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LABORATORY STUDIES OF SILICON VAPOR DEPOSITION

PHASE A

FINAL REPORT

Contract No. NAS 1-14650

August 22, 1977

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Prepared for

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
Langley Research Center
Hampton, Virginia 23665

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Space Sciences Laboratory
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ABSTRACT

A system is described capable of carrying out silicon vapor deposition experiments in the low 10^{-10} torr vacuum range. This system has been assembled and tested preparatory to a program aimed at exploration of vacuum heteroepitaxy studies of silicon on several substrates of potential interest for devices, in particular upon conducting substrates of possible interest for photovoltaic applications. An initial experiment is described in which a silicon layer 2.5 microns thick was deposited on a pyrolytically cleaned tungsten substrate held at a temperature of 400°C. Using a resistance heated silicon source, thicker layers can be deposited in periods of hours by utilizing closer source to substrate distances than the 2 cm employed in the first experiment.

LABORATORY STUDIES OF SILICON VAPOR DEPOSITION

PHASE A FINAL REPORT

1.0 PURPOSE

The following report describes results obtained in the first phase of a program[1] to explore possibilities for ultra-high vacuum vapor heteroepitaxial growth of silicon films. The overall objectives of this program are to extend the limited experimental data available on epitaxial growth of silicon films under ultra-clean conditions to determine the influence of substrate surface condition and temperature, deposition rate, and vacuum conditions upon the grain size of the crystalline deposits obtained and to begin initial explorations as to whether device grade thin films can be produced. The Phase A[2] portion of this study was to prepare the evaporation facility and to explore various techniques for silicon evaporation and for monitoring of the many experiment variables which must be controlled (including mass spectrometer analysis of residual gases within the system). A short introduction is included describing the rationale for the program in terms of later possibilities for continuation of this work in the higher vacua obtainable in a proposed earth orbiting facility. Appended is a plan for the Phase B[2] portion of the present program to investigate vapor deposition on a variety of substrates.

2.0 INTRODUCTION

Limited experimental data, supported by theoretical considerations, indicate that residual gases play a dominant role in experiments in which silicon is grown epitaxially upon a silicon substrate (homoepitaxy) or substrates of other materials (heteroepitaxy). Recent reviews of the existing literature by Cullen[3] and Turnbull[4] indicate the dominant role played by adsorbed gas atoms in providing an undesirably high density of nucleating centers for crystallization and in interfering with mobility of silicon atoms on the surface during the growth process. By experiments carried out in the 10^{-10} torr pressure regime, Widmer[5] and Jona[6] were able to grow silicon homoepitaxially at temperatures of 520 and 400°C

respectively. The growth direction was the (1, 1, 1) crystal direction. Other experiments by Jona indicated even lower temperatures for homoepitaxial growth in the (1, 0, 0) direction,and Widmer's results are not inconsistent with this finding. More recently, Mayer[7] indicated crystallization rates for amorphous silicon prepared from zone refined material by Si ion bombardment as high as 1000 Å per minute for the (1, 0, 0) direction at a temperature of 550°C. These rates, not yet published, are being analyzed by Turnbull and apparently fit the latter's model for crystallization of the pure material. It is to be noted that recrystallization rates at such temperatures are negligible in systems of conventional cleanliness.

Successful vacuum vapor heteroepitaxial growth of silicon has been achieved by Chang[8], Gassman[9] and Jona[10, 11, 12]. Chang found temperatures for heteroepitaxial growth of silicon on sapphire only 50° higher than for homoepitaxial growth. Gassman was able to deposit silicon of sufficient quality for MOS applications at 900°C on spinel substrates. Jona noted an ordered growth of silicon on substrates of nickel, aluminum and beryllium at room temperature. It is to be noted that the deposition rates utilized by Jona are several hundred times lower than that used by the other investigators quoted. For his experiments on the metal substrates, deposition rates were inadequate to keep up with the diffusion rate of silicon into the substrates at the elevated temperatures which would be required for epitaxial growth of thick films so that he did not succeed in obtaining thick heteroepitaxial films. All of these investigators utilized vacuum systems with total pressures in the low to mid 10^{-10} torr range. Because the partial pressure of reactive gases is expected to be of greater importance than the total pressure and since residual gas analyses are not available from these experiments, comparison of results of this work is difficult.

Many experiments have been carried out on vapor vacuum deposition of silicon at pressures above the 10^{-10} torr range. The work of these other experimenters furnishes evidence that the temperature for epitaxial growth drops with pressure. The theoretical reasons for this have been summarized by Turnbull[4].

In all of the ultra-vacuum work referred to above, apparently defect-free silicon was obtained. Gassman measured essentially bulk mobilities for silicon on spinel but found lifetimes in the nanosecond regimes. Cullen[3] has argued that lifetime should increase for thicker films. Of course, lifetimes approaching a microsecond are required for high quality bipolar devices.

3.0 OBJECTIVES

The objectives of the program are to extend the existing data and to explore possibilities for depositing device grade silicon heteroepitaxially on practical substrates. It is desirable to attempt to reproduce, to a limited extent, some of the previous experiments carried out by other investigators for purposes of comparison. This is particularly important in the case of homoepitaxial growth of silicon on silicon since this is the process which necessarily occurs after one has deposited beyond the first few layers on any type of substrate. In addition, exploration of the lowest practicable temperatures for this process is of importance in screening other substrates to be explored in terms of chemical and physical compatibility at the required deposition temperatures.

It is planned that experiments on heteroepitaxial growth of silicon include an early experiment with sapphire, of interest both for comparison with the work of Chang, and also because of the potential importance of such a technique for producing films of sufficient quality for bipolar devices on insulating substrates. For solar cell applications, a conducting substrate is required and experiments are planned both with compatible close packed metals and with an amorphous conductor such as glassy carbon.

The immediate objective of the work on heteroepitaxial growth is to explore the variation of grain size with substrate temperature and residual gas pressure during deposition. This is particularly important since it is estimated that grain widths as small as 20 to 30 microns may be of practical interest for solar cell applications, whereas the previous investigations referenced typically did not characterize polycrystalline deposits other than by noting their polycrystallinity.

When grains in the desired size range are obtained, further characterization by scanning electron microscopy, X-ray diffraction, defect studies and electrical characterization will be carried out. Periodic examination must also be made of chemical purity of the depositing films to ensure that contamination from substrate reactions or other sources is not occurring.

Since establishment of the effect of substrate temperature during deposition is a starting point for any systematic investigation, it is believed necessary to carry out experiments in which depositions are made simultaneously on two or more substrates held at different temperatures. Otherwise, it is expected that other run-to-run variables, such as system pressure or possible variations in amounts of reactive gases in the system, may tend to complicate interpretation. In most cases adequate techniques for in situ cleaning of the substrates have been developed and published elsewhere, and so a detailed program for further study of these techniques and in situ characterization of substrate surfaces is not proposed (with the possible exception of limited experiments utilizing contact potential differences and thermal desorption mass spectrometry where sufficient correlation with surface contamination or other properties has been established).

4.0 EVAPORATION FACILITY

4.1 VACUUM SYSTEM

Several types of vacuum pump were considered for the present program. Although the highest pumping speeds in the ultra vacuum level can be achieved by means of cryopumping, a large triode ion pumped facility with four sorption roughing pumps was selected rather than modification of an existing large cryo system to provide oil-free forepumping.

Titanium sublimation pumps are very effective at the pressures required in this program, but work reported by both Monsanto Chemical Corporation and by Westinghouse (working in conjunction with Dow Chemical Corporation) indicates

that titanium concentrations as low as 10^{13} atoms per cubic cm in silicon can affect performance of the material in solar cells. For this reason titanium sublimators are not used in the vacuum system because of the relatively significant amounts of titanium which might be able to reach the substrates even through a baffle system.

4.1.1 General

The vacuum system employed is shown in Figure 1 and consists of a 46 cm diameter, 74 cm high water cooled stainless steel bell jar with two 15 cm diameter access ports. This is mounted on a feedthrough ring containing sixteen 6.98 cm Cu gasketed flanges. The bell jar bolts to the feedthrough ring and is sealed by a Cu wire gasket. A manifold leads to a 1200 ℓ/s GE 22TP410 triode ion pump and via a valve to a smaller manifold containing a valved outlet to air and valved outlets to 4 GE sorption pumps. The ion pump is run by a GE 22TC401 power supply and 22TC402 control. One glass viewing port is used for observations into the chamber interior; the other has been replaced by a bellows and valve assembly leading to a Varian 400 ℓ/s Noble (Triode) ion pump (model 912-7022) run by a Varian control (model 921-0066). This pump is used during initial pumpdown and bake.

The bell jar, manifold and 1200 ℓ/s pump are equipped with integral heating elements and temperature sensors for bakeout. These are capable of heating to at least 320°C. Other accessory elements of the vacuum system, such as the bellows and valve to the 400 ℓ/s pump, are baked out using Variac controlled heating tapes.

A GE Model 8HG 1A020322 multi-point potentiometer recorder is used during bakeout to monitor temperatures at various locations using chromel alumel thermocouples.

Figure 2 shows a schematic of the vacuum system with shut-off valves. Figure 3 shows characteristic pumping speeds for various gases typically obtained with triode ion pumps of the type employed here.

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Figure 1. Basic GE Triode Pumped Vacuum Facility, 1200 ℓ/s

