotational speeds and higher pressures, the reactant incident rate on the surface may otherwise not be uniform without using high flow rates of pure reactants, which may not be desirable.

Design and Maintenance of System Integrity. The apparatus has been constructed to minimize the impurity levels, especially water and oxygen, in the system. The reaction chamber is evacuated to 10^{-7} torr and baked out prior to deposition to remove impurities adsorbed on the walls. The RF coils located outside the quartz chamber are used to heat up the graphite sample holder for processing as well as for high temperature annealing of the sample to remove the oxide deposited after ex situ pre-cleaning.

Further precautions have been taken to isolate the reaction system from the atmosphere and reduce the chances of oxygen and water contamination. The entire deposition chamber is enclosed in a glove box filled with dry nitrogen. All electrical and vacuum connections, as well as gas lines, are sealed with O-rings to the walls to prevent moisture from entering the box. The glove box is kept maintained slightly above atmospheric pressure by constantly flowing nitrogen into the system and regulating the internal pressure with a bubbler, which is vented to an exhaust system. For entry and removal of samples and other necessary equipment into and out of the system an antechamber is attached to the glove box. The antechamber has an O-ring door to the atmosphere and another one inside of the glove box. A vacuum line and a line to the glove box itself are connected to the antechamber. For entry of samples the chamber is pumped out and purged with nitrogen from the box several times in order to remove the atmosphere from the antechamber. At this point the glove box and antechamber atmospheres are the same and the sample can be brought into the system for loading into the reaction chamber.

The deposition chamber is shown in Figure 9. The sample is easily loaded and unloaded via an O-ring sealed port and raised to the quartz reaction chamber using a programmable lift motor. The sample holder is heated by RF coils located outside the quartz chamber and is rotated by simple programming of the rotation motor. Two pumping systems are employed. One is for baking and purging the system and operates at a base pressure of 10^{-7} torr. The pump used for deposition regulates the system pressure and can be set in the torr to atmospheric range. This pressure control system operates by means of a Baratron pressure gauge and a butterfly valve. Once the desired pressure is set, the reading from the pressure gauge is automatically monitored and the butterfly valve adjusted continuously to increase or decrease the pumping speed and keep the pressure constant.

The system is designed for easy modification for future research. The susceptor (sample holder) and quartz chamber may be removed for modification if desired. The loading port can be replaced with a load lock system to further isolate the reaction chamber from the atmosphere. The gas lines are constructed for addition of dopant sources into the inert argon lines for doped deposition studies.

Gas Purification. Purifiers have been placed in line with the reactant gases and the argon. These are Nanochem purifiers which reduce the total impurity levels to the low ppb concentrations. The purification processes are trade secrets and are based on lithium-phenyl compounds for hydrogen and on chlorinated compounds for DCS systems. Water and oxygen contamination are especially harmful to Si epitaxy, due to rapid oxide formation. The DCS/hydrogen system is selective under many conditions and will not deposit on the oxide. Therefore, even a minute amount of oxide on the surface can destroy the epitaxial quality. Sedgwick [40] has recently examined the effects of oxygen and water on the DCS/hydrogen silicon epitaxial growth system at atmospheric pressure. His studies show that even a

99.999% hydrogen source is not pure enough for deposition to occur. As little as 50 ppb of water and 20 ppb of oxygen can substantially affect growth to allow only polysilicon deposition. However, using a Nanochem hydrogen purifier, like the type we have installed, he is able to obtain high quality epitaxial silicon growth.

C. Equipment Design and Development for the Deposition of Si and SiC (Davis Group)

To accomplish the ALE of Si and, ultimately SiC, a special high vacuum system has been designed and completed. Initially the system is configured to process 1 inch wafers. Ultimately, the apparatus may be adapted to handle samples up to 2 inches in diameter. The system consists of three chambers; a load lock, a cleaning chamber, and a growth chamber. A composite schematic drawing of the system is shown in Figure 11 and a photograph of the chambers and operations cabinet in Figure 12. The system is made from stainless steel with knife edge seals. Process gases are regulated by thermal mass flow controllers. Process pumping is handled by a rotary vane pump. High vacuum is achieved through diffusion pumps.

The load lock is a simple five way cross that can hold up to four samples. All samples are introduced to and removed from the system through this chamber. In the present design, the load lock may be evacuated to the millitorr level.

After passing through the load lock, the samples are cleaned using a remote hydrogen plasma in a chamber specially designed for this purpose. The cleaning chamber is pumped by a diffusion pump to high vacuum, and the process gas is removed from the chamber by a rotary vane pump through a throttle valve. To assure identical sample cleaning within a run, up to four samples may be simultaneously cleaned in the chamber. In current silicon technology, many different plasma cleaning routes are employed through varying flow rates, substrate temperatures, plasma power, and process pressure. This chamber and its associated power supply is also capable of performing many variations on the plasma cleaning operation.

