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

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As the first step in the chemically-controlled atomic layer epitaxy (ALE) of SiC, research has been conducted regarding the ALE of Si. Good quality single crystal epitaxial films of Si on off-axis (100) Si have been produced in the Davis group. Equipment related to the deposition of high-quality Si only is virtually completed in the Bedair group. Dichlorosilane has been used (or is being considered) by both groups. A deposition system that will achieve ALE of CeO_2 on Si has also been designed.

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I. Atomic Layer Epitaxy of Silicon Carbide (Davis Laboratory)

A. Introduction

This report details progress in the continuing research program on Atomic Layer Epitaxy (ALE) of Group IV Materials conducted in the laboratories of Dr. R. F. Davis. At present, research concerned with the growth of films on silicon via atomic layer epitaxy is being conducted as the first step to producing films of silicon carbide by ALE. Several films of silicon have been grown on (100) silicon substrates with dichlorosilane in our large ALE reactor. These films were studied using secondary ion mass spectroscopy (SIMS), scanning electron microscopy (SEM), and reflection high energy electron diffraction (RHEED). Good quality epitaxial single crystal films of silicon have been grown with dichlorosilane gas at 670°C. In the attempt to lower the growth temperature, thermal hydrogen cracking filaments have been installed in the system to create atomic hydrogen that is expected to aid growth.

B. Experimental Procedure

1. Technique

To explain the technique involved in chemically-terminated ALE, a process to grow silicon will be surveyed. Firstly, the Si surface is exposed to a flux of SiH_2Cl_2, the hydrogen atoms break away from the molecule as the SiH_2Cl_2 nears or is adsorbed onto the heated substrate and a monolayer of Si having a terminating layer formed by the remaining chlorine atoms now resides on the Si surface. This molecular surface configuration now prevents the adsorbtion of another layer of Cl-terminated silicon until the chlorines are removed. Secondly, a flux of hydrogen impinges on the substrate, and removes the chlorine termination via the formation of HCl and leaves a virgin silicon surface. The cycle is then repeated. The technique may be expanded to allow growth of compound semiconductors.

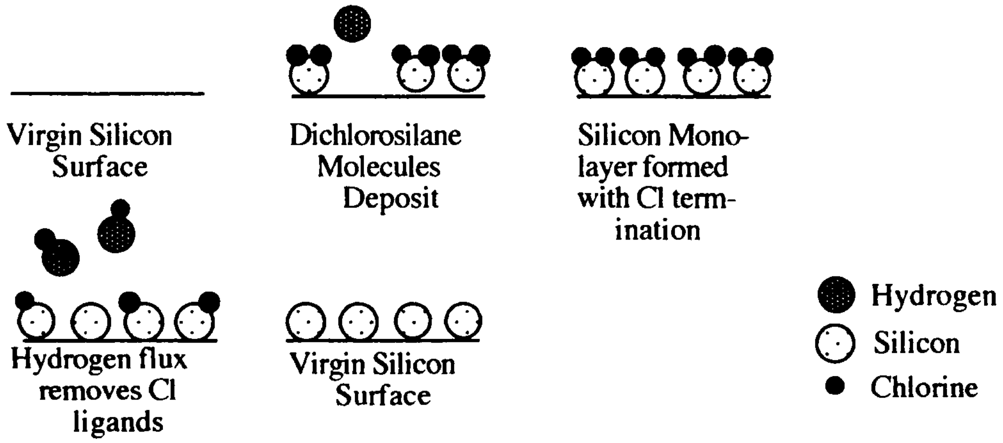


Figure 1.

2. *System*

To accomplish ALE, a 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 remote hydrogen plasma cleaning chamber, and a growth chamber. The system is high vacuum capable, and is of stainless steel with knife edge seals. Base pressure in the cleaning and growth chambers is in 10^{-9} torr range. Process gases are regulated by thermal mass flow controllers, process pumping is handled by a rotary vane pump, and high vacuum is achieved through diffusion pumps.