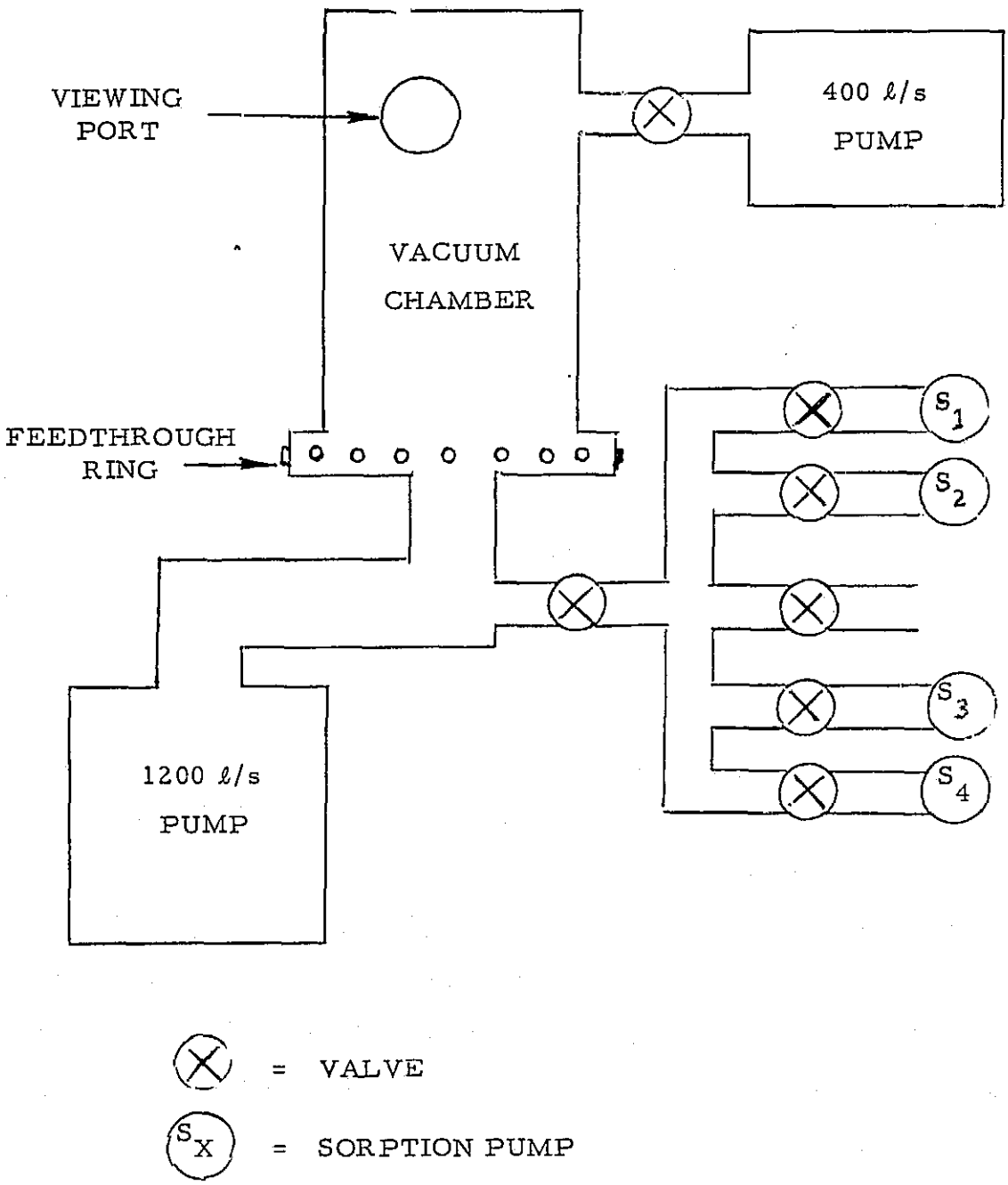
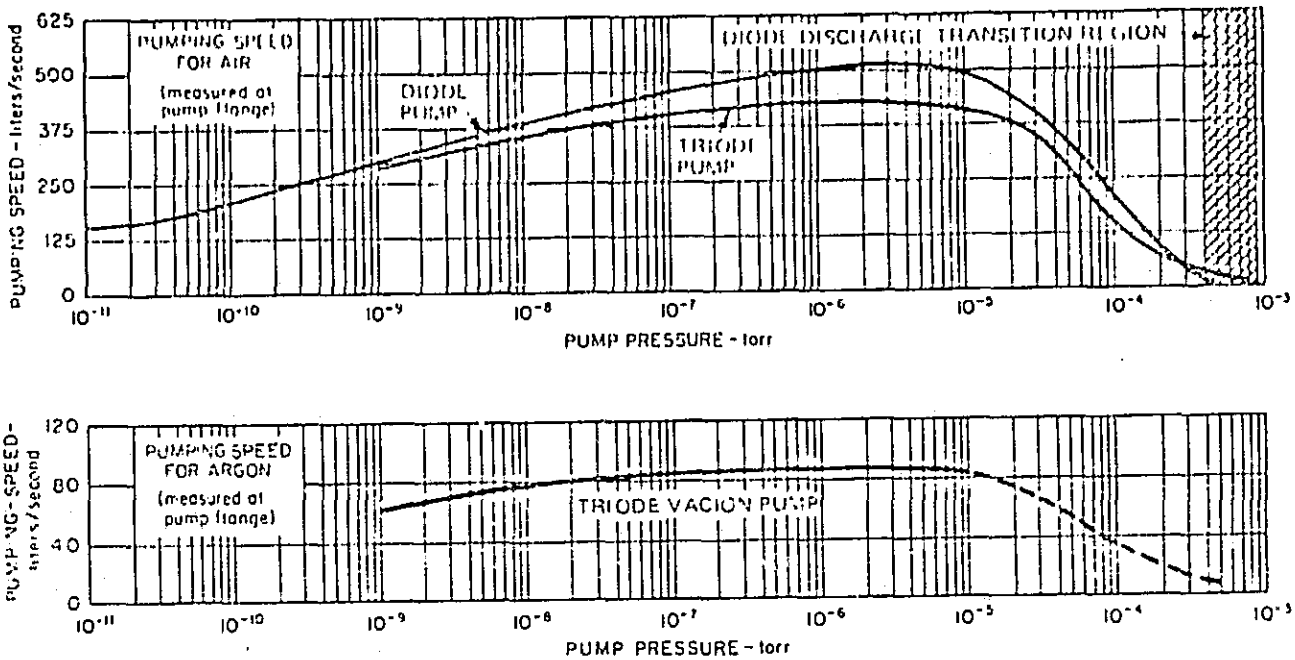


Figure 2. Schematic Diagram of Vacuum System



Pumping Speed Characteristics - Air, 100%

Hydrogen	200%	Light Hydrocarbon 90	105%
Nitrogen	95%	Water Vapor	100%
Oxygen	57%	Helium	20%
Carbon Dioxide	100%	Argon	30%

Figure 3. Typical Pumping Speeds for Large Triode Ion Pumps

4.1.2 Ion Gauges

Pressure is monitored by a GE 22GT103 ionization gauge with 22GC101 control and by a Varian UHV-24 ionization gauge with dual range control (model 971-1008 with automatic ranging from 1×10^{-11} T to 10×10^{-4} T). The output of either of these gauges or of the 400 ℓ/s pump gauge can be continuously recorded on a Heath Sclumberger SR-204 strip chart recorder with 10 chart speeds variable from 0.025 cm/min. to 25.4 cm/min.

The GE ionization gauge is mounted at the end of a tube outside the feedthrough ring. The Varian gauge is nude and located inside the feedthrough ring. Since, as described below, the latter gauge was sensitive to scattered electrons from the electron beam heater source within the chamber, it has been provided with an electrostatic shield to which a negative potential can be applied for the purpose of blocking entrance of inelastically scattered and secondary electrons.

4.1.3 Evaporation Chamber and Internal Mechanisms

Interior to the main vacuum chamber is a 10 kw, 270° magnetic deflection water cooled electron gun used to heat and melt a cylindric slug of silicon serving as evaporant source. This source is mounted on a thin tantalum support which allows the entire silicon mass to be sufficiently thermally isolated to provide for removal of any surface oxide layer by thermal desorption. In addition, the silicon cylinder is surrounded by a non-contacting concentric sheet of tungsten which can be brought to incandescence by passing through it an electric current. This auxiliary tungsten heater is used to assist in outgassing of the silicon and its support.

The substrates are mounted on the end of a movable arm with provisions for simultaneous exposure of up to three substrates. This substrate assembly can be moved into position over the electron gun evaporant source by rotation of the arm through a worm gear mechanism. The worm is driven directly through a mechanical rotating vacuum feedthrough. The substrate assembly at the end of the arm can move along a track to other substrate stations provided. One of these,

for substrate outgassing, is located opposite a port provided with a Veeco GA-4R residual gas analyzer for observation of gases evolved during initial substrate heating prior to deposition.

Figure 4 is a simplified plan view showing the rotating substrate arm and several stations to which the substrates can be moved by articulating the arm. Figure 5 is a photograph of the interior mechanisms prior to closing of the bell jar. In Figure 5, auxiliary silicon evaporant sources in the form of directly electrically heated silicon rods have been added and their electrical leads show prominently in the center of the photograph. We shall describe each of these internal mechanisms in more detail in separate sections below. At this point we note that the track upon which the moving end of the substrate arm rolls has various inclinations from a horizontal plane in order to bring the substrates into desired vertical positions for the various stations.

A third substrate position is provided for possible use with in situ vapor deposition of substrate material (aluminum). A final position provided at present can be utilized for measurement of contact potential differences by utilizing a technique described by Hopkins[13] in which the substrate is mechanically vibrated near another electrode (e.g., tungsten) which has previously been outgassed by thermal desorption. When a d.c. bias (equal to the difference in contact potential) is applied between the two plates of this vibrating electrical capacitor, a null a.c. signal at the vibration frequency is observed. This technique has been tested in breadboard form but is not presently incorporated in the vacuum system.

The radius of the arc traversed by the substrate assembly is 22 cm. The track upon which the substrate arm rests describes an 28 cm radius arm as viewed from above. The worm (single thread) and gear for driving the arm have a 48 pitch, a $3\text{-}1/2^{\circ}$ lead angle and 100 teeth on the gear. This provides for an angular rotation of 3.6° or 1.5 cm movement of the substrate assembly per worm revolution.