After cleaning, the samples are transferred to the growth chamber. Like the cleaning chamber, the growth chamber is pumped to high vacuum using a diffusion pump, and the

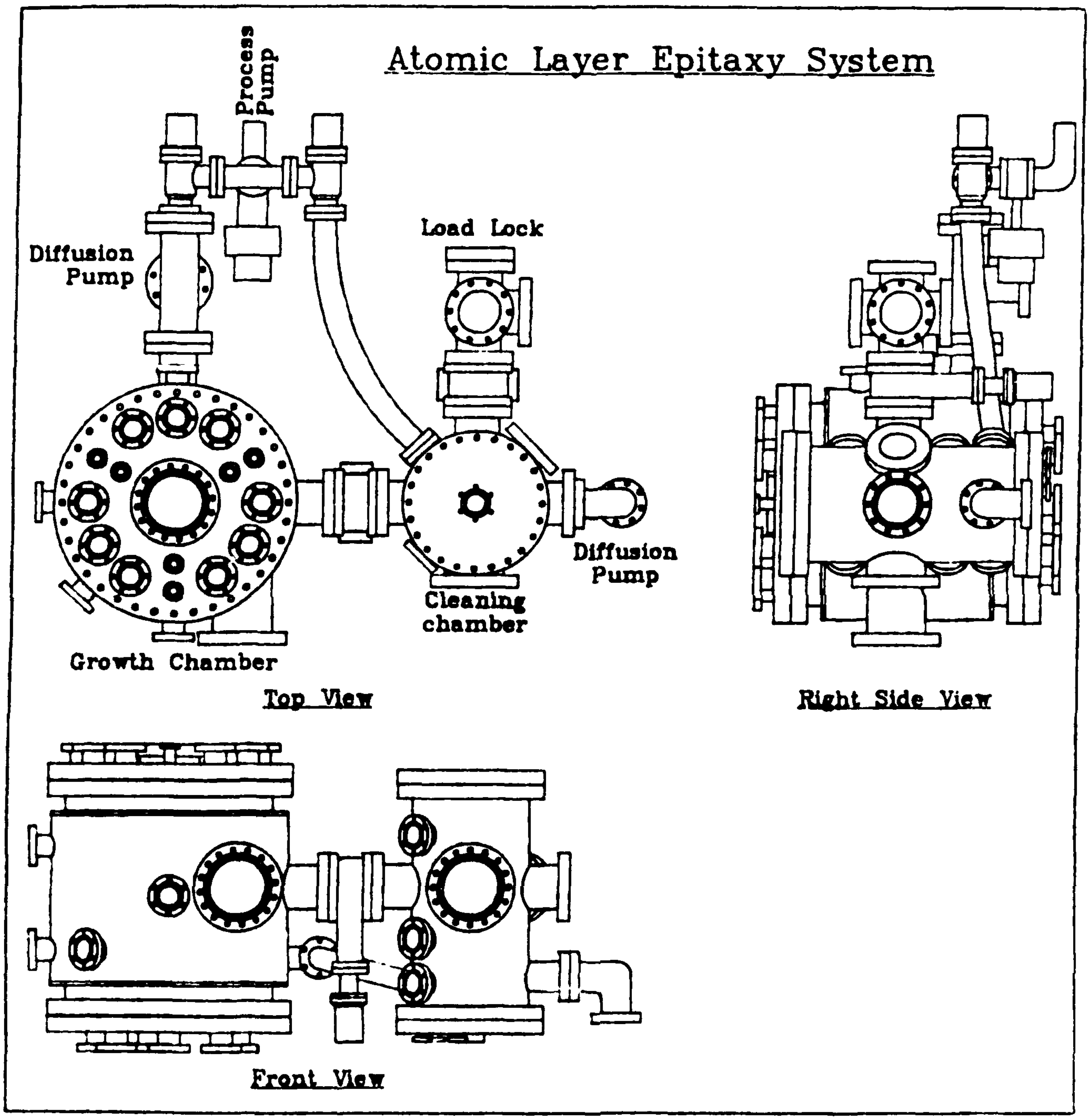


Figure 11. Schematic of Entire ALE growth chamber and associated cleaning chamber and lode lock used by Davis and coworkers for the ALE of Si, SiC and device structures from these two materials.