Growth chamber. After cleaning, the samples are transferred to the growth chamber where the samples on their travelers are mounted on a revolving, receiver stage above the heater body that will introduce them to up to eight independent gas fluxes distributed by the vane assembly. Figure 2 depicts the internal arrangement of the growth chamber. The vane assembly is divided into 16 sections, each supplying a different gas, so as a sample rotates below the vane assembly it will see the sequence: Ar-SiH$_2$Cl$_2$-Ar-H$_2$ ... etc, repeated 4 times per revolution. Heater design allows heating the samples as high as 1000°C, however we process at substantially lower temperatures. Due to the potential for high temperature employment of the system, appropriate heat shielding, and a water cooled chamber are also a part of the design. In addition, thermal hydrogen cracking filaments have been installed in those zones that handle the hydrogen.

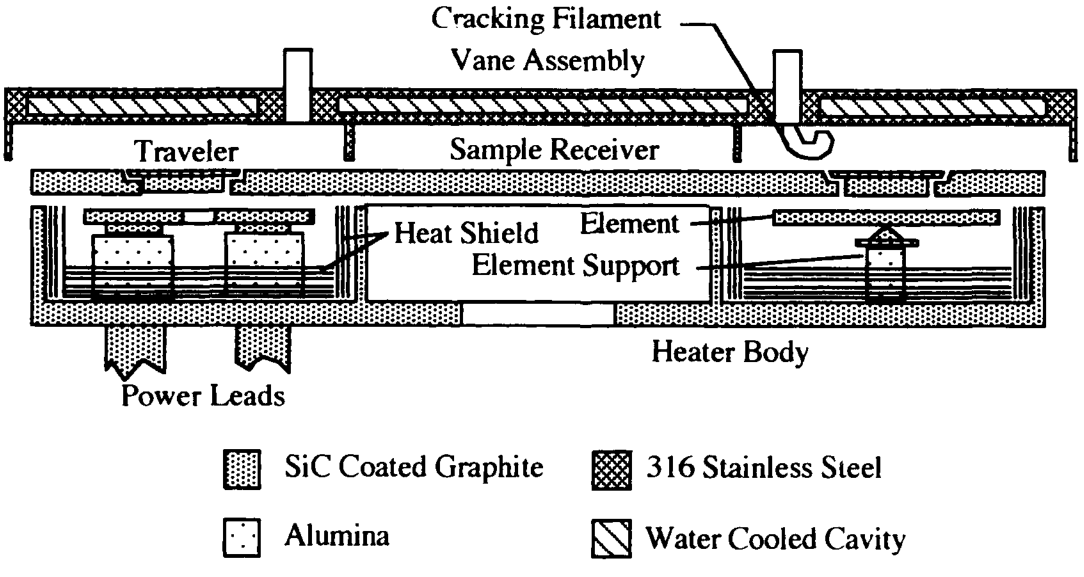


Figure 2.

3. *Sample Processing*

Sample preparation and loading. All samples have been grown on heavily arsenic doped silicon (100) wafers having a resistivity of <.005 ohm/cm. 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 solution to strip the oxide, quickly loaded into the load lock and transferred to the plasma cleaning chamber. The samples are under 10^{-7} torr vacuum within 15 minutes.

Plasma cleaning samples. During plasma cleaning, the samples are heated to 250°C under flowing purified argon at .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.[1] 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, the 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. Once installed in the growth chamber, the samples are heated to growth chamber under a flux of purified hydrogen. Once at growth temperature, dichlorosilane and argon purge flow is started and stabilized. 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. *Sample Analysis*

The system has no in-situ analytical instruments, so samples 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 regarding film contamination and cleanliness of the interface. 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

Experiments were run at differing temperatures, pressures, and rotation speeds. Flow rates are set so that in the time a sample spends in each zone, it is “washed” three times by that particular gas. Table I shows the results of these runs. Target thickness is the film thickness that would result if each SiH_2Cl_2-H_2 cycle resulted in the deposition of one monolayer. Actual thickness is the measured thickness by SIMS. Crystallinity was determined by SEM and RHEED.

Table I

Run	Temp.	Press	Time per Zone	Crystallinity	Thickness (Target/Actual)	Time
1	830°C	15 torr	1875 sec.	Poly	1520 Å / 4400 Å	15 min.
2	830°C	15 torr	1 sec.	Poly	716 Å / 6800 Å	35 min.
3	690°C	15 torr	1 sec.	Ordered Poly	1220 Å / 735 Å	1 hr.
4	670°C	15 torr	1 sec.	Single Crystal	1220 Å / 320 Å	1 hr.