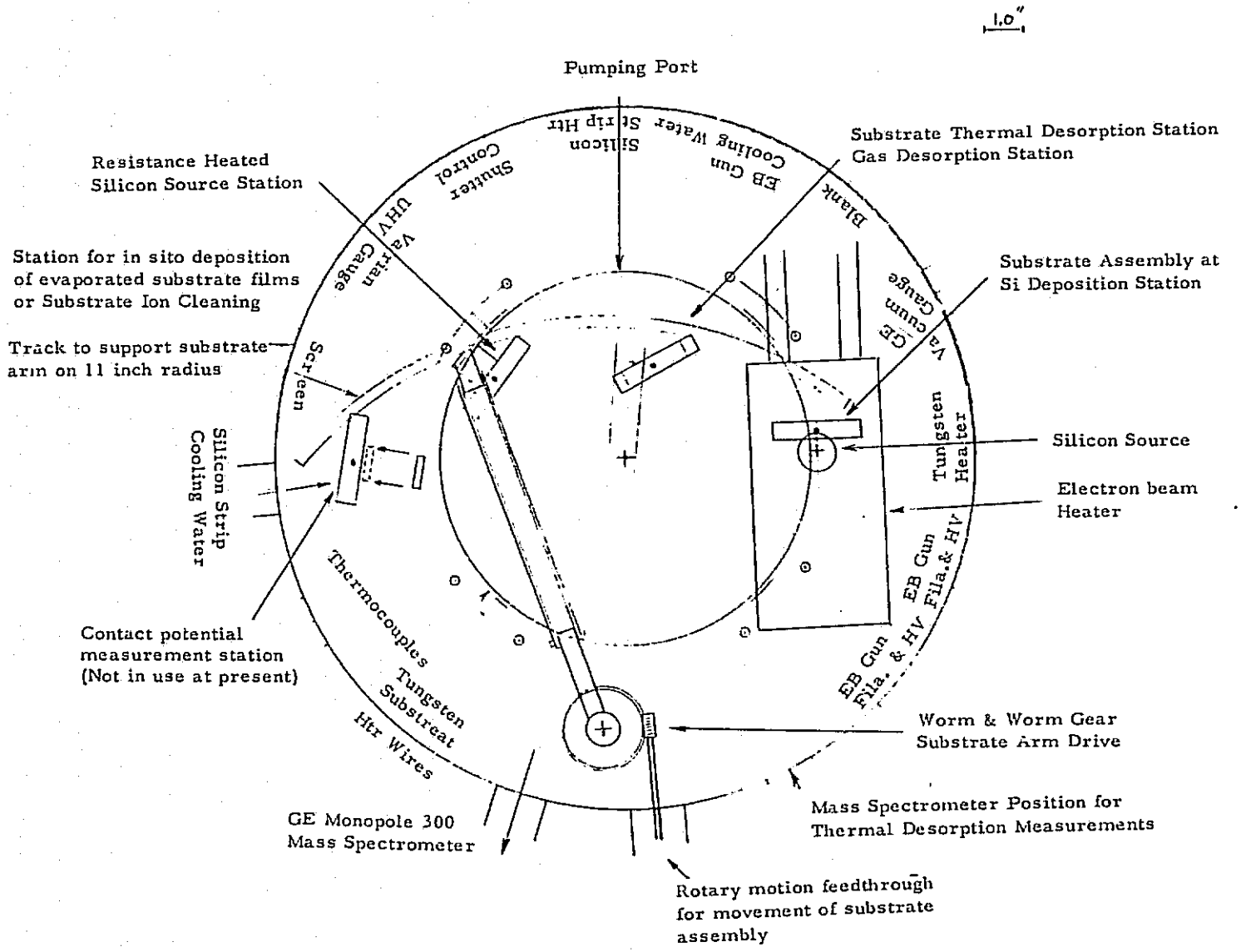


Figure 4. Schematic Plan View of Rotating Substrate Arm and Substrate Stations

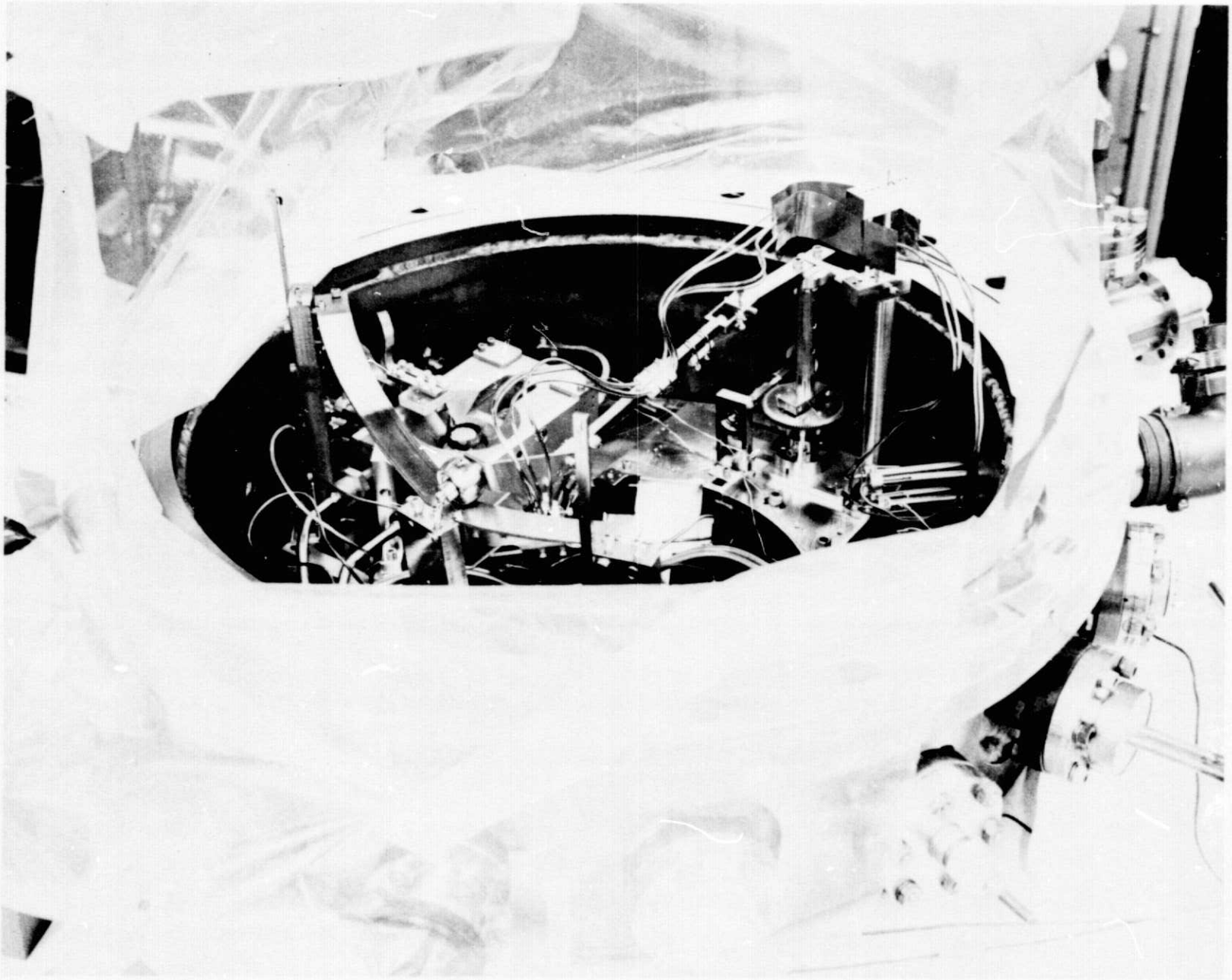


Figure 5. General View of the Mechanisms Interior to Vacuum Deposition Chamber.

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At a distance of 6.3 cm from the vertical axis through the worm wheel, there is a horizontal axis about which the main part of the substrate arm is free to rotate as it rests on the supporting track 28 cm from the vertical axis. The main arm is a 0.63 cm square rod terminating in the substrate/heater assemblies. At the end of the arm is connected a wheel with ball bearings resting upon the track. This track serves two purposes: it minimizes vibration of the arm which could result in relatively large oscillations of the position of the substrates and also provides for proper vertical positioning of the substrates at each of the stations. The bearings, roller and track are coated with molybdenum disulfide to provide lubrication and to prevent welding under ultra-high vacuum conditions.

Silicon vapor emitted from the electron gun heated source can leave the conical well within which the silicon is located only in an upward cone of directions. A stainless steel plate mounted above the rotating arm blocks this cone of escape from above in order to minimize deposition of silicon upon the chamber walls, window and upper mirror. Mirrors are provided for observing, through the viewport, the silicon sources and the substrate, and for optical pyrometry of the source during evaporation and the substrate during initial outgassing prior to evaporation.

4.1.4 Cleaning Procedures

All materials placed into the vacuum system were first thoroughly cleaned. Unassembled pieces were degreased by sequential ultrasonic agitation in baths of trichloroethylene, acetone and methanol, and were then vapor degreased in freon. A few large pieces did not fit in our ultrasonic cleaners and were only scrubbed sequentially in the above solvents. Also, the electron beam gun, which was received as an assembled unit, was not disassembled but was ultrasonically agitated in methanol and vapor degreased in methanol.

After the above degreasing, materials were additionally cleaned as follows:

Stainless steel - key pieces (track, etc.) - acid etch in 10:2:88 = HNO_3:HF: H_2O at 40°C - 50°C for 1 to 2 minutes. Rinse in 20% HNO_3 in H_2O at 60°C for 5 minutes and then rinse in H_2O. (Note: all H_2O is deionized.)

Molybdenum - Rinse in H_2O_2 and quickly transfer into ultrasonically agitated H_2O.

Tantalum - Etch 15-30 sec. in 5:3:2 = H_2SO_4:HNO_3:HF, rinse in H_2O.

Copper - Etch several seconds in 1:3 = HCℓ:H_2O, rinse in H_2O.

Tungsten - Ultrasonically rinse in H_2O.

Silicon - Polish in 1:3 = HF:HNO_3 about 1 minute. Add H_2O to etchant to stop reaction, rinse in H_2O. Clean in 1:1:4 = NH_4OH:H_2O_2:H_2O at 80°C for 10 min. Rinse in H_2O, immerse in HF for 2 min. Clean in 1:1:4 = HCℓ:H_2O_2:H_2O at 80°C for 10 min. Rinse in H_2O.

After water rinse, the parts were blown dry using dry nitrogen. The above procedures are basically standard recipes. The action of the peroxide Si etches is described by R. C. Henderson[13] and by W. Kern and D. Puctinen[14].

It had originally been intended to prebake many pieces in a separate vacuum oven pumped by a turbomolecular pump. Failure of that pump at a critical time prevented this and all baking was performed in the system after assembly and pumpdown for the first system test.

4.1.5 Bakeout Procedures

1. Use sorption pumps, with 400 l/sec ion pump operating and valve to it closed, to bring system pressure down to 2 - 5 millitorr and then open valve to 400 l/sec pump (and close valve to sorption pumps).

2. When pressure is 10^{-6} torr or less, operate electron beam heater to verify proper beam position control via beam voltage.

3. Attach leak detector and check for leaks.

4. Operate substrate heater to verify operation.

5. Operate E-beam gun to verify operation.

6. Heat the system to 300°C. During heating, do not heat so fast that the pressure rises above 10^{-5} torr.

7. After the system has been at 300°C two or more days and after the pressure has fallen to 10^{-6} torr, outgas vacuum gauges, substrate and its heater wires, and, for short periods of time and/or at less than full filament power, heat the electron beam heater and silicon source. Because the temperature of parts in the vicinity of the filament is not known, care must be taken not to overheat them (e.g., ceramic insulators, stainless steel parts and, farther removed from the filament, the magnet).

8. Start the 1200 l/sec pump occasionally to outgas for several minutes.

9. Start the 1200 l/sec pump. Pump with both pumps for a while and then turn off heater power and allow the system to cool to room temperature.

10. After the 400 l/sec pump becomes a source of gas, rather than a pump or sink, close the valve to it.

11. After the temperature of the system is approximately 100°C or less outgas everything again (gauges, substrate and, as soon as water may be introduced into the electron beam heater, the electron beam heater and silicon).

12. After room temperature has been reached, again operate the electron beam heater to observe the rise in pressure.

13. If pressure is adequately low, heat the substrate to clean it and begin deposition of silicon. If pressure is not adequately low, repeat the entire baking cycle, unless specific components have been identified as being prime contributors to outgassing. In that case, remove them from the system and bake them at high temperatures separately in another vacuum chamber.

4.2 EVAPORANT SOURCES

A number of heat sources can be considered for evaporation of silicon. These include direct resistance heating, r.f. heating of a pedestal melt or a pendant drop, radio frequency heating of an electromagnetically levitated melt or electron beam heating. Of these techniques, radio frequency levitation and heating is probably ideally the best because of the possibility of outgassing the silicon above its melting temperature without any physical contact with cooler silicon or other material. Although it is possible to levitate silicon terrestrially, which has been accomplished in this laboratory, severe instabilities are encountered due to the rapid decrease of silicon resistivity with temperature. The two types of heating source provided in the facility described here are the electron gun and direct resistance heating. These will be described below.

4.2.1 Electron Gun

The electron gun is an Airco Temescal Model SFIH-270-1, 270° magnetically deflected type. The main body of the gun is water cooled. Magnetic deflection is provided by permanent magnets. A sweep coil is also available for sweeping the beam in two orthogonal directions, but this sweep magnet has been temporarily removed so as to allow baking of the entire system to 300°C. The gun power supply can provide up to 10 kw at a 10 kv beam energy. Filament power can be provided up to 300 watts, but only about 100 watts is required for bringing the 2 cm diameter silicon cylinder up to the melting point in the region of beam impingement. This gun is currently being used with a diffuse beam which strikes

the top of the silicon source cylinder in a crescent shape approximately 1/4 inch wide and 3/4 inch long. The cathode is brought to the full negative accelerating potential, and the accelerating anode is near ground potential. Outgassing from the incandescent filament and nearby focussing electrodes constitute a major limitation to pressures achievable in the vacuum system during evaporation of silicon, and long outgassing with the filament operated at powers higher than utilized during silicon evaporation is required. Tungsten evaporating from the gun filament cannot reach the substrate and contaminate it because of the 270° deflection feature of the gun. Despite degassing difficulties, a study of the capabilities and limitations of this type of source in the present work is of significance for planning any continuation of this type of work in the space vacuum environment where an electron gun is probably the ideal type of heat source to consider because of its high efficiency.

4.2.1.1 Silicon Source and Mount

In order to be able to bring the entire silicon cylinder to sufficient temperatures for removal of surface oxides which are inevitably present despite the most careful precleaning, the cylinder is thermally isolated from the electron gun base through a thin tantalum sheet mount provided with six legs which rest upon the top rim of the electron gun crucible. This arrangement is shown in Figure 6. Waves can be seen in the top of the silicon resulting from melting by the electron beam. Also shown is a molybdenum crucible provided for the use of the gun with molten pool sources. This crucible was mounted directly below the silicon source during initial tests in order to catch any silicon that might drop (although this did not actually occur). Dark markings can be seen at the edges of the crucible where it was struck by the electron beam in initial outgassing runs at relatively high pressure levels. The silicon used was vacuum float zoned and was obtained from Monsanto Chemical Co.

4.2.1.2 Auxiliary Heater

For preliminary thermal desorption of the silicon oxide layer and to obtain a more uniform temperature in the silicon cylinder during evaporation, an auxiliary tungsten heater strip surrounds the silicon cylinder in a concentric manner. This auxiliary heater can be seen in Figure 5. Estimates of the radial

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Figure 6. Silicon Source Cylinder, Mount and Molybdenum Crucible

temperature distributions at the top of the silicon cylinder, with the central region brought to melting with the electron beam and with the auxiliary heater at various temperatures, are shown in Figure 7.

Figure 8 shows the electron gun controls in the top two rack mounted panels. The lower two panels are the varian ion gauge control and the auxiliary 400 ℓ/s pump control unit. To the right is shown a 24 point recorder used for recording various thermocouple temperature and pressure data.

