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System for the Growth of Bulk SiC Crystals by Modified CVD Techniques

Final Report

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System for the Growth of Bulk SiC Crystals by Modified CVD Techniques

I. ABSTRACT

The goal of this program was the development of a SiC CVD groe growth of films thick enough to be useful as psuedo-substrates. The cold-walled CVD system was designed, assembled and tested. Extrapolating from preliminary evaluation of SiC films grown in the system at relatively low temperatures indicates that the growth rate at the final temperatures will be high enough to make our approach practical. Modifications of the system to allow high temperature growth and cleaner growth conditions are in progress. This program was jointly funded by Wright Laboratory, Materials Directorate and NASA LeRC and monitored by NASA.

II. INTRODUCTION

One of the critical limitations in the use of electronics in the automotive and aerospace industries is the ability to operate at high power and/or elevated temperatures. Examples of such applications include airborne (and shipborne) power supplies, high power electronic controls (for automobile, tank, jet engines), high temperature sensors, etc. The clear front-runner technology in fulfilling these requirements is based on the wide bandgap semiconductor silicon carbide (SiC). The state of Ohio is in a very strong position to take the leadership in introducing and developing the new technology which will provide the needed high temperature and high power electronics. The reason for this is the unique concentration in Ohio of organizations working in and possibly benefitting from SiC technology. This includes government laboratories involved in SiC technology (WPAFB and NASA), automotive and aerospace companies, component supplier companies and universities. If successful this project can be of benefit to many of these organizations by providing the material needed for their own development efforts.

Silicon carbide (SiC) is a material historically well-known for its high wear resistance, and chemical and thermal stability. SiC single-crystals are extremely hard and impervious to chemical attack (by acids and bases). SiC is the only intermediate phase in the Si-C equilibrium diagram. It forms a number of different crystal structures called polytypes which differ only in the stacking sequence of double layers of Si and C atoms. Depending on the stacking sequence different lattice structures are obtained: cubic, hexagonal, rhombohedral. The polytype is identified in the Ramsdell notation by the number of layers before the sequence repeats itself and by the crystal structure. For example, the 4H polytype has four double layers before repeating itself (ABAC ABAC....) and has a hexagonal structure.

More recently, SiC has received renewed attention due to its potential usefulness in semiconductor devices. The most common polytypes used for electronic device applications are cubic 3C-SiC (or b-SiC) and hexagonal 6H-SiC. SiC is the material of choice for electron device applications involving extremes of temperature, radiation, power and frequency. A comparison of the properties of SiC, Si and GaAs is shown in Table 1, along with the related advantages of SiC-based devices. SiC is a wide band-gap semiconductor with E_g of 2.2 and 2.9 eV in the cubic (3C) and hexagonal (6H) polytypes, as opposed to 1.1 eV for Si and 1.4 for GaAs. The SiC melting point is much higher than that of either Si or GaAs. This results in a current ability to operate at temperatures in excess of 600°C and in principle as high as 1200°C. The electric field breakdown in SiC is 10X higher than that of Si and GaAs, which can lead to improved high power and high density devices. SiC also has an excellent thermal conductivity and radiation-resistance, as well as being impervious to most acids, bases and other corrosives. Interestingly, while SiC has many superior properties to Si, it also has several important similarities. Most important among these is the fact that the oxidation of SiC results in a high quality SiO_2 layer similar to that obtained during thermal oxidation of Si.