General trends in film properties are depicted in Figure 3.

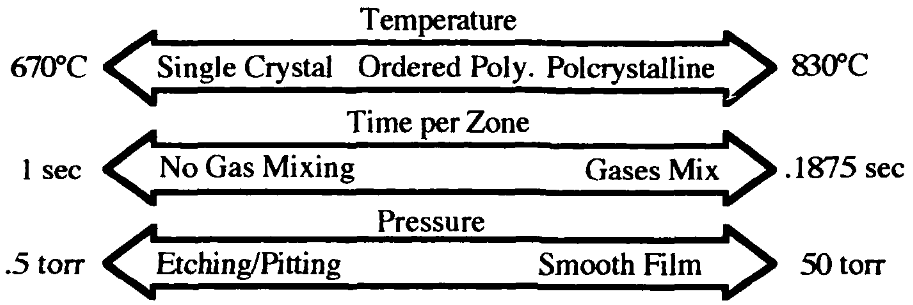


Figure 3.

SIMS data for runs 1-4 are shown in Figures 4-7 respectively, RHEED spectra for runs 3 and 4 are shown in Figures 8 and 9 respectively.

From the SIMS plots, one can see that the grown films contain very little of the arsenic dopant found in the wafer even when grown at 830°C. As a result, SIMS depth profiling allows one to find the interface by locating the step in arsenic concentration. After SIMS, the samples were taken to a contact profilometer where the depth of the sputtered pit is measured, and thus the film thickness may be extrapolated. On the SIMS plots, one can see the build-up of carbon and oxygen at the interface, an immediate goal is to minimize this contamination. Also the films contain slightly more carbon in the bulk than the wafers. This is probably attributable to oil back streaming through the diffusion pumps.

From the RHEED spectra, Figure 8 shows the (100) reflection, and Figure 9 shows the (110) reflection. Kikuchi line are barely visible in both patterns, and the cloudiness is due to a native oxide.

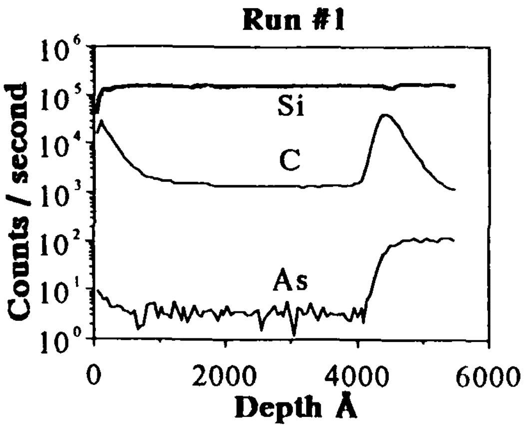
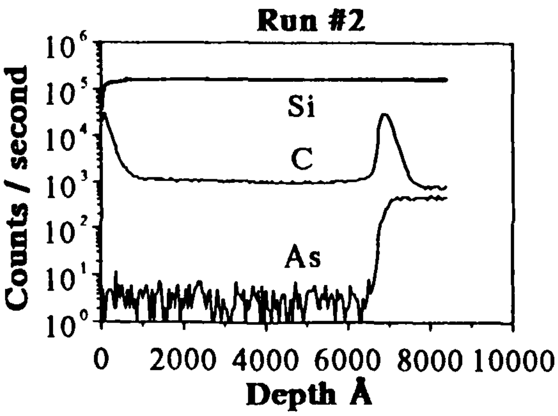


Figure 4



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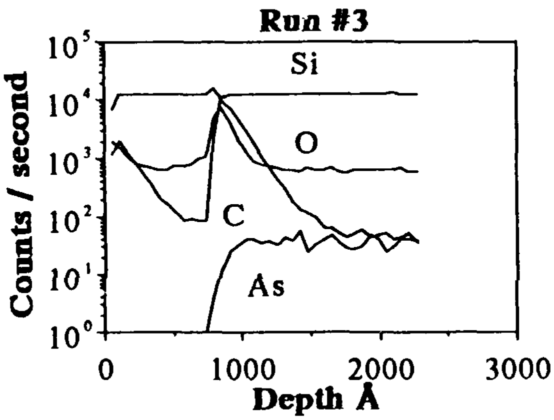