4.2.2 Alternate Resistance Heated Source

Because of difficulties of outgassing the electron beam heated silicon source and the electron gun itself as described below under "Operating Experience" an alternate silicon source was installed consisting of a pair of silicon rods of 2 mm x 2 mm cross section and 3 cm length. These rods are heated by passage of an electric currently directly through them. The electrical connections to the rods, which also serve as their physical mount, consist of tungsten wire wrapping at either end. This source technique has been previously described by Kilgore and Roberts[15] and has also been used by Widmer[5] and Chang[8]. Such a source exhibits unusual electrical characteristics as viewed from its terminals; the voltage developed across the silicon continually drops as the current through the silicon is raised due to the heating of the silicon and the consequent rapid reduction in silicon resistivity with temperature. These sources, thermally isolated from one another, were mounted near the track along which the substrate assembly is moved so that the substrate could be brought within 1 cm of either source. The sources are mounted on a water cooled base. One of the prime purposes of the installation of this alternate source was to obtain outgassing characteristics of the silicon itself uninfluenced by outgassing from the electron gun. Since this direct heated source proved much easier to outgas than the electron beam heated source, it was actually used in addition for a deposition onto the substrate as described below under "Operating Experience." Figure 9 is a photograph of the

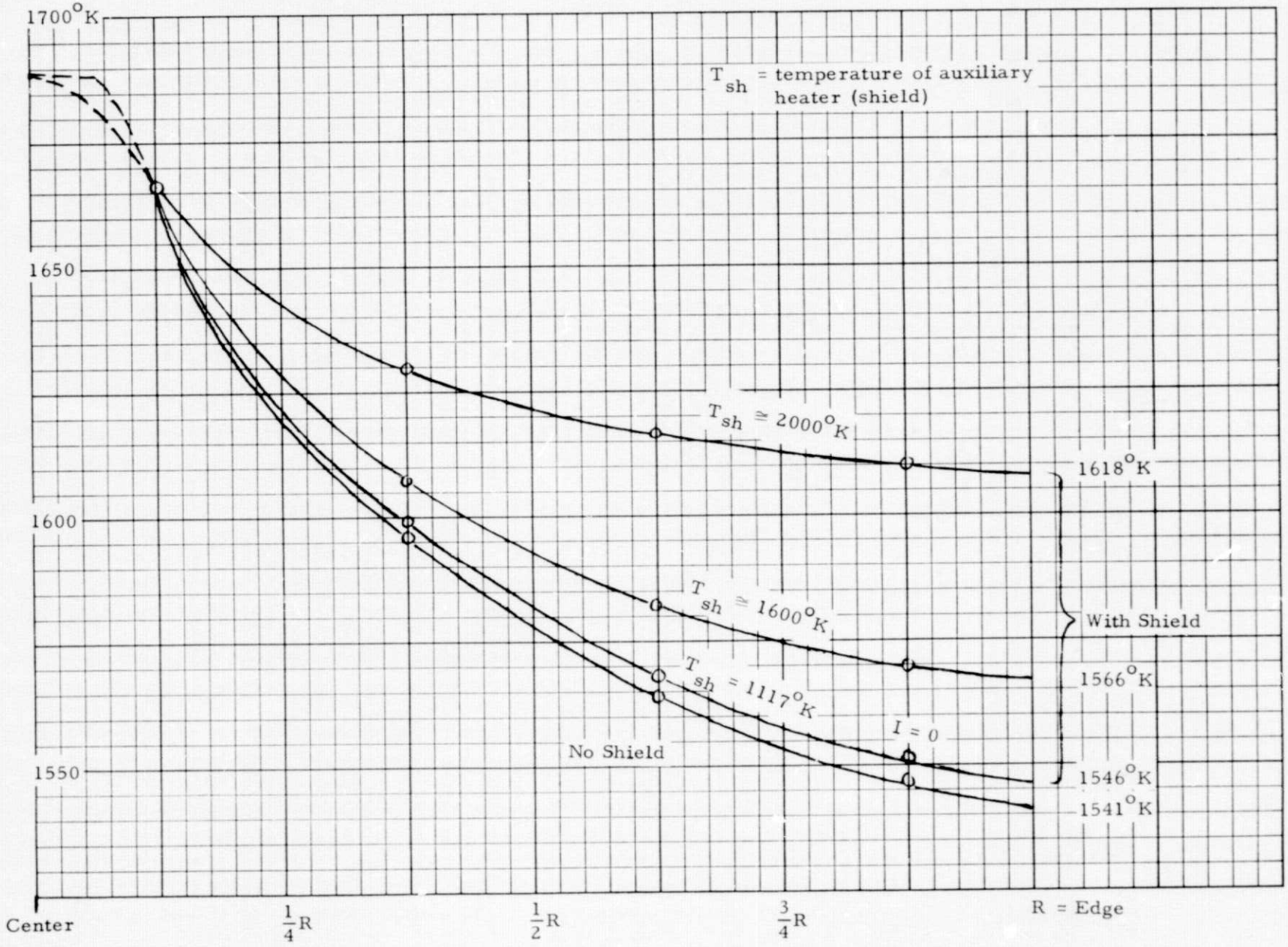


Figure 7. Calculated Temperature Profiles at Top Surface of Silicon Source

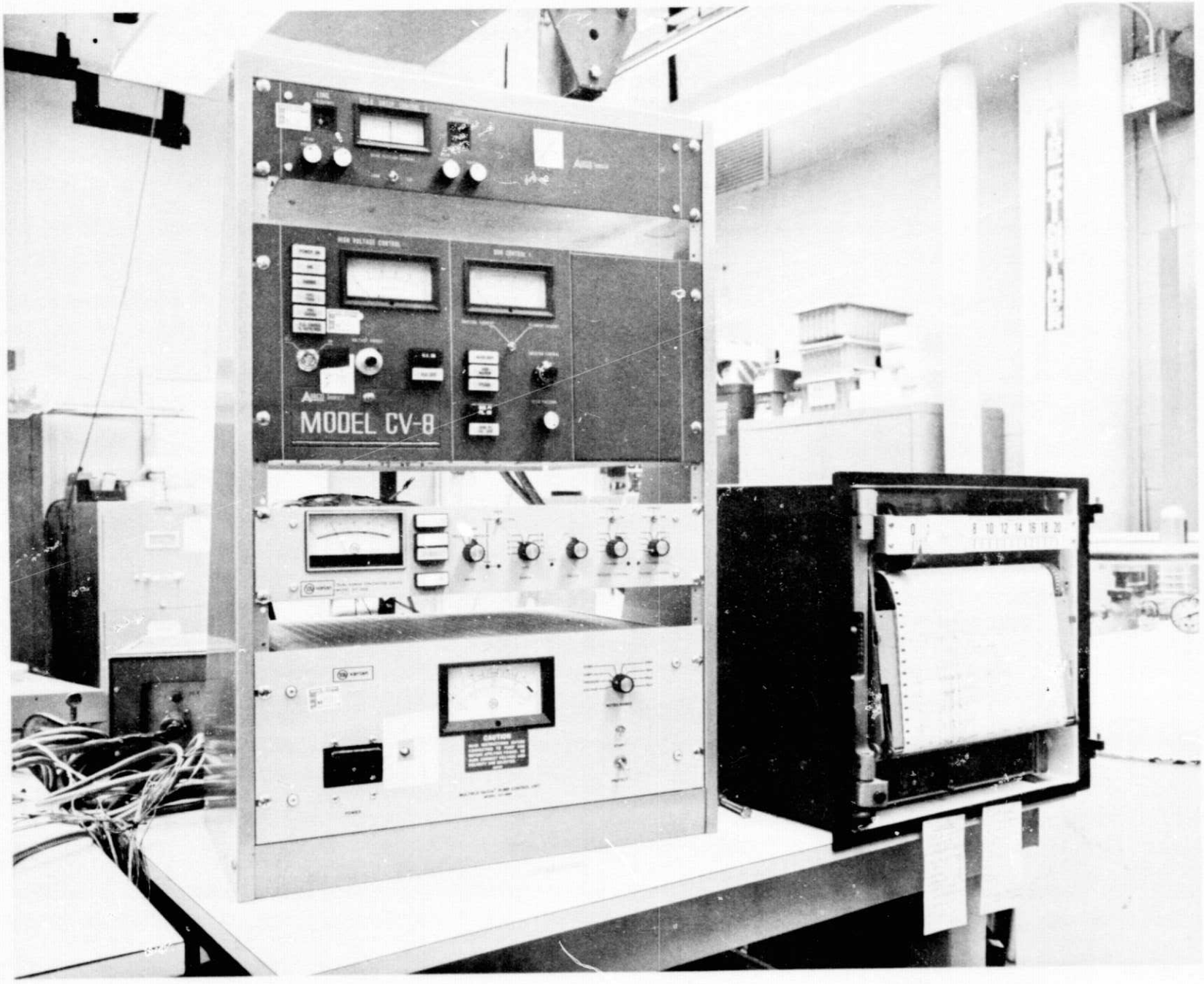


Figure 8. Electron Gun Controls (top), Varian Gauge Control and 400 ℓ/s Pump Control (bottom)

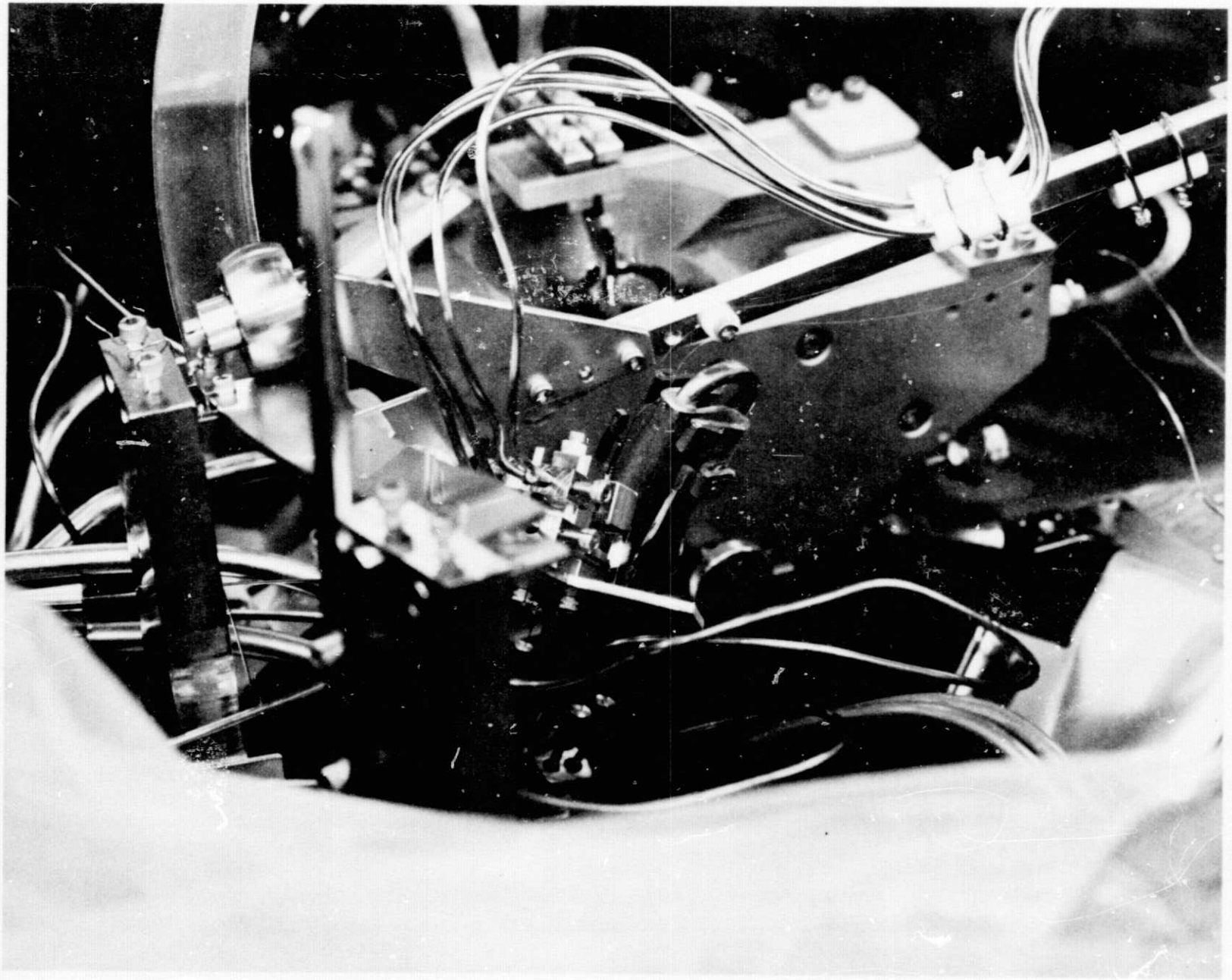


Figure 9. Alternate Silicon Evaporant Source Comprising 2 Resistance Heated Silicon Rods with Tungsten Substrate in Position for Deposition

direct heated silicon rod source with the substrate and holder in position for deposition. This photograph was taken prior to closing of the vacuum system.

This source technique was tested in an auxiliary vacuum system and was found to be quite reliable. Currents of approximately 15 amperes at 12-1/2 volts were found sufficient to bring the main central section of the silicon rod within about 65°C of the melting point. The ends, due primarily to their larger radiation area and, to a smaller extent, heat reduction by the tungsten wires, keep the silicon/tungsten junctions at a temperature some 50-100° lower, thereby avoiding a tungsten-silicon reaction. This type of source was used under similar conditions by Chang[8] at Bell Telephone Labs where he achieved successful heteroepitaxial depositions in ultra-high vacuum.