	SiC	**GaAs**	**Si**	**Advantages of SiC-Based Devices**
Band-gap energy - E_g [eV] 6H 3C	 2.9 2.2	1.43	1.12	• High Rad. Environment Operation • Blue Light Emission • UV Detection • Ultra Low Leakage
Maximum Operating Temperature [°C] 6H 3C	 > 1200 > 800	60	360	• High Temperature Operation
Breakdown Electric Field [V/cm (for 1000 V operation)]	$2.5x10^6$	$3x10^5$	$2.5x10^5$	• High Power • High Density Integration
Thermal Conductivity [W/cm-K@ RT]	4.9	0.5	1.5	• High Thermal Conductivity (greater than any metal)
Saturated Electron Drift Velocity [cm/sec (@ $\leq 2x10^5$V/cm)]	$2.0x10^7$	$1.0x10^7$	$1.0x10^7$	• High Frequency Operation in High Electric Fields
Oxidation Properties	excellent	poor	excellent	• Superior Passivation Capability
Resistance to Acids, Other Corrosives	excellent	poor	fair	• Superior Physical Stability

Table 1 Properties of SiC, GaAs and Si materials

Two methods have been commonly used to grow SiC: sublimation and CVD. In the sublimation process, the source material (SiC powder) is heated up to above 2100°C, while a single crystal SiC seed also located in the furnace is heated to a lower temperature. SiC-related molecules sublimed from the source redeposit on the cooler seed, leading to the growth of an ingot. Successful bulk growth of 6H-SiC by sublimation has been achieved by many researchers [1-4]. Almost all of the growth chambers are made of high-quality graphite. The heating power is provided by either rf induction or resistive heating. Ar ambient has been always used to: (1) suppress evaporation from the SiC source and SiC seed as well as from the graphite chamber during heat-up; (2) provide a desired vacuum level for growth. The substrates are usually 6H-SiC crystals made by the Acheson process. The growth temperatures range from 1800 to 2400°C. The growth pressure ranges from ~1 to 760 Torr. Typical growth rates are from 100μm/hr to 4 mm/hr depending on growth temperature and pressure.

CVD is known for its ability to obtain single crystal material at growth temperatures lower than the melting point. CVD has also been shown [5 - 15] to produce monocrystalline SiC thin films on various substrates at a reasonable growth rate (several μm/hr) at temperatures between 1200 - 1350°C with separate C- and Si-bearing precursors. Even lower growth temperatures (to 1000°C) has been reported [16, 17] in a few cases. The C-bearing precursor is typically a simple hydrocarbon, such as propane, ethylene, or acetylene. The Si-bearing gas is either a silane or chlorosilane gas, which are both highly toxic and pyrophoric.

Alternative precursors for SiC deposition by CVD have been investigated. In general, a precursor designed for this purpose [18] would contain directly bonded Si and C atoms and would decompose at relatively low temperatures into a film of stoichiometric SiC. Examples of such precursors reported to date include methylsilane [19, 20] (CH_3SiH_3, $MeSiH_3$), methyltrichlorosilane [21] (CH_3SiCl_3, MTS), tetramethylsilane [22] ($\{CH_3\}_4Si$, TMS), diethylsilane [22] ($\{C_2H_5\}_2SiH_2$, DES), tripropylsilane [22] ($\{C_3H_7\}_3SiH$, TPS), hexamethyldisilane [23] ($\{CH_3\}_6Si_2$, HMDS), dimethyldichlorosilane [24] ($\{CH_3\}_2SiCl_2$, DMDS).

Compared to the sublimation technique, CVD growth of SiC films is relatively slow. If this growth rate can be increased dramatically, CVD will be a strong competitor to the sublimation technique for SiC growth. Efforts are under way in this direction at the University of Cincinnati. Recently, a new class of single-source organosilane SiC precursor with a cyclic structure has been investigated [25, 26, 27]: mono- and di-silacyclobutanes. Silacyclobutane ($c\text{-}C_3H_6SiH_2$, SCB) is a cyclic molecule containing one Si atom bonded to two C atoms in a four-member ring structure. SCB has been synthesized by the Dow Corning Corp. The SCB ring structure contains significant strain energy, thereby reducing the decomposition temperature. Such a precursor possesses many advantages, including the simplicity of single source organosilane, the decreased operational hazards compared to silane, the possibility of deposition with pre-existing Si-C bond. Monocrystalline SiC films have been deposited on Si using SCB as described below.