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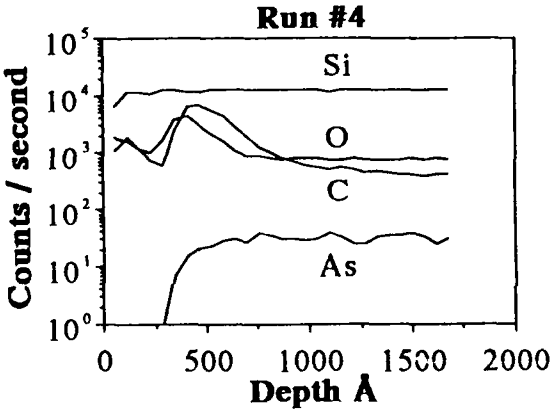

Figure 7

Figure 8

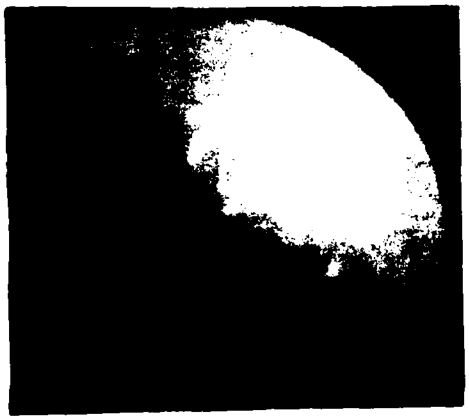

Figure 9

D. Discussion

Early runs used highly arsenic doped (100) wafers 3° off axis toward <011>. Two problems plagued the early runs. Surface oxidation prevented deposition. If deposition occurred, the films were pitted. We determined that the surface oxidation was mainly due to argon, and to a lesser extent, the hydrogen. To surmount the oxidation problems, three changes were made to the system: all gas lines were replaced with electro-polished tubing, a titanium gettering furnace was installed on the argon line, and a Nanochem® purifier was installed on the hydrogen line. These changes ended the oxidation problems.

The pitting occurred in a regular pattern and produced geometrical pits indicative of the thermal etching of defects. To avoid the pitting, higher growth pressures were employed to reduce the driving force for etching. In addition, also on-axis wafers were used to reduce the surface defect density.

Chemically-terminated ALE growth requires that the various source gases be individually "pulsed" across a sample. In this system the "pulsing" is achieved by rotating the sample from one zone where one source gas flows to another where the other is present. The zones are separated by a third through which flows a "curtain" of purge gas. In the present configuration, the purge gas is argon. It is important to assure that minimal gas mixing occurs. From the work by Kermani [2], and Regolini [3] growth rates of silicon from SiH_2Cl_2 at 830°C, 690°C, and 670°C are found to be 900 Å/min, 50Å/min, and 25 Å/min respectively. Although this data is for a slightly lower pressure, namely 10 torr, around these temperatures growth is surface reaction rate limited, not transport limited [4], so that the data are useful. Table II compares growth rates for runs 1-4 assuming the sample experiences the SiH_2Cl_2 only $^1/_4$ of the time.

Table II

Run	Thickness	Time	Measured Growth Rate	Expected Growth Rate
1	4400 Å	15 min.	1173 Å/min	900 Å/min
2	6800 Å	35 min.	777 Å/min	900 Å/min
3	735 Å	1 hr.	49 Å/min	50 Å/min
4	320 Å	1 hr.	21 Å/min	25 Å/min

From the results of these computations, it appears that the gases were mixing in run 1, because the growth rate is higher than expected. In run 2 (at slower rotation) the growth rate is lower than expected, therefore the following runs were performed at 1 second per zone rotation to minimize mixing.

In the course of these experiments, it was found that polycrystalline growth occurs at temperatures of 720°C and above (from another run not reported here because the data are questionable). At 690 °C a highly ordered polycrystalline film grows, and at 670°C, a single crystal film grows that is of good quality as determined by the presence of Kikuchi lines in the RHEED pattern.

SIMS data reveals the presence of considerable carbon and oxygen at the interface between the film and substrate. More work is required to optimize our cleaning technique to reduce this contamination.

E. Conclusions

We have produced good quality single crystal epitaxial films of silicon on silicon. Conclusive proof that the growth mode is chemically-terminated ALE has not yet been determined. The growth rate corresponds roughly to a coating of $^1/_4$ monolayer per cycle. We have found that we can minimize mixing of process gases in our continuous flow reactor.