4.2.3 Outgassing Procedures

With vacuum float zone silicon, included gases are expected to be low in concentration. On the other hand, surface oxides are expected due to the unavoidable exposure of the silicon between final etching and achieving a high vacuum in the evaporation system. In fact, the etching procedure chosen is one which purposely leaves a thin oxide layer in preference to other contaminants which can result from alternate procedures since the oxide layer can be removed by simple pyrolysis. The stable oxide near the silicon melting point is a monooxide and vapor pressure data is available[16]. On the other hand, little data is available on the conversion of the dioxide to the monooxide as pyrolysis temperatures are reached in an ultra-vacuum system. Because the electron beam source heats only the top surface of the silicon, the auxiliary concentric tungsten heater was added to raise the outer cylindric surface temperature adequately into the pyrolysis range.

The outgassing procedure utilized with the electron beam heated source consists first of outgassing the electron gun by operation at filament currents considerably higher than those used during silicon deposition but with the

high voltage disabled, followed by a long period of outgassing of the silicon slug by electron bombardment and by use of the auxiliary tungsten resistance heater. This outgassing is begun at relatively low power levels in order to prevent large pressure rises in the system. The power is gradually increased in steps until silicon temperatures are reached corresponding to reasonable evaporation rates at a desired pressure level.

The auxiliary tungsten heater surrounding the electron gun heated silicon source outgasses quickly as it is first raised to incandescence. It is then left operating for a period of hours in order to outgas, by the action of its radiant heating, the silicon mount and other objects which will be heated by thermal radiation from the silicon. The silicon cylinder is outgassed by electron beam bombardment with the substrate removed to a large distance and out of direct view from the source. Experience has shown that literally days of electron bombardment with a portion of the silicon molten are required in order to reduce desorbed gas loads sufficiently to reach pressures in the 10^{-10} torr regime.

By contrast, degassing of the direct resistance heated silicon sources is relatively rapid, and outgassing can be accomplished in a matter of hours to a level allowing system operation in the low 10^{-10} torr region with silicon source temperatures about 50° below melting.

4.2.4 Silicon Vapor Pressure and Evaporation Rates

The evaporation rate from the silicon source is determined by the silicon vapor pressure corresponding to the source temperature. Considerable uncertainties exist regarding these vapor pressure values as can be seen by the following Table 1 of measurements and reports giving the vapor pressure at 1481°C. In terms of silicon mass evaporated, a vapor pressure of 0.001 torr at this temperature corresponds to an evaporation rate of approximately 7.5 μgrams $cm^{-2} sec^{-1}$. In the case of the directly heated rod source, the temperature is reasonably constant over the central portion away from the ends and one can,

Table 1

			P (torr) at 1481°C
*	1926	O. Ruff & M. Konschak, Z Electrochem 32, 68 (Ref. by Honig (1))	0.08
*	1934	E. Baur & R. Brunner, Helv. Chim Acta 17, 958 (Ref. by Honig (1))	0.10
*	1950	L. Brewer, Paper 3 in "The Chemistry & Metallurgy of Misc. Materials," L. E. Quill, ed. McGraw Hill, N. Y., p. 13 (Ref. by Honig (1))	0.10
*	1954	R. Honig, J. Chem. Phys. 22, 1610 (= Honig (1))	0.009
***	1957	R. Honig, RCA, Rev XVIII, 195 (= Honig (2)) (also in S. Dushman, "Scientific Foundations of Vacuum Technique, John Wiley, N. Y. (1962))	+ 0.0036
*	1958	J. Drowart et al, J. Chem Phys, 29, 1015	0.0003
*	1959	R. Batdorf & F. Smits, J. Appl. Phys., 30, 299	0.00076
*	1961	J. Davis, et al, J. Chem. Phys. 34, 659	0.00091
*		"	0.00030
***	1967	R. Honig in "The Characterization of High Temperature Vapors," J. Margrave ed., Wiley, N. Y. (Ref. = Honig (3))	0.0015

+ Dushman (2nd ed.) & Honig (2) agree exactly $T > T_m$. At T = 1357°C they differ.

T	Dushman	Honig
1177°C	$10^{-2}\mu$	$9 \times 10^{-3}\mu$
1282	$10^{-1}\mu$	10^{-1}
1357	1	0.4

* Independent
** Dependent upon Honig (1)
*** Combination of Honig (2), Batdorf & Davis

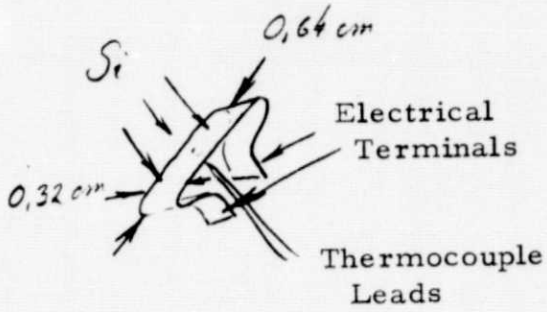
to good approximation, assume a uniform evaporation rate. In the case of the electron gun heated silicon source, temperatures can vary significantly over the silicon surface and account must be taken of this variation. To rough approximation the evaporation rate drops an order of magnitude for 200°C drop in temperature.

4.3 SUBSTRATE HOLDER AND HEATING TECHNIQUES

Various techniques for heating of substrates during vapor deposition experiments have been described in the literature. In the Phase A program experiments were carried out with two of these techniques. The first was used with tungsten substrates and can be extended to other metallic substrates. The second technique was developed as a byproduct of the direct heated silicon source, since by selecting

oriented silicon rods, these same techniques can be used without change in the case where silicon substrates are utilized.

The tungsten substrates consist of a one mil (0.0025 cm) tungsten ribbon as illustrated which is directly heated by passage of an electrical current. Temperatures are monitored by a thermocouple contacting the back side of the substrate. The substrate is thermally desorbed by operation at temperatures in the neighborhood of 2100°K. It is well established in the literature that this treatment desorbs surface gases. Substrate temperature during degassing can be monitored by optical pyrometry as well as by use of a thermocouple. During deposition experiments at lower temperatures only the thermocouple monitor is available.



TUNGSTEN SUBSTRATE

4.4 DEPOSITION RATE MONITOR

The deposition rate monitor is a quartz crystal microbalance. It consists of a cut quartz crystal resonant at 5 MHz with low temperature coefficient mounted on a water cooled stainless steel head. The crystal is mounted in the vacuum chamber so as to be exposed to the source. Deposition onto the crystal lowers its resonant frequency. Approximately, the change of frequency is given by $\Delta f = T\ell/2$ where Δf is the frequency change of the crystal oscillator in Hz, T is the film thickness on the crystal in Angstroms, ℓ is the bulk density of the deposited film in gm/cm^3. Each crystal is capable of ~ 100 kHz excursion corresponding to

~8μ deposit of Si. Placement of the crystal at a distance from the source and/or use of a perforated screen between source and crystal permit monitoring deposits much thicker than that.

To measure the thickness of a film being deposited, the changing frequency of the sensor head is compared against a tunable reference signal. The beat frequency is then suitably treated and read out on a meter to indicate thickness and rate of deposit.

Deposition monitors of this type are used routinely in the laboratory during vapor deposition experiments and one is incorporated in the auxiliary vacuum system used for initial tests of the resistance heated silicon source rods. The monitor used in the ultra-high vacuum deposition system is a 900007 Sloan sensor head UHV bakeable with remote oscillator on 5.94 cm diameter flange mount, read out on a Sloan Deposit Control Master Omni II.

As noted below under "Operating Experience" the bakeable deposition rate monitor had to be removed from the system during the experiment in which tungsten was successfully deposited at pressures below 5×10^{-10} torr and estimates of total deposition thickness during the run were made by monitoring of source temperature and comparison with previous tests with a similar filament mentioned in the interim tests, by quantitative observations of darkening of a glass slide located within the system and by visual observations of the decrease in lateral dimensions of the silicon source ribbon.

4.5 MASS SPECTROMETER

The mass spectrometer incorporated into the system at the port opposite to the substrate thermal desorption station is a Veeco GA-4R residual gas analyzer utilizing magnetic deflection and an electron multiplier. This instrument has been used for a number of routine residual gas analyses in this laboratory for a number of years and has the following specifications.

- Sensitivity - 10^{-13} torr for nitrogen
- Mass Range - 2-300 amu covered in two intervals - 2-50 amu and 12-300 amu
- Resolution - Unit resolution at mass 75 as measured at 1% of peak heights
- Scanning - Automatic or manual; restricted mass range and single peak monitoring
- Readout - Customarily by means of x-y recorder

As mentioned below under "Second System Test" leaks associated with the method of mounting the spectrometer to the ultra-high vacuum system were encountered after bakeout and cooldown and necessitated temporary replacement of this spectrometer with a General Electric monopole 300 mass spectrometer. The characteristics of this spectrometer are as follows.

- Sensitivity - 10^{-12} torr for nitrogen.
- Mass Range - 1-300 atomic mass units in a single range
- Resolution - Unit resolution over entire mass range where resolution is defined in terms of 10% peak height
- Scanning - Linear, automatic or manual
- Readout - Customarily by means of x-y recorder

Mass spectra were read out on a Keithley 417 high speed picoammeter with a 4170 Input Head and on a Mosely 135A X-Y recorder set at 0.5 V/inch.

This spectrometer was attached, through a right angle valve, at the position noted in Figure 4. Results obtained during pumpdown, source outgassing and deposition are described below under "Operating Experience."

5.0 OPERATING EXPERIENCE

The ultra-high vacuum vapor deposition system was subjected to two operational tests. The first of these tests, carried out during March and April, was a preliminary attempt to utilize the electron gun heated source, without auxiliary tungsten resistance heater, to outgas the gun and source and to make a test deposition on a heated tungsten substrate at the lowest possible pressure. Premature failure, through fracture, of the electron gun filament terminated this attempt at a time when the total system pressure with the central portion of the silicon source at the melting temperature was 5×10^{-9} torr. With the silicon source at a slightly reduced temperature, the system pressure was 3.8×10^{-9} torr. This first run did, however, give a check on most other system components which were found satisfactory. Some unsatisfactory features were corrected, as noted in detail below, and a second operational test was carried out during early August which included tests of both the electron gun heated source with auxiliary heaters and the direct resistance heated silicon source. Since the latter source proved much easier to outgas, it was utilized for the actual deposition onto a heated tungsten substrate carried out at pressures ranging from 2 to 4×10^{-10} torr. In addition, mass spectrometer analysis of residual gases was carried out within the system at various stages preparatory to and during the deposition run. Although the electron gun was not used for the actual deposition experiment, its outgassing and operating characteristics were thoroughly explored with and without the auxiliary tungsten heater operating and no failure was encountered. These two system tests are described in more detail below.

5.1 FIRST SYSTEM TEST

The first run included most of the hardware and assemblies expected to be needed in subsequent runs. This included all of the apparatus in the system description above with the exception of the auxiliary tungsten heater, the resistance heated silicon, the mass spectrometer and the deposition monitor.

5.1.1 Pumpdown and Bakeout

After the apparatus was cleaned and assembled in the vacuum system, the vacuum chamber and the 1200 ℓ/s pump were evacuated and baked at 320°C while pumping with the 400 ℓ/s pump. During this period, both ion gauges were outgassed, the tungsten substrate was heated to 1300°K for several minutes to aid outgassing of its supporting material, the 1200 ℓ/s pump was turned on for short periods to aid its outgassing, and the shutter and substrate arm were moved to test their operation. Finally, the 1200 ℓ/s pump was turned on with the system at 320°C and 1.5×10^{-6} torr, and run at this temperature for a day. Pressure was then 5×10^{-7} torr and cooling of the system was begun. After the run was ended, the system was left under vacuum and reached a pressure of 8×10^{-11} torr after several days.

5.1.2 Gun and Source Outgassing

A tungsten block was clamped to the electron beam gun to serve as an alternative target during outgassing of the electron beam filament and anode assembly. Variation of the electron gun voltage permitted moving the beam to strike either the tungsten or the silicon source. The beam could also be moved to strike portions of the Mo crucible and Ta support. 10 kV was required to make the beam hit the tungsten. 5.5 to 6 kV was required to make the beam hit the silicon. Outgassing of the filament could also be accomplished by disabling the high voltage and running the filament at a high current. Since this did not contribute additional gas from the tungsten target, considerable time was spent in this outgassing mode.