II. SIC TECHNOLOGY

We have been pursuing SiC technology for the past six years. As part of our SiC program, we have investigated: (1) SiC thin film growth by rapid thermal CVD [28 - 30]; (2) SiC-on-Si growth mechanisms [31, 32]; (3) growth of SiC nanometer-scale films [33, 34]; (4) atomic force and scanning tunneling microscopy of SiC surfaces [35, 36]; (5) reactive ion etching of SiC [37 - 39]; (6) device structures, including SiC/Si heterodiodes, Schottky diodes and 3C- and 6H-SiC [40, 41].

For the past two years we have been using SCB as a precursor for SiC growth with the aim of lowering the growth temperature. The deposition experiments using SCB are carried out in a rapid thermal CVD system equipped with a quartz chamber, IR lamps, a molecular drag pump, etc. SCB is a liquid at room temperature (boiling point ≈ 42°C) with a vapor pressure of approximately 400 Torr, which enables its use without the need for a bubbler. The SCB was chemically synthesized by fractional distillation [42, 43]. The SCB reaction was performed at 5 Torr with a 5 sccm flow rate accompanied by a 2 lpm H_2 flow. The reaction time for the experiments described here was 10 min.

Transmission electron microscopy (TEM) and diffraction (TED) have been used to investigate the structure of relatively thin layers obtained by a short reaction time. In Fig. 1 are shown TEM plan view image and TED pattern of a SiC film grown on a Si (100) substrate at 900°C. The SiC film exhibits a TED pattern which indicates a crystalline (periodic array of spots) and poly-crystalline structure.

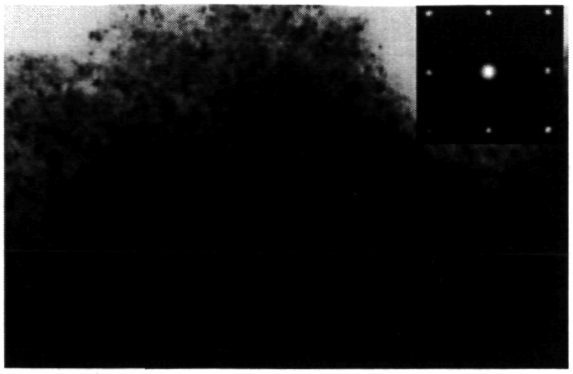


Fig. 1 TEM and TED pattern of SiC films grown with SCB on Si (100) substrate at 900°C.

Thicker SiC films were grown with SCB on Si (100) and (111) substrates by increasing the reaction time to 10 min. At a reaction temperature of 900°C, the resulting growth rates were 3 and 6 μm/hr for the (111) and (100) substrates, respectively. Plan-view and cross-sectional SEM microphotographs of these SiC films are shown in Fig. 2. The surface morphology of the SiC film grown on Si (111) is considerably smoother than that of SiC grown on Si (100). The SiC/Si interface appears to be uniform in both cases.

Conventional (θ-2θ) x-ray diffraction (XRD) spectra for the thicker SiC films grown at 900°C on (100) and (111) Si substrate are shown in Fig. 3a and 3b. The SiC film grown on (100) Si displays major peaks for the SiC (200) reflection at 41.44° and the SiC (400) reflection at 90.13°. Only very small peaks were observed for SiC (111) and (220), indicating that the dominant film structure is (100) with minor components of other orientations. The full width at half-maximum (FWHM) of the SiC (200) peak is 0.45°. If we remove the 0.08° system broadening , we obtain a corrected value of 0.315°. The XRD spectrum of the SiC film grown on Si (111) exhibits a very large and sharp peak at the (111) reflection (35.63°). With the exception of the second order (222) reflection at 75.46°, no other SiC peaks are observed, indicating monocrystallinity of the grown film. This has been verified by the TED inset in Fig. 3b. The measured FWHM of the SiC (111) peak is 0.17° and the corrected value is 0.125° or 450 arc-sec.