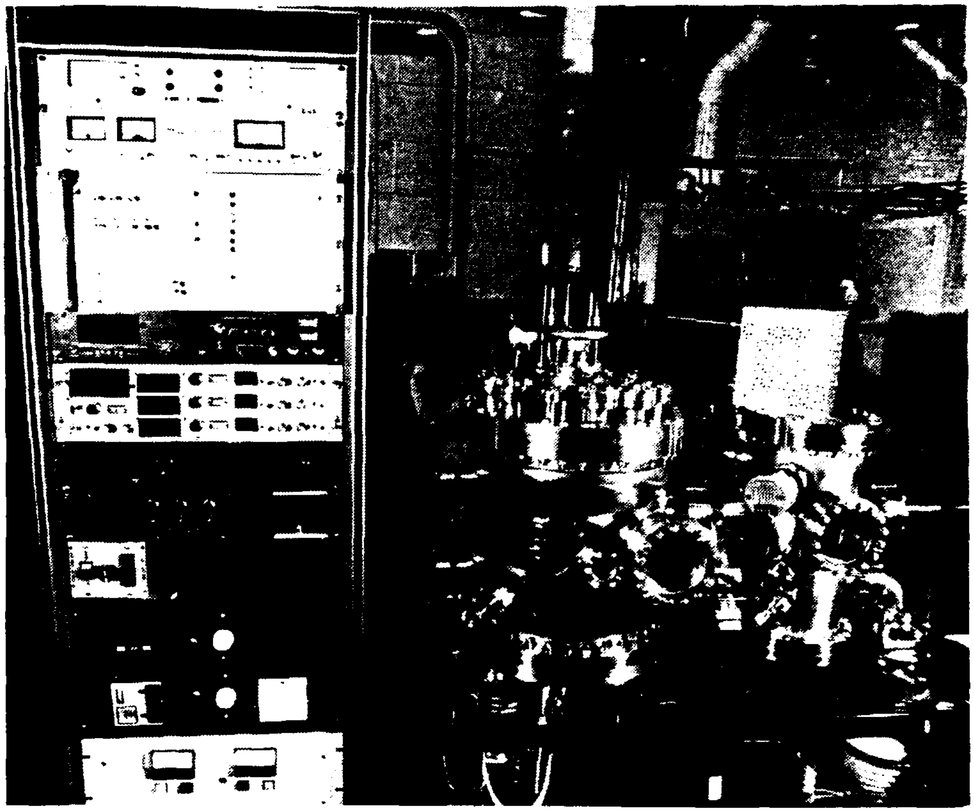


Figure 12. Photograph of completed ALE deposition system used by Davis and coworkers of the ALE of Si, SiC and device structures from these two materials.

product and residual process gases are removed through the throttle valve using a rotary vane pump. Inside the growth chamber, the samples and their travelers are mounted on a revolving, receiver stage above the heater body that will introduce them to as many as eight independent gas fluxes distributed by the vane assembly. A schematic of this growth assembly is shown in cross section in Figure 13. The vane assembly is divided into 16 sections, each supplying a different gas. Thus, as a sample rotates below the vane assembly it will see in turn: Ar-SiH_2Cl_2-Ar -H_2 ... etc. repeated 4 times per revolution. The heater design allows heating of the samples as high as 1000° C, however the present intent is to ascertain process routes which will allow the deposition of both Si and SiC at substantially lower temperatures.

Due to the large mass that will be heated inside the growth chamber, and the possibility for high temperatures, appropriate heat shielding, and a water cooled chamber are employed.

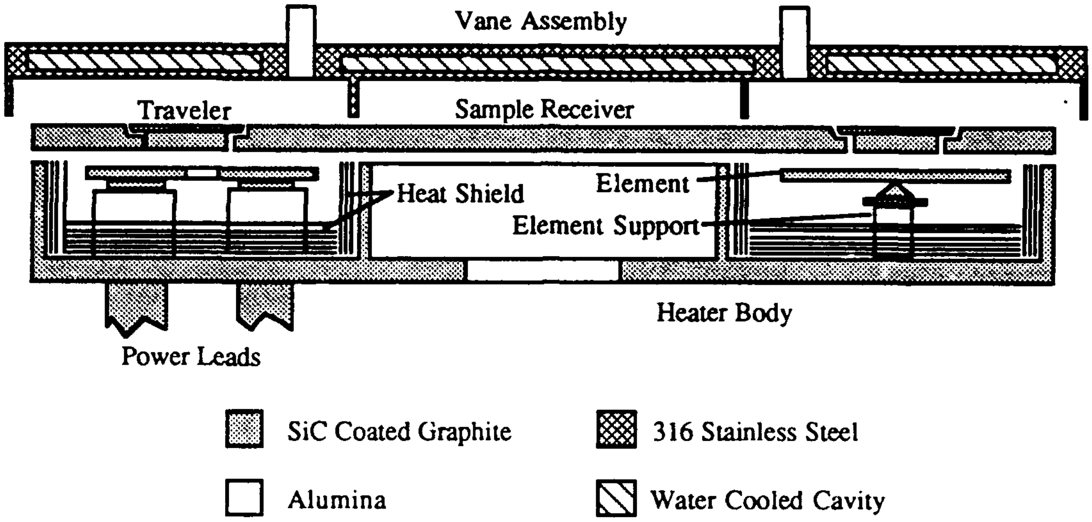


Figure 13. Cross-sectional view of the ALE growth assembly for the deposition of Si and SiC.

The system described above has been completed and commissioned. The cleaning chamber reaches a base of $< 3 \times 10^{-8}$ torr, and the growth chamber has been evacuated to $< 3 \times 10^{-9}$ torr after an appropriate bakeout. Four cleaned samples can be loaded into the system and be under a 10^{-7} vacuum in less than 10 minutes. The heaters in the cleaning and the growth chambers have achieved sample temperatures of 500°C and 960°C, respectively.