Except at the very lowest pressures, the GE gauge indicated slightly lower pressure than the nude Varian gauge. However, the Varian gauge yielded spuriously low pressure indications when there was a large electron beam current. The GE gauge did not show this effect. The cause of the dependence of the nude gauge reading on electron beam current was explored by use of an electrostatic shield grid in the second system test described below.

There were three sources of heat which can cause a pressure rise during a deposition: the electron gun filament, the heated Si source and the heated substrate. Considerable time after cooldown was spent outgassing the areas around the first two of these. The electron gun filament failed prematurely after about 83 hours of use before outgassing had been completed.

Degassing of the gun filament and nearby parts was carried out by disabling the high voltage in order to outgas the filament and its surroundings while using a high current. This also permitted better identification of gas sources by isolating filament heating effects from Si heating effects. When this was done, it was obvious that although little gas was desorbed from the filament itself, much gas was desorbed from the surroundings. A small gas burst from the filament lasting a few seconds was observed when the filament was first heated. Then a much larger gas quantity began evolving as the surroundings were heated and took about one hour to peak before beginning to fall.

Application of 19 amp. filament current resulted in a pressure peak of 2×10^{-9} torr. After outgassing the filament overnight at 22 amp., the pressure peak for 19 amp. current was 1×10^{-9} torr. The filament was heated overnight on April 5-6 at 36 amp. Peak pressure was 6.5×10^{-8} and pressure fell to 2.5×10^{-9} after 17 hours at 36 amp. After various other outgassings during the day, the filament was again set to 36 amp. for an overnight heating. Peak pressure was then only 3.8×10^{-9} torr and fell to 2.2×10^{-9} torr and was declining after 3 hours when the filament failed. Since the required filament current was only 19 amp., it is believed that the pressure rise from heating the filament and its surroundings would not have been enough to prevent evaporation at 5×10^{-10} torr after further outgassing. This speculation was confirmed by the results of the second system test, described below.

Prior to failure of the gun filament, the Si source was electron beam heated several times for a total period of about 24 hours. At first pressure rose to

10^{-8} torr with the Si at 1000°C. On April 6, pressure was 5.5×10^{-9} torr with portions of the Si molten and 3.8×10^{-9} torr with the hottest spot of the Si just below melting.

An undetermined fraction of the gas evolved while heating the Si originated in the Ta and Mo support structure and other surrounding materials. The electron beam was used to heat these much hotter than their temperature during the Si heating. One result of these outgassing tests was a decision to reduce the area and mass of the support for the second system test and to include an auxiliary resistive heater to aid in the outgassing process.

5.1.3 Substrate Outgassing

After the electron gun failure, substrate assembly outgassing was investigated and yielded satisfactory results. The substrate temperature was gradually raised to 2250°K and the pressure rose to $\sim 5 \times 10^{-8}$ torr. Cooling to 1500°K, pressure dropped to 3×10^{-10} torr in about 1-1/2 hours. Temperature was then raised to 1900°K. Pressure rose to 1×10^{-9} torr and then decreased steadily. After 3 hours pressure was $< 7 \times 10^{-10}$ torr and declining steadily.

Total use of the electron beam filament was 83.1 hours as follows:

Establishing operating characteristics of gun	2.4 hr.
Beam impinging on tungsten target	5.2 hr.
Heating of Ta and Mo support	7.6 hr.
Outgassing gun filament with high voltage disabled	42.2 hr.
Heating of Si source	25.7 hr.

5.1.4 Observations of Silicon Source

The silicon was partially molten for less than two hours. Melting was easily detected by observation of the reduced emissivity (darkening) of the molten area. Total molten area could be varied from a just visible spot to a lens shaped area having maximum dimensions 5 mm x 14 mm. Varying the high voltage allowed moving the molten area across the face of the Si source. Pyrometer measurements indicated a maximum temperature difference of 200°C between a small molten central zone and the periphery of the silicon.

Areas of the source which were melted can be seen in Figure 6. As can be seen it was possible to melt a substantial portion of the source surface, though not all at once. Careful examination of the top surface of the source shows shallow depressions, indicating that a significant quantity of silicon was evaporated during the outgassing process. A layer about 1.5μ thick was deposited on the tungsten alternative target which overhung the hearth somewhat and was approximately 2 cm away. A glass slide located on the shutter 20 cm away had a deposit of approximately 0.5 microns. It should be noted that the two numbers cannot easily be related to distance because the tungsten was heated by the electron beam and some of the silicon deposition was probably reevaporated. Also the glass slide was not continuously exposed to the hot Si because of periodic operation of the shutter.

5.1.5 Conclusions from First Run

Several conclusions were reached from the first run and applied to the preparations for the second.

The substrate and its assembly did not present a serious outgassing problem and were not modified.

The electron beam filament and its surroundings present a serious outgassing problem. In order to reduce the outgassing time needed, the filament assembly for the second run was baked at T > 1000°C before attachment to the gun base. Although the gas evolved was reduced in the second run, it is not clear whether

this was the result of the preliminary bake or of the outgassing done in the first run. In any event the effect, though positive, was not dramatic.

The silicon source and its surroundings are difficult to outgas. It is difficult to overheat the surroundings prior to deposition and then reduce their temperature during deposition as can be done with the electron beam filament.

It was obvious that a residual gas analysis of the system would be helpful in determining the origin of the principal sources of gas and that a mass spectrometer should be incorporated into the system before the next run. This was planned in any event so as to be able to characterize the partial pressures of reactive gases in the system during deposition since these are expected to be of greater importance to the achievement of epitaxial growth than the total pressure.

It was concluded that vacuum firing of the silicon source mount and those parts of the electron gun which are not effectively water cooled should be carried out at as high as possible a temperature. Since it was suspected that a large contribution to the outgassing could arise from the silicon source itself and since the cylindric surface cannot be heated by the electron beam as effectively as the central region, it was decided to add a concentric resistance heater surrounding the silicon cylinder in order to obtain a higher temperature for the bulk of the silicon. Since no problems were encountered with pouring of molten silicon over the edge of the cylinder, it was also learned that the size of the silicon source could be reduced in order to reduce the outgassing area and to speed up silicon outgassing.

Since the molybdenum crucible cup furnished with the gun and used to protect the gun from any spilled molten silicon was suspected to be a significant gas source, based on observations of the pressure rise when the electron beam was directed to it, it was decided to replace this with a thin sheet of tantalum which was known from previous vacuum work to be relatively clean and easy to outgas.

It was obvious that redundant ion pressure gauge readings are required in the program and that the possibilities of electrostatic shielding around the Varian gauge should be explored. Since the crystal deposition rate monitor available in the laboratory was not bakeable, a Sloan rate monitor capable of baking to 450°C was ordered.

One of the two magnetic rotary feedthroughs (the one operating the movable substrate arm) proved unreliable in the first run. It was decided to replace this with a direct coupled bellows type actuator rather than to rely on adjustments of the magnetic device.

5.2 INTERIM TESTS OF RESISTANCE HEATED SOURCE AND AUXILIARY HEATER FOR GUN-HEATED SOURCE

As described above, alternate silicon sources of the type described by Kilgore and Roberts[15] consisting of thin silicon rods heated directly by passage through them of an electric current were prepared. A source of this type was constructed and tested in an auxiliary vacuum system prior to incorporation into the main ultra-high vacuum system for use in the second system test. During these auxiliary tests of the resistance heated source, experience was gained in preheating and operation of the resistance heated source taking account of its peculiar voltage current relationships mentioned above as brought about by the rapid decrease of the resistivity of intrinsic silicon with temperature.

In a vacuum chamber at a pressure of 10^{-6} torr, a current of approximately 15 amperes through the 0.2 cm x 0.2 cm x 3 cm silicon rod gave a surface temperature of 1610°K over most of the rod length except at the ends. A vapor deposited layer of silicon approximately 0.5 micron thick, as determined by interference fringe measurements, was deposited in 40 minutes.

The auxiliary tungsten sheet heater for the electron gun heated silicon source was also tested in this auxiliary vacuum system. Forty amperes passing through the 0.0062 cm thick tungsten foil raised its temperature to 2000°K. In the initial

design tested, sagging was noted after prolonged operation due to bending of the hot tungsten foil in the region where it passed to the electrical connections. A new design with the feature that the hottest tungsten sheet material lay nearly in a vertical plane corrected this deficiency.

5.3 SECOND SYSTEM TEST

5.3.1 Preparation

For the second run, the size of the silicon source was reduced to 1.5 cm diameter and the support was redesigned. Also the large Mo crucible which functions as a protection for the copper hearth in the event the Si should melt and run down was replaced by a thin Ta cup covering only the bottom of the Cu hearth. In addition, a tungsten strip heater was added surrounding the source as described above. This can be used to overheat the surroundings before deposition since W can be heated much hotter than Si.

The Veeco mass spectrometer was added to the system. A stainless steel shield with controllable electrical potential was installed around this gauge. The new rotary feedthrough was installed.

Two major leaks were encountered after bakeout; one associated with the Veeco mass spectrometer, the other with the electrical feedthrough for the deposition rate monitor. Because the former appeared associated with the mounting of the spectrometer which could not be quickly corrected, the Veeco spectrometer was replaced for the run with the GE monopole spectrometer as noted above. The leak in the deposition rate monitor flange required its removal. Since a substitute for this bakeable device was not available, deposition thicknesses were estimated by observation of the gradual reduction in silicon ribbon source size, by quantitative observations of darkening of a glass slide used as a temporary deposition monitor and by measurements of source temperature and relating to previous measurements with this silicon ribbon source geometry.

5.3.2 Pumpdown and Bakeout

Except for the occurrence of a number of leaks associated with the addition of the mass spectrometer and the deposition rate monitor, which necessitated starting over, the second pumpdown was similar to the first. The 1200 ℓ/s pump was turned on at 1.7×10^{-6} torr and run for only two hours at 320°C before the heater was turned off at a pressure of 3.7×10^{-7} torr. After start of cooldown, pressure dropped to 2×10^{-10} torr in 24 hours and to 7×10^{-11} torr over the weekend. About a day was spent outgassing ion gauges and mass spectrometer after which pressure was 1×10^{-10} with these in "On" condition.

5.3.3 Source and Substrate Outgassing

One of the resistive silicon sources was gradually heated in order to outgas it. This was done very conservatively keeping the pressure below 2×10^{-9} torr and generally in the 10^{-10} torr range. At the end of 8 hours the temperature had been raised to 1525°K at a current of 12 amp. through the filament. Pressure was then 4.8×10^{-10} torr. The filament was then cooled to room temperature so substrate outgassing could be studied the next day.

The tungsten substrate was heated as in run #1 by passing current through it. Temperature was raised to ~2000°K, as measured using the pyrometer with pressure still in the low 10^{-10} torr range before heating of the surroundings began to cause a slow pressure rise. The substrate was heated to a maximum temperature of 2200°K causing pressure to rise to 2.4×10^{-9} torr before beginning to fall. Substrate temperature was left at 2100°K and pressure fell to 3.8×10^{-10} torr in a few hours. Left at this temperature overnight, pressure fell to 2.5×10^{-10} torr by morning. Since there was no noticeable pressure rise when the substrate assembly was later brought close to the hot Si filament for deposition of Si, it appears that most of the substrate assembly outgassing time was unnecessary.

Substrate temperatures mentioned above are all pyrometrically measured. Comparison of the temperature measured with the pyrometer with that measured

with the tungsten/3% rhenium - tungsten/25% rhenium thermocouple showed that the thermocouple indicated a lower temperature ($\sim 70^{\circ}$ lower at 1200°K). This is not unexpected since heat is conducted down the thermocouple wires reducing the temperature at the junction and since the contact of the thermocouple to the substrate may not be optimum. As the temperature is lowered these effects should become less pronounced. Thus the substrate temperature as measured by the thermocouple at deposition temperature should be accurate within about 50°.

5.3.4 Silicon Deposition

Finally the silicon filament was reheated to $\sim 1510^{\circ}$K and the substrate was moved into position at 2 cm from the filament. Pressure was 3×10^{-10} torr. The Si temperature was then gradually raised to increase the deposition rate while always maintaining pressure below 3.5×10^{-10} torr. Si temperature was raised to 1550°K in 5 hours and to 1625°K in 3 more hours. Heating was continued 14 more hours (total of 22 hours). Substantial deposit could be seen on a glass slide located about 20 cm from the source. During the latter hours of the run, the system pressure had reduced to 1.5×10^{-10} torr. Substrate temperature was $400^{\circ} \pm 50^{\circ}$C.