In summary, monocrystalline, stoichiometric β-SiC thick films have been grown on Si using CVD with SCB. The grown films can serve as seed for subsequent bulk growth in two ways: (1) SiC film with Si substrate; (2) SiC film only, with the Si substrate being dissolved. For the latter case, thicker films are needed for handling. This can be achieved by the extension of the reaction time. In addition, a 6H-SiC crystal wafer can also be used as the seed. In all occasions, since wafers are the starting material this approach can lead to large-area SiC growth.

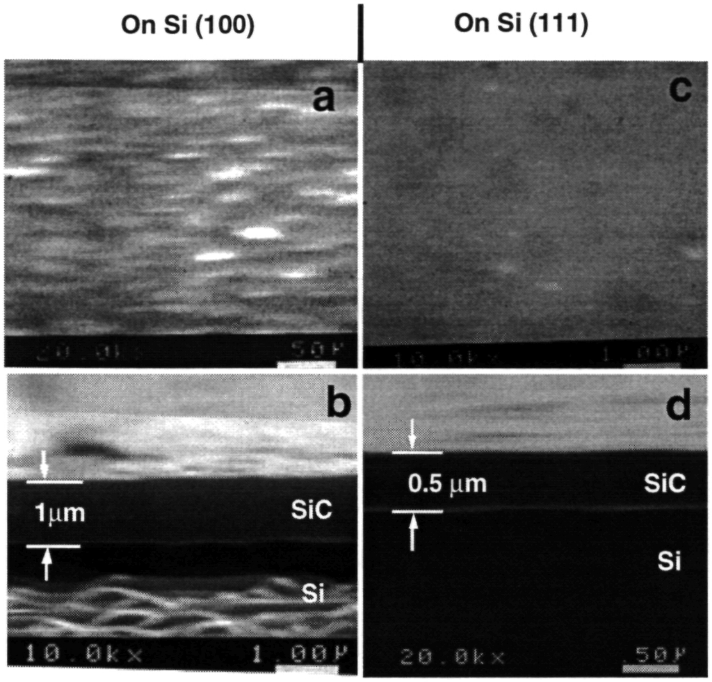
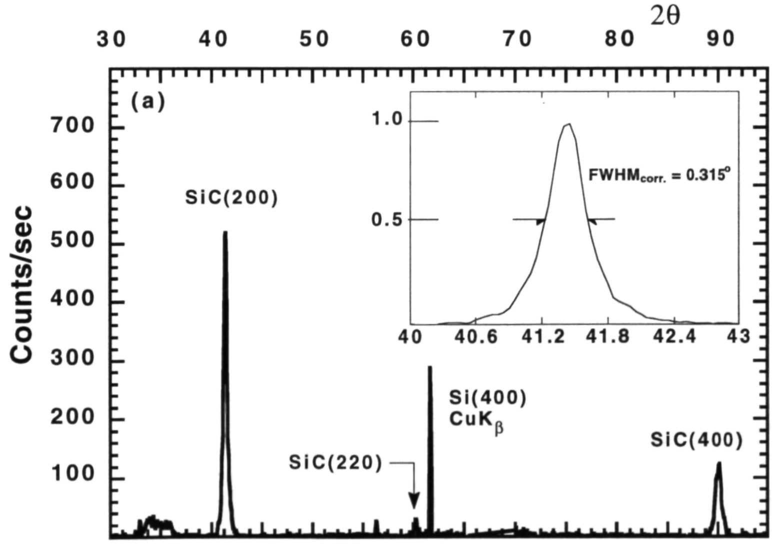


Fig. 2 Plan-view and cross-sectional SEM micrographs of SiC films grown for 10 min at 900°C on AP carbonization: (a), (b) on Si (100); (c), (d) on Si (111).