Based on the studies with SOLGASMIX–PV discussed in the Section II and other limiting factors, the following initial experimental growth parameters were selected:

Pressure:	1 torr
Temperature:	600°C to 700°C
Gas Flow ratio:	1 Ar:1 SiH_2Cl_2:1 H2
Rotation speed:	20 rpm

To determine the thickness of the ALE films, Secondary Ion Mass Spectroscopy (SIMS) will be employed. For this, heavily As-doped Si(100) wafers ($n=10^{19}$) were used. It is known that at these temperatures, arsenic is not mobile. Given the sensitivity of SIMS for As with the use of a Cs primary ion beam, it is possible to sputter the samples until As is detected. Then using a profilometer, one can determine the depth of the sputtered pit, and hence the film thickness. For our equipment, the optimal film thickness is around 500 angstroms. Since ALE would not necessarily grow a complete monolayer per cycle, a target thickness of 750 angstroms was sought.

For this run, four samples were processed in the following manner:

- Modified RCA clean
- Remote Hydrogen plasma clean
- ALE growth of 750 angstroms (560 cycles = 760 angstroms)

The details of each of these steps is shown in Table II.

TABLE II. The details of each of the process steps used to prepare the Si(100) wafers and load them in the growth chamber prior to the ALE of Si.

1. Modified RCA clean:
   - 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 Buffered Oxide Etch
   - D.I. water rinse

2. Load samples into load lock, transfer to cleaning chamber.

3. Remote hydrogen plasma clean:
   - Heat samples to 310°C
   - Admit Ar at 90 sccm
   - Admit H_2 at 15 sccm
   - Pressure at 300 mtorr
   - RF power 35 watts
   - 30 minutes
   - Heater off, let cool to 250°C
   - RF power off
   - Gases off, evacuate to high vacuum

4. Transfer samples to growth chamber:
   - Heat samples to 620°C
   - Ar at 104 sccm
   - H_2 at 52 sccm
   - $SiCl_2H_2$ at 52 sccm
   - Pressure at 1 torr
   - Rotate 20 rpm for 140 rotations
   - Gases off, heater off
   - Evacuate to high vacuum

The samples are subsequently angle lapped on a 17' holder with 1 micron diamond paste, and polished for 20 minutes with Syton® solution to determine the presence of a film in a manner shown in Figure 14 below. At 620°C, no growth of Si was observed.