F. Future Research Plans/Goals

Our immediate plans are to prove *conclusively that* the growth mode of the silicon film is ALE by repeating the experiment at slower and faster rotation speeds, ALE should occur on a plateau that is relatively insensitive to exposure time. Once satisfactory ALE growth of silicon is achieved, we will address the ALE of silicon carbide. As SIMS indicates substantial carbon and oxygen at the film/substrate interface, we will also work to refine our cleaning process to minimize this contamination.

II. Near Atmospheric ALE of Silicon (Bedair Laboratory)

A. Introduction

As the size of semiconductor devices is reduced and the speeds increased, there is a greater need for better control of the deposition process. Atomic layer epitaxy (ALE) provides ideal control of the crystal growth since the deposition is regulated on an atomic scale. The current system has been designed for high speed ALE and has been constructed specifically for atomic layer epitaxy of silicon. The ALE process insures high quality, low defect density single crystal silicon growth, with uniform deposition over the surface at exactly the predetermined growth height. The development toward high speed deposition allows optimization of the process and is appealing for practical industrial applications. The essential features of this system are high purity source gases and isolation of the reaction chamber from the environment while allowing easy access to the sample stage for loading and unloading. This prevents water from contaminating the system, which is crucial for Si deposition [5], while allowing short lag times between depositions.

The system has been designed for deposition using dichlorosilane (DCS) and hydrogen as source gases. The deposition is a two stage process, involving exposure of the substrate to first one, and then the other gas. The DCS exposure forms one monolayer of a silicon chloride compound. The sample subsequently passes through the hydrogen stream which reacts with this surface chlorine to liberate HCl and leave an atomic layer of silicon on the substrate surface[6].

B. Experimental Procedure

As mentioned above, the system has been designed for ease of sample loading while not breaching the system integrity. The sample is first pre-cleaned and loaded into the antechamber of a glove box. This chamber is purged with dry nitrogen and the sample transferred into the glove box and then into the reaction system through an O-ring sealed port. The graphite sample stage is raised into the quartz reaction chamber where another graphite susceptor is already in place. RF energy is applied to the susceptor to raise the sample to the desired temperature. The fixed susceptor helps keep the purified reaction gases separated from each other by providing a physical barrier as well as directing an inert argon stream which creates a buffer zone between the DCS and hydrogen. The sample stage rotates to expose the sample to one of the reactants at a time. Between each exposure the stationary graphite also helps to shear away any gases carried along with the rotating substrate. The gas flow rates are controlled by metal seal mass flow controllers and by needle valves, which allow dilution of the reactants with inert argon. A thermocouple extending into the fixed susceptor provides the feedback necessary for the RF coils to regulate the graphite temperature. The rotation of the susceptor is computer controlled and may be programmed to vary the speed within any given cycle and increase the cycle speed to 40 revolutions per second.

C. Results

Upon final testing and examination of the system, two major problems were encountered. One is that the DCS steel cylinder had been corroded at the CGA fitting, apparently by the dichlorosilane. Although this cylinder may have been used for initial testing, the risks of contamination of the lines, long term effects on the system, and the safety risk of possible leaks at the connection outweighed the short term benefits that might be gained. The replacement tank, made of stainless steel, had not been sealed properly before shipment, and rust formation at the CGA fitting presented the same problems as the first. A new tank was immediately ordered and should be received by mid June.

The other problem was with the temperature uniformity over the graphite susceptors. The stationary piece showed a wide range of temperature variation over its surface, and the rotating piece remained at least two hundred degrees cooler than the fixed susceptor. The thermocouple also read about three hundred degrees less than the optical pyrometer indicated. The quartz tube for the thermocouple was first extended so that it would penetrate deep into the susceptor. Both susceptors were redesigned so that they would adsorb more RF energy and reach higher temperatures. The rotating susceptor now exhibits even temperature distribution and can reach 1100 C. The top fixed piece was then modified to attain uniform temperature distribution and to match the temperature of the bottom sample stage, since it had a great deal of variation and was initially about two hundred degrees hotter than the sample holder. The temperature variations could be detected by the eye for the initial adjustments, for fine tuning an optical pyrometer was used. The modifications involved cutting notches in the susceptor, to reduce temperature variations over the surface, and reducing the total thickness by milling, to lower the temperature to that of the rotating susceptor.