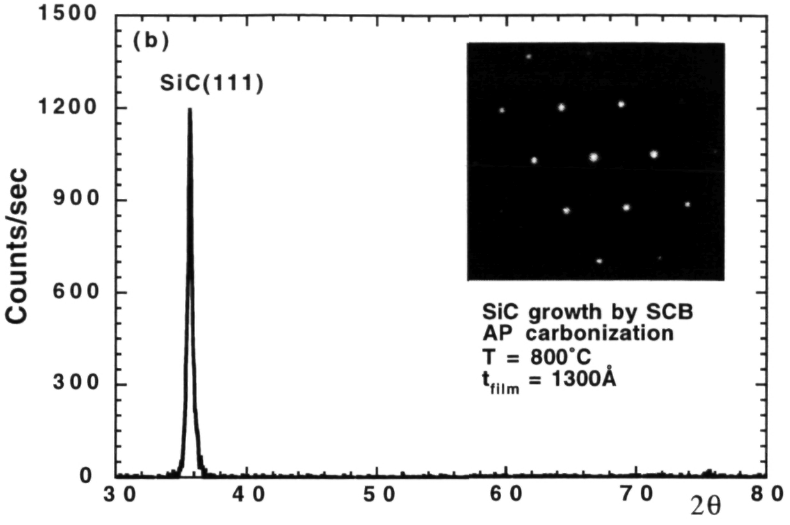
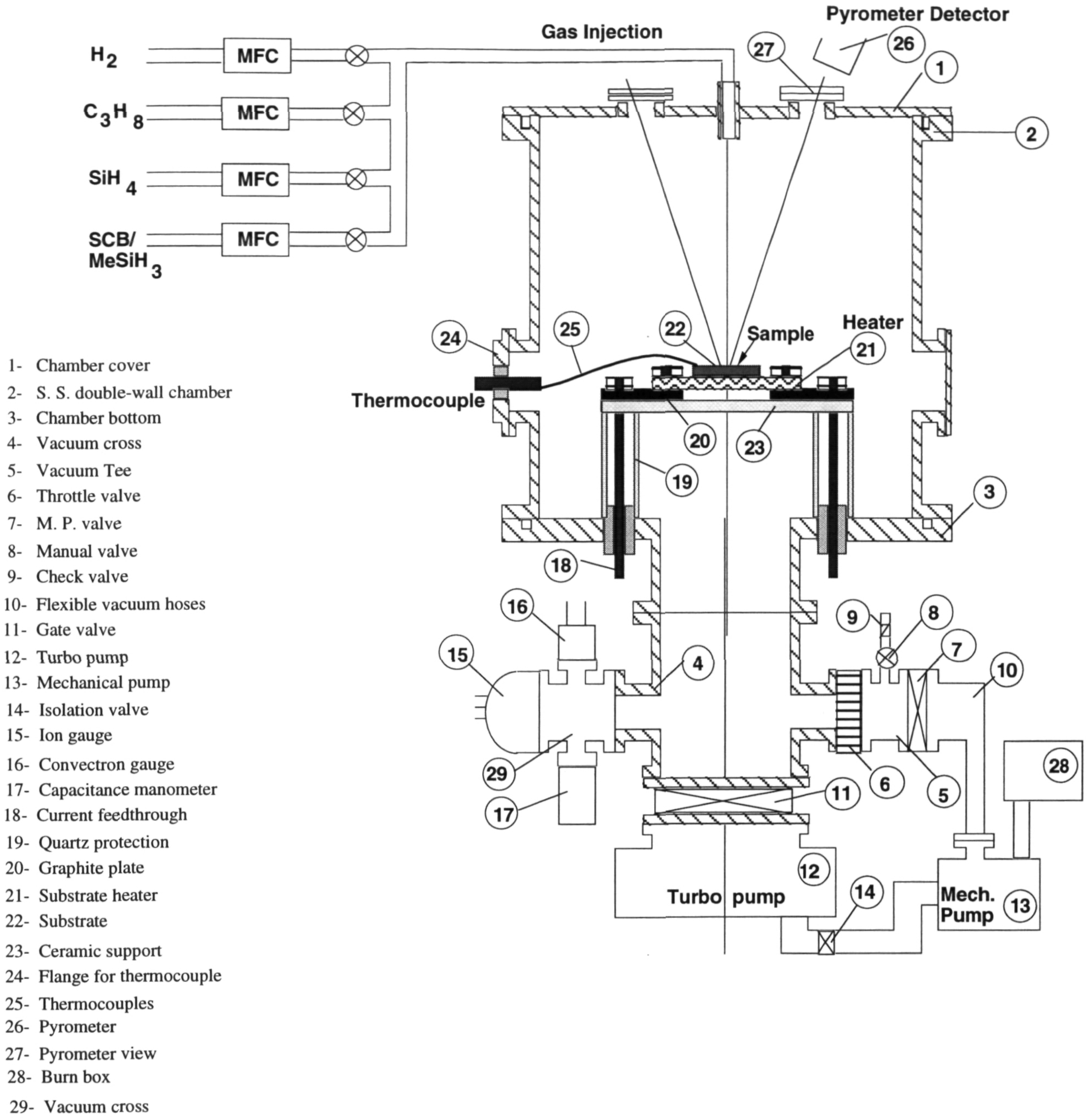