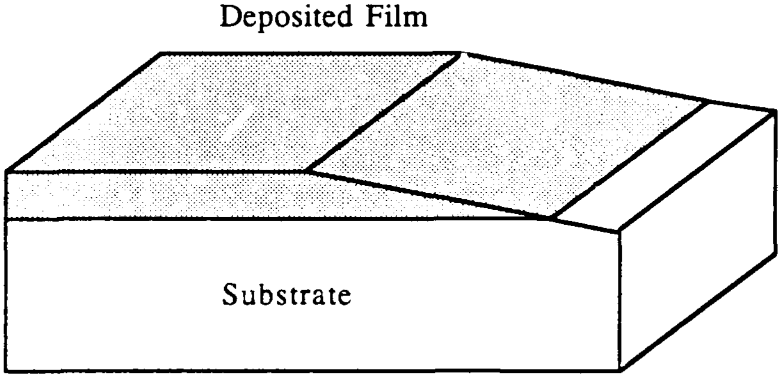
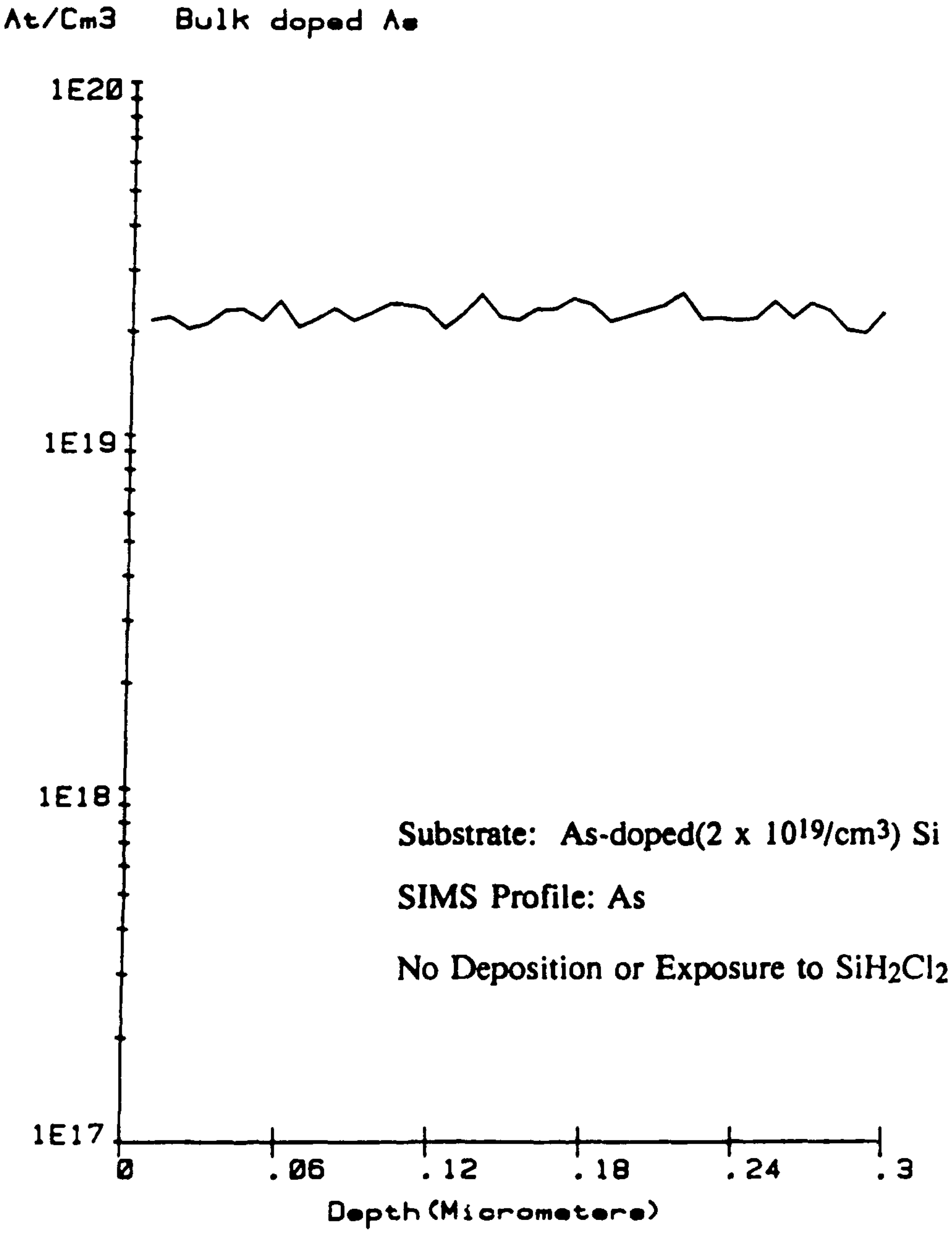


Figure 14. Schematic of angle lapped sample showing the magnification effect on the deposited film and its thickness.

Much additional research will be conducted to fully comprehend the details of the reactions ongoing in the growth chamber. These results will be correlated with those derived from the thermal desorption studies described above.

V. ALE of Silicon Using a Chemical Vapor Deposition System

One of the co-principal investigators of this proposal has also demonstrated ALE of Si using alternate flows of SiH_2Cl_2 and H_2 at 815°C and an As-doped Si substrate. Briefly, As profiles were obtained from the bare substrate (Fig. 15) and with the substrate exposed only to SiH_2Cl_2 for 30 minutes (Fig. 16). As shown in Figure 16, only ≈ 0.01 µm of Si was deposited (the profile from 0.01-0.03 µm shows the beam is already overlapping the Si substrate—as diffusion into the growing film was not detected). By contrast, the alternate introduction of SiH_2Cl_2 and H_2 under the conditions and for the times shown in Figures 17 and 18 strongly indicate that the SiH_2Cl_2 is decomposing to a precursor species (presumably $SiCl_2$) which is chemisorbing to the surface of the Si substrate and subsequently reacting with the introduced H_2 to produce deposition of Si. Some of the SiH_2Cl_2 also decomposed