Concurrent with these modifications, the computer software controlling the system has been upgraded to allow better control of the growth process and provide error checking for situations that can crash the computer. The initial programs, written for an older DEC micro computer, were transferred to an IBM At compatible, which has more versatility and better error handling capabilities. The software allows manual control of the rotation or fully automated control. The exposure time of the substrate to each reactant gas as well as latency times between each exposure may be controlled separately. The program may also be adapted to allow full control of the pneumatic valves controlling the inlet gases. This will be useful for automatic switching of the source gases, purge gases, or dopant gases being used.

D. Discussion

The susceptor design and modifications resulted in the desired temperature uniformity. The temperature variation along the surface of the stationary piece is at most 25 degrees, as measured with an optical pyrometer. The rotating sample holder has no significant temperature variations and is at about the same temperature as the top susceptor. More importantly, the new thermocouple position results in accurate temperature readings of the sample stage itself, as measured with the optical pyrometer. The computer software to control the stepper motors has been written and tested. The program handles user errors, errors that may come from the stepper control unit, and timing problems that occasionally arise between the computer and the motor controller.

E. Conclusions

The present system design has been aimed at high speed, high quality, low temperature silicon ALE. The construction allows for high purity source gases, system integrity and isolation from the atmosphere, ease of sample loading without breaching system integrity, and good control of the reaction conditions. All of the design goals have been met and the system will be ready for full operation once the new DCS source has been received.

F. Future Research Plans/Goals

During the idle time when outside labor was being used for alterations, designs and modifications were made to the system for future research plans. One obvious desire will be for dopant gases for silicon deposition, once ALE has been achieved. This was fairly simple, since the Si ALE chamber is adjacent to an existing GaAs ALE system. The dopant source lines have been connected to the DCS inlet line so that in the future the dopants can be added to the DCS stream.

Additional plans have been made for germanium epitaxial deposition. The manifolds and purifications systems have been designed and lines have already been run from the ALE system to the gas cabinet. The source gases considered are HCl and germane. This would be used for examination of germanium deposition on silicon as well as silicon on germanium. The ultimate goal of this exploration will be silicon germanium superlattices[7,8].

III. Epitaxial Growth of CeO_2 on Si (Bedair Laboratory)

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%[9]. Also, CeO_2 has a dielectric constant of ~26, which could potentially allow it to be used in stable capacitor devices of small dimensions[9].

B. Experimental Procedure

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[10,11]. 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). This produces a "plume" of CeO_2 molecules free to move in UHV and form 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 have reported it necessary to flow oxygen at low pressure (10^{-7} – 10^{-8} torr) during growth[9,10]. Cerium, 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. This indicates that auxiliary oxygen flow may be unnecessary[11,12].

Characterization of thin films. In order to observe quality, crystallinity, orientation, and 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 preliminary design has been proposed for a system suitable for growing epitaxial CeO_2 on Si. This system will be added onto an existing UHV system currently being used for gas-source molecular beam epitaxy (GSMBE) of III - VI compounds (see Figure 10.)

The proposed system consists of two chambers, one for sample introduction, and the other for oxide deposition. The introduction chamber will use a 220 l/s ion pump capable of achieving 1×10^{-10} torr. This chamber will allow Si substrates to degas unwanted contaminants, while insulating the growth chamber from exposure to the atmosphere. The deposition chamber will use a combination of a 400 l/s ion pump and a 300 l/s turbomolecular pump to provide a base pressure of 1×10^{-10} torr. The turbomolecular pump will allow oxygen to be introduced at very low pressures to control stoichiometry if necessary. The laser to be used is a Lamda Physik excimer laser.

The substrate holder and transport mechanisms will be compatible with the existing GSMBE 3" format. Requirements for the internal manipulator are that substrate be capable of at least 180° angular rotation for RHEED purposes, and that the substrate can be heated up ~800° C. A schematic plan is presented in Figure 11.