Fig. 3 XRD spectra of SiC films grown at 900°C for 10 min: (a) on Si (100); (b) on Si (111).

III. GROWTH SYSTEM DESIGN, IMPLEMENTATION, AND OPERATION

§ 1. Current System

As part of the program, a growth system suitable for thick film SiC CVD has been designed and assembled. A schematic diagram of the system is shown in Fig. 4. A photograph of the system is shown in Fig. 5. The growth chamber is made of stainless steel with metal gasket sealing. The inner chamber surface is mirror finished to reduce gas adsorption and outgassing. A turbo pump backed with a mechanical pump is capable of achieving vacuum of 10^{-8} torr. The growth chamber is isolated from the turbo pump by a gate valve. Low pressure growth is achieved by a throttle valve and the mechanical pump. The vacuum is monitored by a convectron gauge and an ion gauge. The growth pressure is monitored by a capacitance manometer. To date we have operated the chamber to a growth temperature of 1000°C. Sample temperature as high as 1800°C will be achieved by a molybdenum resistive heater to be installed in the near future. The temperature is measured and controlled by a thermocouple and/or a pyrometer. The system is equipped with four gas lines with electronic mass flow controllers. Silane and propane as well as organosilanes such as methylsilane and sylaclobutane can be used for SiC formation.



1- Chamber cover
2- S. S. double-wall chamber
3- Chamber bottom
4- Vacuum cross
5- Vacuum Tee
6- Throttle valve
7- M. P. valve
8- Manual valve
9- Check valve
10- Flexible vacuum hoses
11- Gate valve
12- Turbo pump
13- Mechanical pump
14- Isolation valve
15- Ion gauge
16- Convectron gauge
17- Capacitance manometer
18- Current feedthrough
19- Quartz protection
20- Graphite plate
21- Substrate heater
22- Substrate
23- Ceramic support
24- Flange for thermocouple
25- Thermocouples
26- Pyrometer
27- Pyrometer view
28- Burn box
29- Vacuum cross

Fig. 4 Schematic diagram of the SiC thick film growth system.