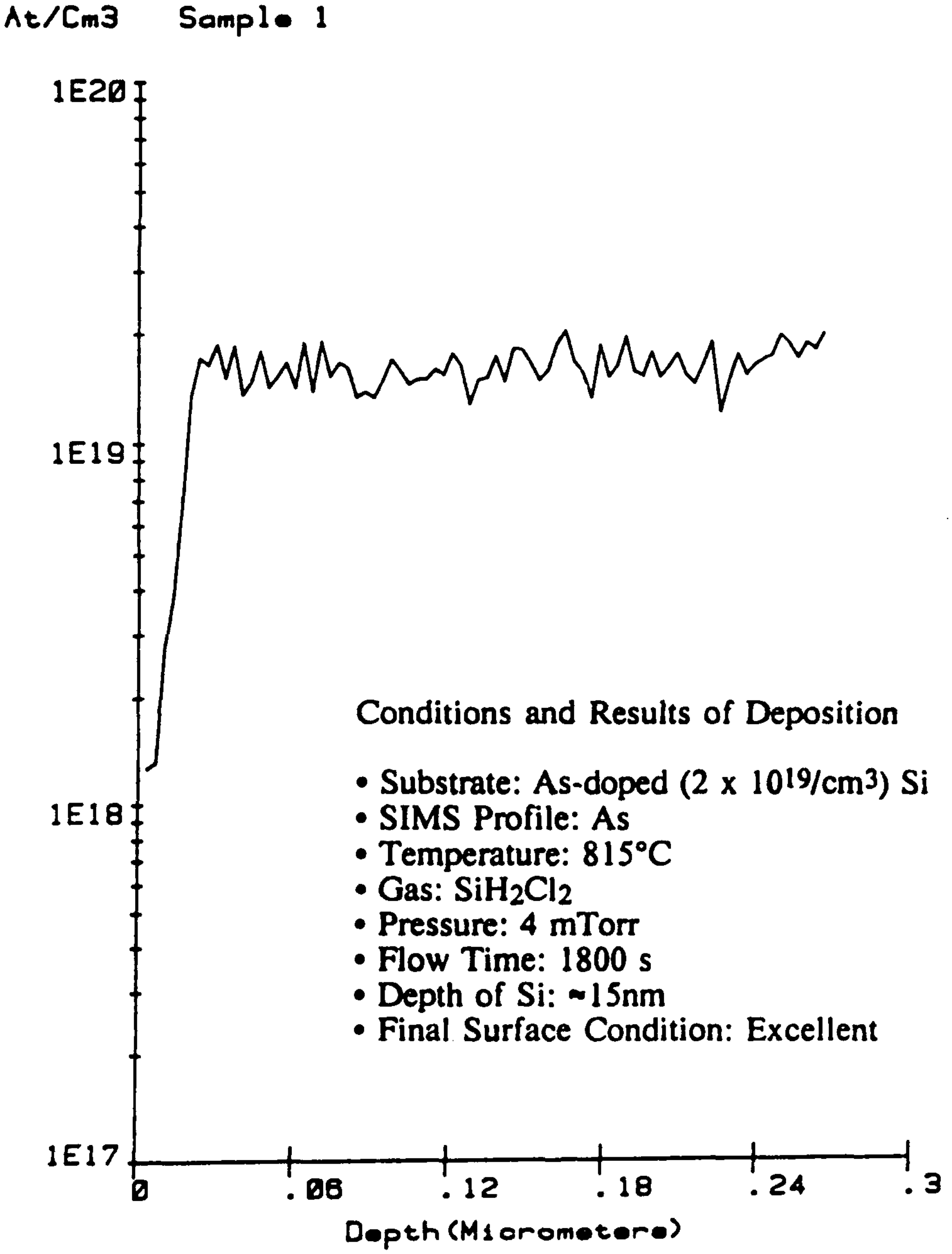


Substrate: As-doped(2 x $10^{19}/cm^3$) Si

SIMS Profile: As

No Deposition or Exposure to SiH_2Cl_2

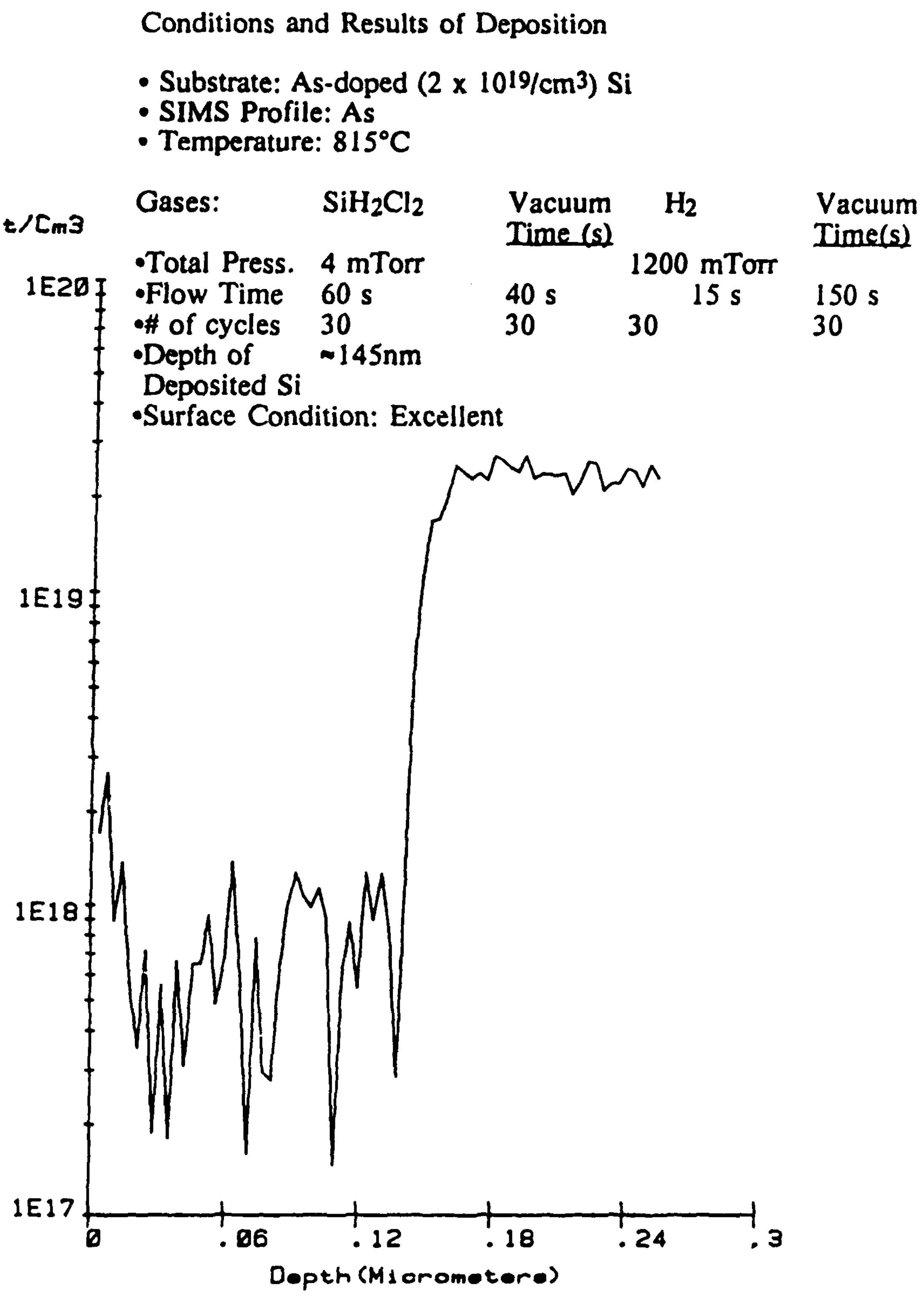
Figure 15. Secondary ion mass spectrometry profile of As-doped Si substrate used for Si ALE research.