5.3.5 Electron Gun Heated Source Tests

Following deposition on the tungsten substrate from the resistively heated source and prior to opening the vacuum chamber, the electron beam gun was operated to establish its outgassing and operating properties, with the substrate in a position protected from further silicon deposition.

The prediction from the first run that the electron beam filament could be successfully outgassed was confirmed. After outgassing with the high voltage disabled for 48 hours at less than maximum filament current of 36 amp., the pressure was 1.6×10^{-10} torr at 18 amp. filament current and 2.6×10^{-10} torr at 25 amp. with no water flowing in the bell jar cooling coil. (Water was flowing in the electron gun cooling coil.)

Efforts were then begun to outgas the Si and its surroundings using the electron beam and the auxiliary heater. After about 15 hours of heating the Si at temperatures up to 1650°K using both heat sources, pressure was 2.6×10^{-9} torr independent of whether the auxiliary heater was on or not. This indicates that the pressure is not a result of heating the area of the gun surrounding the Si. Continuing to heat with both sources overnight reduced the pressure to 1.6×10^{-9} torr. Turning off the electron beam, the pressure dropped to 4×10^{-10} torr in about 30 minutes with the auxiliary heater at 1940°K. When the auxiliary heater was also turned off, pressure dropped to 2.2×10^{-10} in 1 hour. Since portions of the apparatus were still warm after this time, this indicated that the base pressure of the system was essentially unchanged. The electron beam heater alone was then turned on and the Si heated to produce a small molten zone. Pressure rose to 2.4×10^{-9}. This was left on overnight. By morning, the beam current had dropped slightly so the molten zone just disappeared. Pressure was 1.4×10^{-9} torr.

The thermal model of the silicon source heated solely by electron beam impingement bringing the central upper surface to the melting temperature was confirmed to ± 50°C and gives a predicted deposition rate of about $1\mu\ hr^{-1}$ at 4 cm distance.

After a total outgassing time of 26 hours with the electron beam impinging on the silicon and with a small molten zone on the silicon, it appeared that although the system pressure was dropping slowly, several days at these conditions would be required in order to bring the total system pressure down to the specified level of 5×10^{-10} torr. Even if this could have been achieved during this run, this would have represented a total time spent outgassing the electron gun and silicon source of approximately one week whereas the direct heated silicon source was outgassed sufficiently within a matter of only 6 or 7 hours before depositions could be begun at pressure levels below this. It was therefore decided to terminate the testing of the electron gun heated source in favor of shutting down the system for removal and examination of the successful deposition made using the resistance heated source.

5.3.6 Ion Gauge Screen Tests

During the first run, during March and April, the pressure readings obtained from the Varian UHV gauge were frequently of no value due to a dependence of the Varian pressure readings upon the operation of the electron beam gun. The Varian gauge was apparently affected by scattered and/or secondary electrons from the electron beam which entered the gauge and caused spurious currents in the ion current circuit. For the second system test during August, a stainless steel screen was installed between the Varian gauge and the vacuum chamber to investigate control of these stray electrons. The potential of the screen could be controlled from outside the vacuum chamber via an electrical feedthrough. During most of the run the screen was left grounded and no obviously erroneous pressure readings were observed. While the electron beam power into the silicon disc was sufficiently large to maintain a small molten region on the surface of the silicon, the potential of the screen was varied from +300 volts to -2000 volts. At all the positive potentials the pressure indication in each gauge increased and approximately 1 milliampere flowed into the screen. Presumably 1 ma of electrons were drawn to the screen and heated it upon impact, causing the temperature of and outgassing from the screen to increase. As the potential of the screen was made negative, the GE gauge readings were unaffected and the Varian gauge pressure readings first increased, by approximately 20% at about 550 volts, and then decreased, going to values of pressure lower than those for the screen at 0 volts, at -2000 volts. When operated with no applied potential, the potential of the screen slowly rose from zero, after being ungrounded, to a measured -10 volts.

These observations tend to confirm the hypothesis that the reduction in the Varian gauge readings relative to those of the GE gauge during operation of the electron gun are due to the impingement of electrons on the ion collector of the nude Varian gauge. Since most of these electrons would be relatively low energy inelastically scattered electrons and secondary electrons, they should be repelled by a relatively low potential applied to the screen. This was in fact observed. With the higher negative potentials applied to the screen, positive ions may be

attracted to the screen with sufficient energy to cause emission of additional secondaries in the neighborhood of the gauge. This could explain the decrease in Varian gauge reading at the higher voltages. With the screen disconnected from ground or a source of potential, its negative potential would rise to a value comparable to the mean energy of the scattered electrons reaching it, at which point it would be able to repel those electrons. This would explain the fact that the gauge readings were approximately the same either with the screen floating or with it connected to a negative potential of several hundred volts.

5.3.7 Observations of Outgassing Characteristics

In the cases where direct resistive heating of silicon or tungsten is used to outgas the elements of the system which are hot during deposition, outgassing is quite straightforward and reasonably easily accomplished. Outgassing to permit use of the electron beam heated source, however, has been more difficult.

Mass spectra from 1 to 50 AMU were obtained on the GE Monopole 300 manually scanning at 75V ionization voltage and 1 ma emission current.

During pumpdown from 10^{-6} torr to 10^{-10} torr, a number of hydrocarbon peaks were observed to reduce in intensity leaving the spectrum shown in Figure 10. The three major peaks in this spectrum are hydrogen to the left, mass 28 attributed to CO (and N_2) and mass 44 attributed to CO_2.

Observations of mass scans, from mass numbers 0 to 50, taken under the various outgassing conditions indicate that the spectrum of gases generated by the electron beam heating differs considerably from that generated during resistive heating.

First consider the relative quantities of mass numbers 2, 12, 28 and 44. Mass 12 is of course associated with carbon.

Figure 11 shows the spectrum during initial heating of the resistance heated silicon source. The upper curve has ~ 3X gain setting of the lower curve. The proportion of mass numbers 28 and 44 has risen compared to the

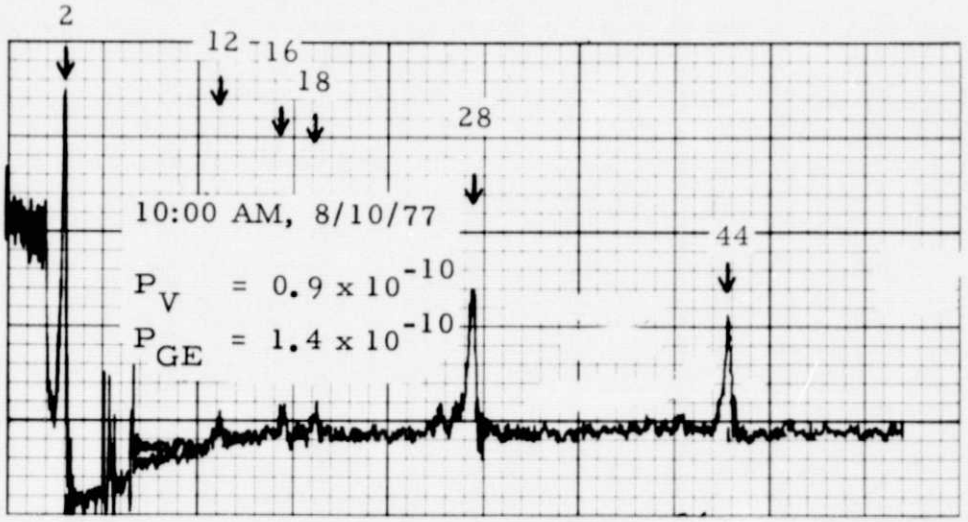


Figure 10. Mass Scan of System After Bake, at a Pressure Near 10^{-10} torr, 0.3×10^{-8} full scale

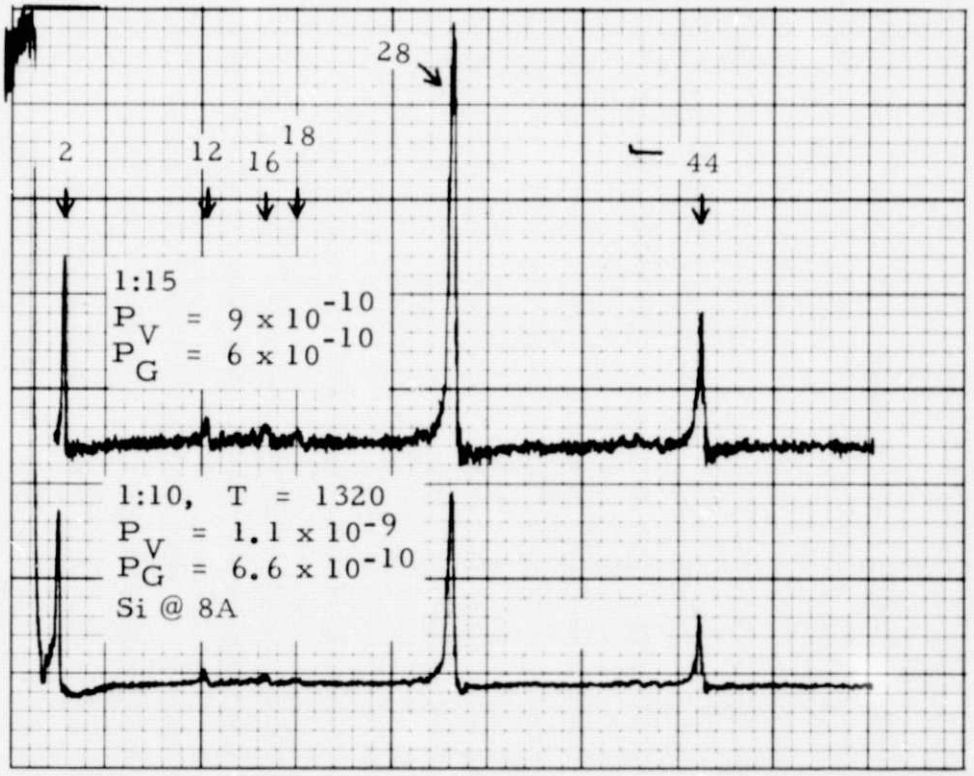


Figure 11. Mass Scan During Initial Outgassing of Resistance Heated Silicon Source
Upper curve - 0.3×10^{-8} A, full scale;
lower curve - 1×10^{-8} A, full scale.

hydrogen. Continued heating returns the proportions to near those of the cool system. Small peaks are observed at mass 12 and 16 and attributed to carbon and oxygen (or CH_4).

Heating the substrate, there is little change in the ratios of the above compared with the cool system except for relatively less mass number 44.

Heating the electron beam filament with the high voltage disabled, the quantity of mass number 28 increases relative to the above.

Heating the silicon with the electron beam, the quantity of hydrogen (mass 2) rises (Figure 12) substantially relative to the others and is still high after many hours of heating. This is much different from the effect of heating the resistively heated silicon.

Scans taken with the system cool, during resistive silicon outgas, substrate outgas, or during deposition of silicon from the resistively heated source, show peaks at mass numbers 16 and 18 comparable to that at mass number 12. During outgassing of the filament of the electron beam heater with no high voltage the peak at mass number 18 was hardly noticeable. When the electron beam is hitting the silicon, peaks at mass 15 and 16 are somewhat larger than that at 12, while mass number 18 is hardly noticeable.

Thus electron beam heating of the silicon generates a different mass spectrum than resistive heating of the silicon filament, and it appears that the high pressure observed during electron beam heating of silicon is not due to simple outgassing of the silicon. Possibly stray electrons heat some other element of the gun or other apparatus.