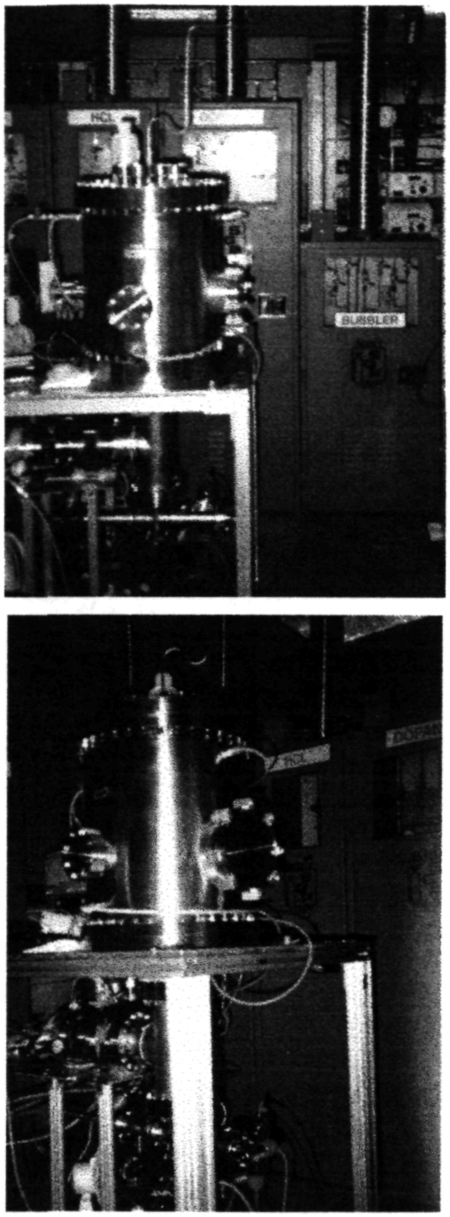


Fig. 5 Photographs of the SiC
thick film growth system.

§ 2 *Preliminary Operation*

It has been shown in the *SiC Technology* section that monocrystalline SiC thin films can be grown with SCB. We have shown the potential for an increase in the growth rate with the current growth conditions at higher growth temperatures. The SiC growth rate from CVD with SCB is plotted in Fig. 6 as a function of temperature from 700 to 900 °C . The extrapolated SiC growth rate at 1400°C is ~0.2 mm/hr. In order to obtain this high growth rate, it is necessary to obtain reaction conditions under which a high enough transition point into the diffusion-dominated reaction region is achieved. In addition, our cold-wall chamber proved necessary to eliminate premature deposition on the chamber walls.

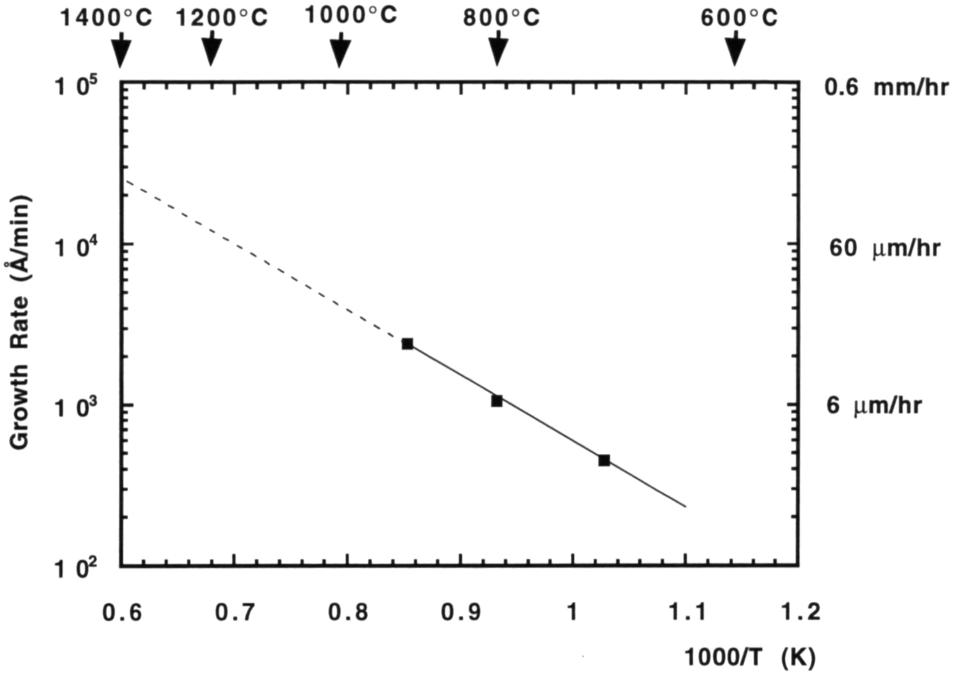


Fig. 6 SiC growth rate with SCB as a function of temperature.