Conditions and Results of Deposition

- Substrate: As-doped (2 x $10^{19}/cm^3$) Si
- SIMS Profile: As
- Temperature: 815°C
- Gas: SiH_2Cl_2
- Pressure: 4 mTorr
- Flow Time: 1800 s
- Depth of Si: ~15nm
- Final Surface Condition: Excellent

Figure 16. SIMS profile of As showing slight deposition of Si from 0 – 0.01 microns from decomposition of SiH_2Cl_2 at 815°C on an As-doped Si substrate.



Conditions and Results of Deposition

- Substrate: As-doped (2 x $10^{19}/cm^3$) Si
- SIMS Profile: As
- Temperature: 815°C

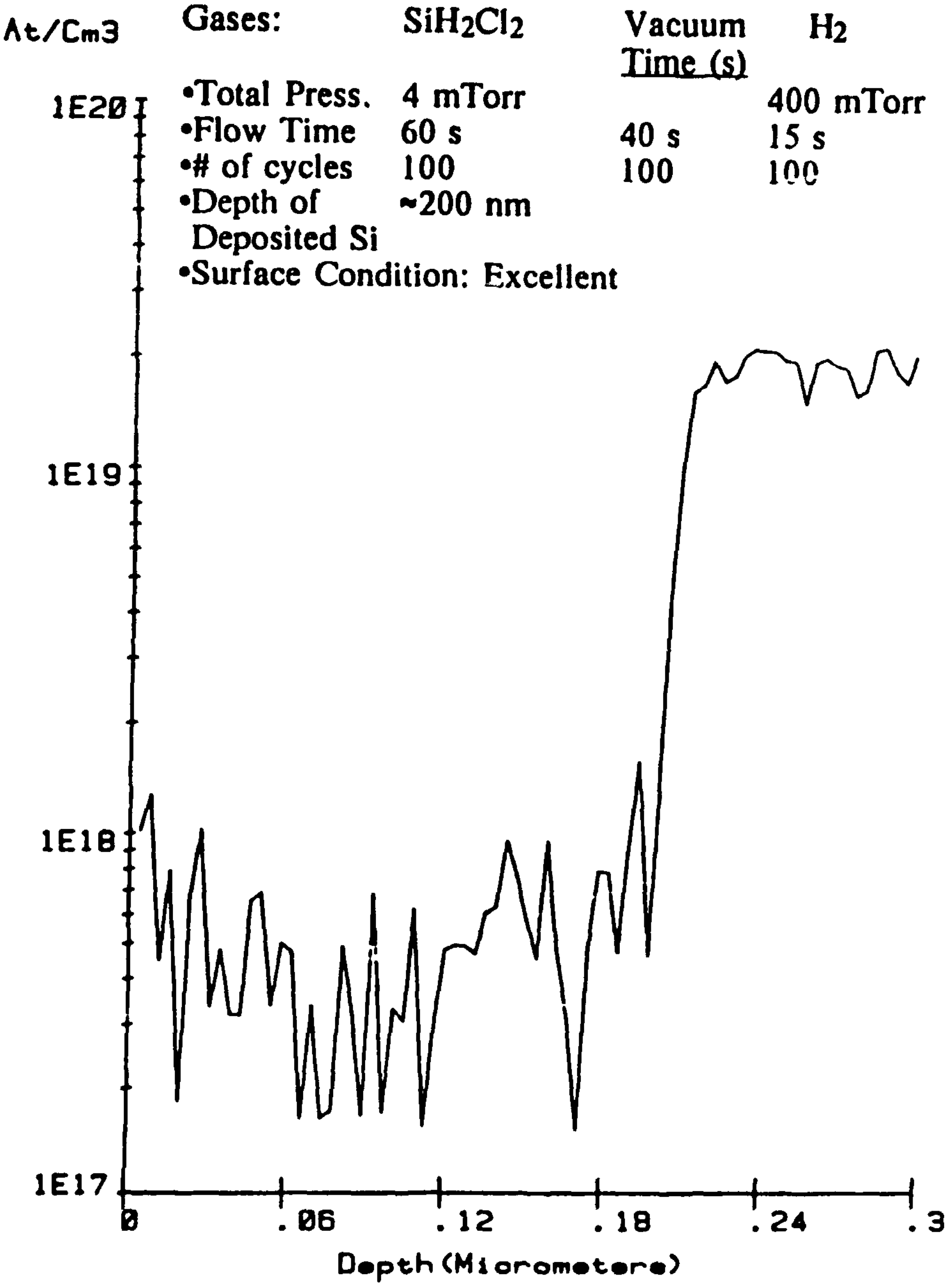
Gases:	SiH_2Cl_2	Vacuum Time (s)	H_2	Vacuum Time(s)
•Total Press.	4 mTorr		1200 mTorr	
•Flow Time	60 s	40 s	15 s	150 s
•# of cycles	30	30	30	30
•Depth of Deposited Si	~145nm			