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. Therefore

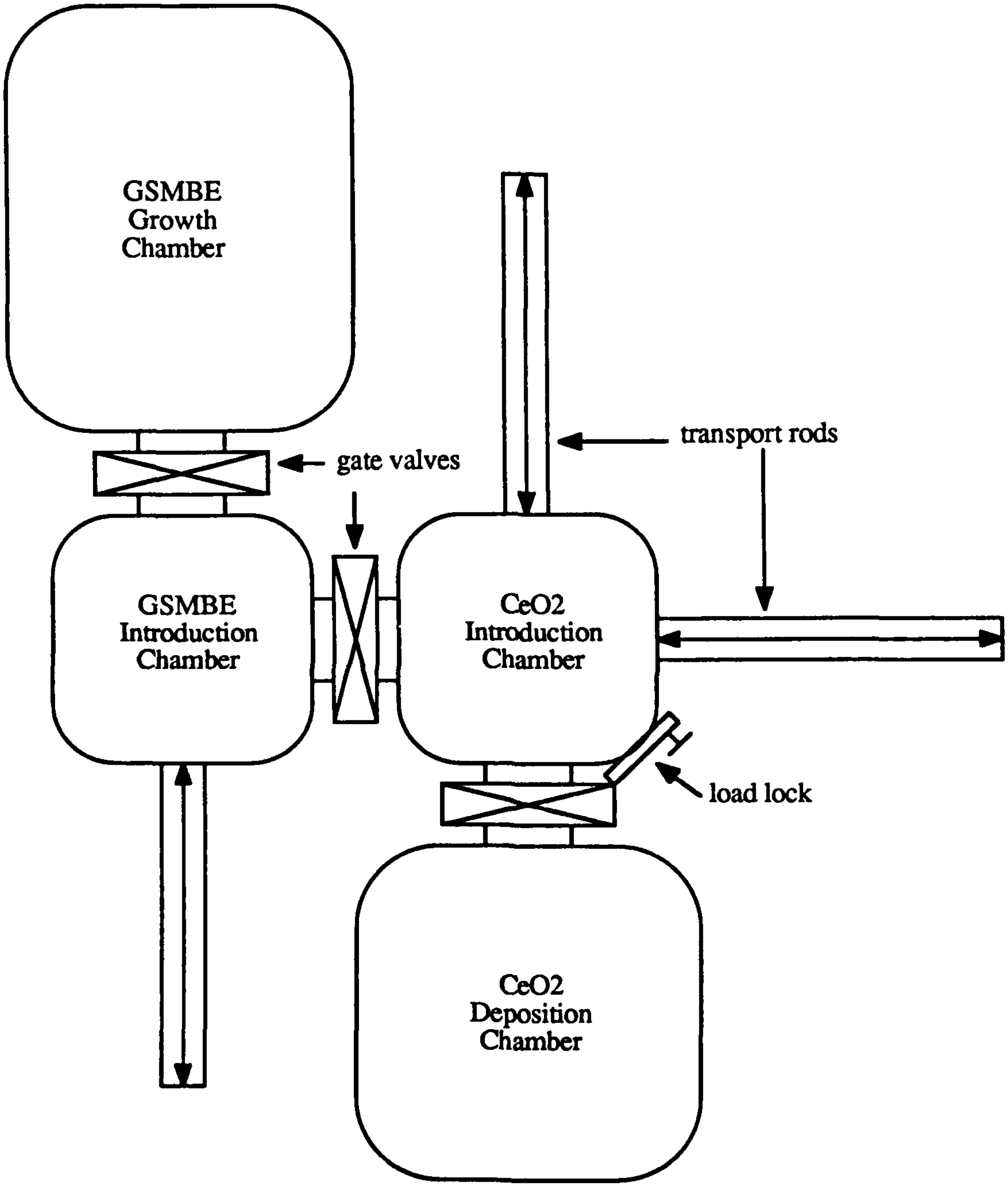

Figure 10. Schematic plan to add CeO_2 system to existing GSMBE system.