§ 3 *Future Modifications*

As mentioned in section *§1*, we plan to install a molybdenum resistive heater capable of reaching temperatures near 1800°C. The SiC CVD growth system will be retrofitted with a load lock and the molybdenum heater mounted on a transferable stage. The load lock will allow lower base pressures and reduced contamination of the CVD system. The transferable heater stage will have a receiver mount inside the chamber with leads for power and a thermocouple to provide feedback to the controller which will stabilize the input current at desired growth temperature. A schematic of this system is shown in Fig. 7.

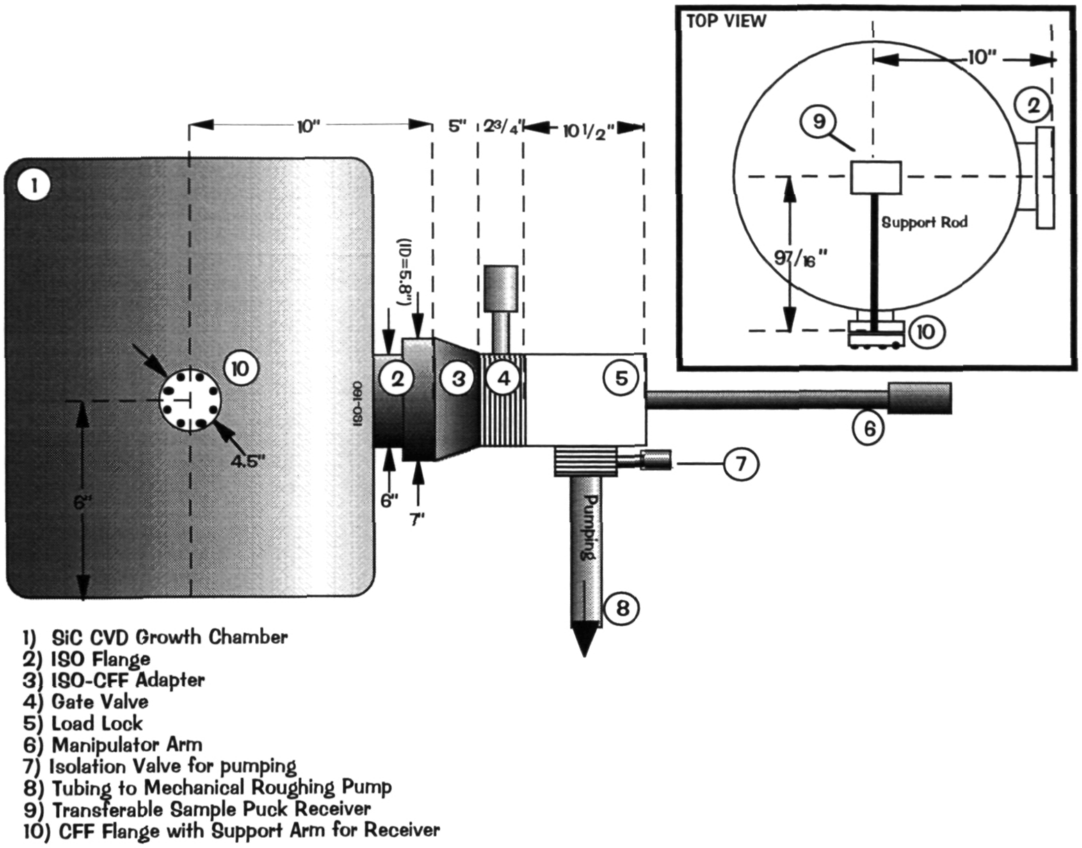


Fig. 7 Load lock mechanism for SiC CVD growth chamber.

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