•Surface Condition: Excellent

Figure 17. SIMS profile of As showing deposition of ca. 0.14 microns of Si by atomic layer epitaxy via the alternate introduction of SiH_2Cl_2 and H_2 under the conditions shown in the table in the figure.

Conditions and Results of Deposition

- Substrate: As-doped (2 x $10^{19}/cm^3$) Si
- SIMS Profile: As
- Temperature: 815°C



Gases:	SiH_2Cl_2	Vacuum Time (s)	H_2	Vacuum Time(s)
•Total Press.	4 mTorr		400 mTorr	
•Flow Time	60 s	40 s	15 s	100 s
•# of cycles	100	100	100	100
•Depth of Deposited Si	~200 nm			

•Surface Condition: Excellent

Figure 18. SIMS profile of As showing deposition of ca. 0.20 microns of Si by atomic layer epitaxy via the alternate introduction of SiH_2Cl_2 and H_2 under the conditions shown in the table in the figure.

on its own, as the initial exposure without H_2 resulted in ≈ 50 unit cells of Si while the 30 alternate exposures produced 400 unit cells and the 100 alternate exposures (with shorter exposures to H_2) resulted in ≈ 450 unit cells. It is believed that some of the SiH_2Cl_2 is not being pumped away in the intervening evacuation. This is indicated by the proportionally smaller thickness of Si when the pumping time increased from 30s to 100s. Reducing the temperature to 770°C did not result in the deposition of Si under any conditions.

VI. Summary

The primary focus of the research for this grant has been the atomic layer epitaxy of Si; however, the ALE of SiC has also received serious consideration. A computer assisted study, based on the free energy minimization of a thermodynamic system undergoing equilibrium reactions has shown that the progressive decomposition of SiH_2Cl_2 (the Si precursor of choice in this study) results in the products of $SiCl_2$, H_2, SiH_2Cl_2, HCl and Si. Moreover, above 600°C, $SiCl_2$ is stable. Thus $SiCl_2$ adsorbed onto the surface will not decompose. It is predicted to react with H_2, forming Si on the surface. The experimental program has primarily involved the design and fabrication of equipment to (1) determine the surface adsorption, desorption and chemical reaction routes necessary to achieve the ALE of Si and SiC and (2) produce Si layers of a desired thickness via ALE processes. The ALE of Si was achieved at 815°C using available chemical vapor deposition equipment and information regarding the chemisorption and decomposition of dichlorosilane on the Si(100) surface in the presence of H_2. Reducing the temperature to 770°C did not result in the deposition of Si under any conditions of flow rate or total pressure.

All growth systems are now operational. The future research will be devoted to the ALE of Si and C as it pertains to the growth of SiC as well as the ALE of diamond and CeO_2. Studies will examine the effects of temperature, pressure, and rotational speed on film quality and coverage per cycle. The results of the thermal desorption studies will be invaluable in selecting the correct starting gas species and the temperature and pressure regimes wherein ALE of these materials can be achieved. The films will be analyzed by SIMS, TEM, SEM and optical microscopy. It should also be noted that the ALE of gallium nitride and aluminum nitride will be addressed. Finally the growth of some of these materials (e.g., SiC) by ALE within a Si(100) trench will be studied.

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