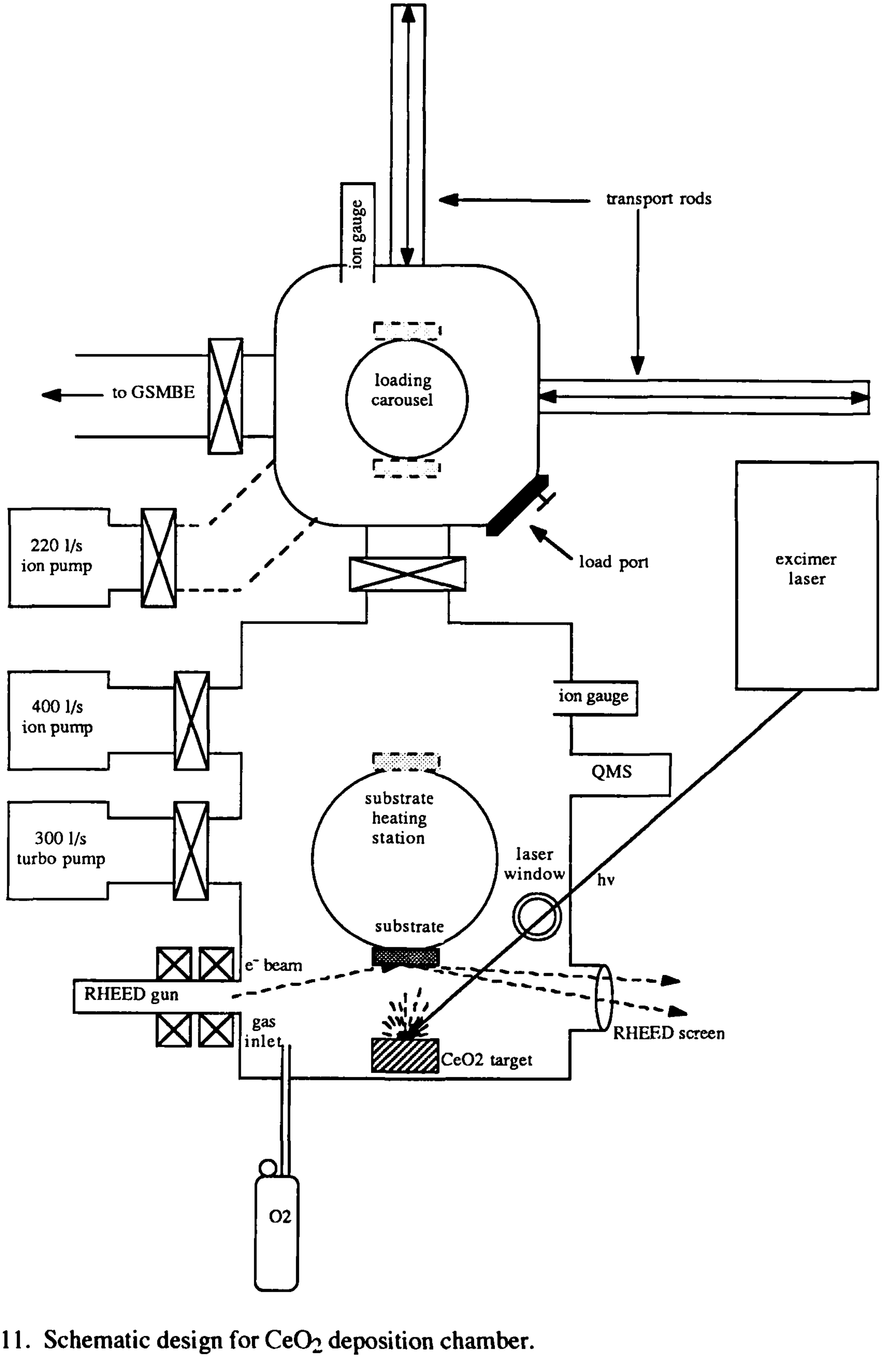

Figure 11. Schematic design for CeO_2 deposition chamber.

alternatives must be found. Also, the method of heating the substrate must be resistant to oxidation. Quartz heater lamps or tantalum filaments may be used.

E. Conclusions

Conclusions regarding the feasibility of the CeO_2 project may be drawn. By building the new system on to the existing GSMBE system, the CeO_2 project gains the use of valuable electronics (i.e. QMS and RHEED gun controllers) which might otherwise render the project cost prohibitive. The GSMBE system will gain another level of vacuum between atmosphere and the growth chamber, which will help eliminate impurities and increase productivity. Also, the literature shows good results in similar systems[9-11]. With careful design there is much room for improvement. This project is indeed feasible.

F. Future Research Plans/Goals

Immediate plans include completing the design, and building the system.

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