5.3.8 Examination of Substrate After Removal From System

Upon removing the substrate assembly from the system it was discovered that a procedural error had resulted in the substrate being located a distance of 2.0 cm

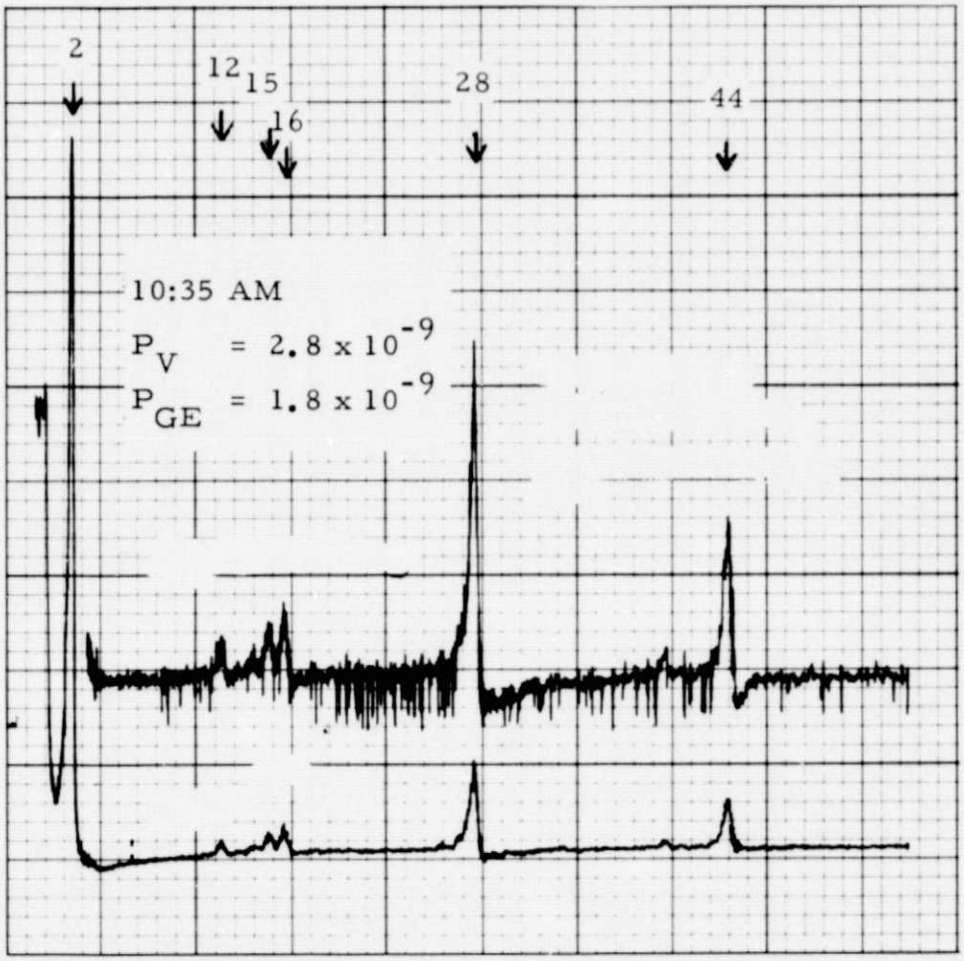


Figure 12. Mass Scan Taken During Outgassing of Electron Beam Heated Silicon Source
Upper curve - 0.3×10^{-8} A full scale;
lower curve - 1×10^{-8} A full scale.

from the silicon ribbon source which was used during the deposition instead of 1.0 cm as planned. This relative position error also resulted in exposure of the substrate surface to the impinging silicon flux at a considerably oblique angle estimated as 70-80° away from the normal to the foil surface. Relatively thick deposits were noted on most of the substrate assembly and, on one stainless steel part of the substrate assembly which was near the source, severe peeling of the deposited layer was noticed. The deposits on other surfaces appeared quite smooth and featureless except that at very large distances on some exposed areas of the bell jar interior optical diffraction patterns were noted due to the thinness of the deposition at those distances.

Upon removal of the tungsten substrate from the holder it was noted that a gray layer had been formed on the exposed portions of the substrate as compared to the bright metallic color of the tungsten in the unexposed portions. Figure 13 shows the front surface of the tungsten substrate with silicon deposit. An attempt was made to remove the central portion of the substrate by cutting. Fracturing occurred due to the embrittlement of the tungsten but a piece of suitable size for examination was obtained. It was noted that the fracture in the tungsten and silicon did not exactly coincide so that a step was observable along most of the edge where the bare tungsten substrate was observable directly in a narrow region. Measurements with a Watson-Barnet interferometer across this step were made to measure the silicon layer thickness. Figure 14 is a photograph at 142X of the white light fringes across the step. The silicon film is to the left and the arrows indicate the darkest fringe formed by reflection from the silicon and from the bare tungsten ledge. Counting of fringes in monochromatic light gave a silicon film thickness of $2.5 \pm 0.1\,\mu$. Grain boundaries are obvious. Since in most cases these are observed to cross the step these apparently depict the grain structure of the tungsten substrate. Their average width appears to be 50-100 μ. It is planned to further characterize this silicon deposit as part of the Phase B program.

The silicon-tungsten ledge along the fracture was examined with the scanning electron probe. A typical region photographed at 750X in the silicon K_α line is

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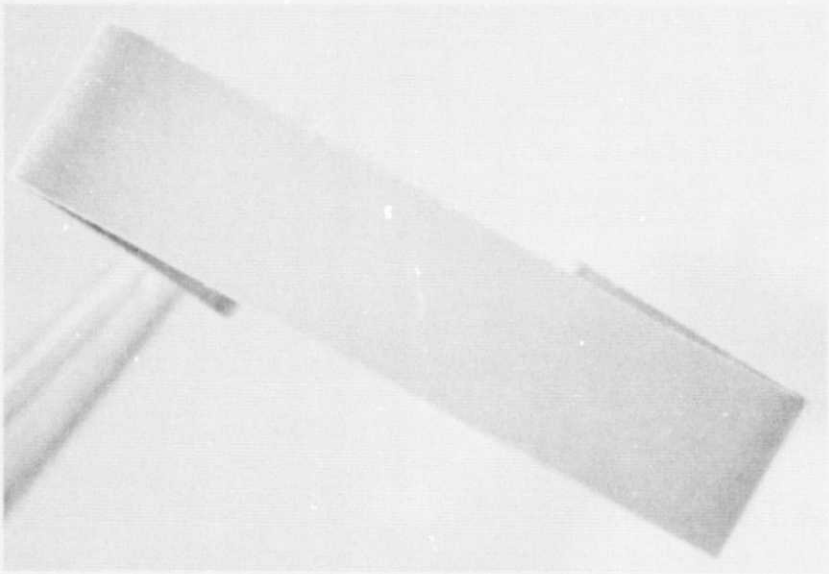

Figure 13. Tungsten substrate with silicon deposit after removal from system. The ribbon width is 0.32 cm.

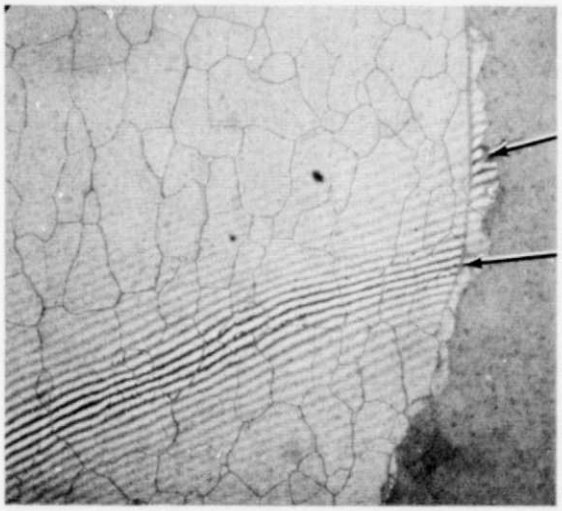

Figure 14. White light fringes observed across the silicon ledge observed near a fracture in the substrate. The silicon film lies to the left. The arrows depict the darkest fringe corresponding to the front surface of the silicon and the narrow bare tungsten ledge, 142X.

shown as Figure 15. The lightest color region is the silicon film and the bare tungsten ledge appears faintly. Figure 16 is a photograph taken in the M_α line of tungsten in the same region. Here the fractured edge of the tungsten appears sharper and the bare tungsten ledge gives the largest signal. Since the 25 kev electrons can penetrate the silicon layer, a lower intensity signal is also received from beneath the silicon film.

One of the silicon peelings from the stainless steel substrate assembly was removed and photographed edge on as shown in Figure 17 taken at 500X. This film thickness was measured as $9 \pm 1\mu$. The steel surface was oriented nearly normally to the silicon flux. Since the steel originally underlying this silicon flake was at a similar distance from the source as the tungsten substrate (2 ± 0.2 cm), the difference in thickness of the two deposits is consistent with the different angles of orientation for the two substrates. The silicon flakes are curved with their convex sides towards the stainless steel. Since peeling was observed only in the regions of the thickest deposits, a tentative conclusion may be made that the silicon ~~tungsten~~ steel bond formed during the deposition is insufficient to carry the stresses due to differential thermal contraction for silicon films thicker than several microns deposited under these conditions.

5.3.9 Conclusions from the Second System Test

From the results of the second system test it is generally concluded that the facility is suitable for carrying out the deposition experiments planned for the Phase B portion of the program provided the resistance heated source is used. Since this has proven far easier to outgas than the electron beam heated source, it is thus planned to emphasize use of this source although further work with the electron gun may be considered in later phases of the program. This will, of course, require gun and source outgassing times of the order of a week and may require some further improvement in procedures, for example a bakeout of the entire gun assembly instead of only its high temperature parts. This may require modifications of the gun assembly since the gun water leads at present do not allow fitting the entire gun assembly into an available baking oven.

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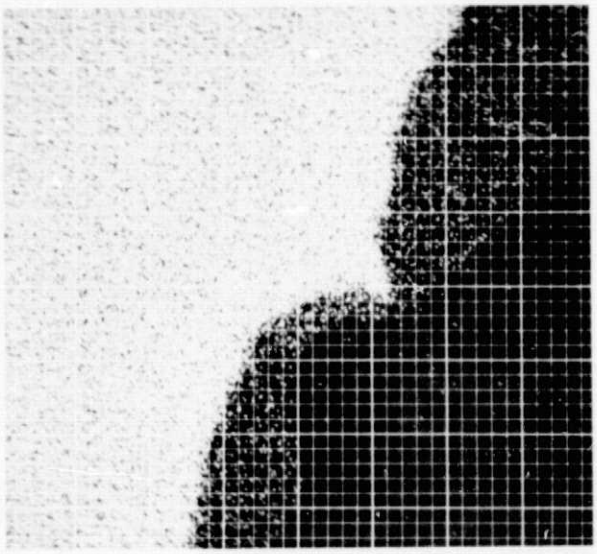

Figure 15. Electron probe micrograph of silicon step and tungsten ledge, K_α silicon X-ray, 750X.

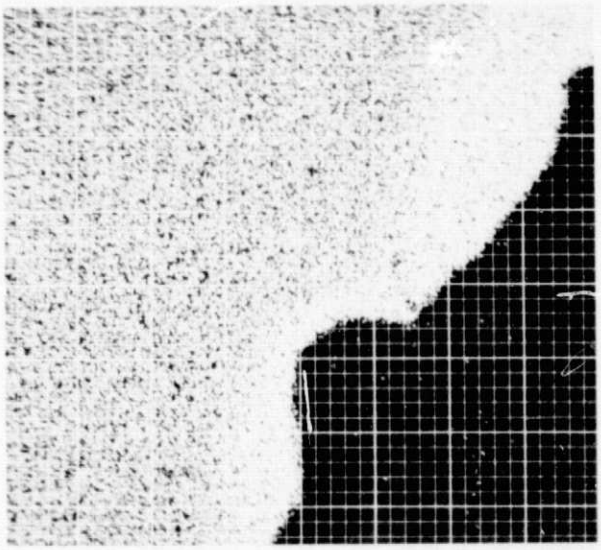

Figure 16. Electron probe micrograph, M_α tungsten X-ray, showing tungsten edge and ledge (brightest area), 750X, same area as Figure 15.

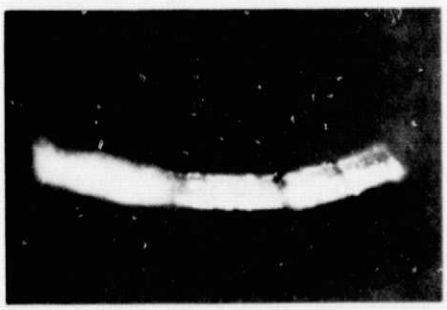

Figure 17. Edge view of silicon film peeled from stainless steel, 500X.

A second major conclusion is that oxygen partial pressure during depositions can be made negligible with respect to partial pressures of hydrogen and other gases. The most prominent gases, other than hydrogen, determined are of mass 28 and 44, probably largely due to CO and CO_2 although the latter was not enhanced by operation of the resistance heated source. Since CO is a highly reactive gas, further work should be done to identify its source in order to attempt to reduce its partial pressure. The possibility for a contribution by SiO to the peak detected at mass 44 should be resolved by an experiment with a mass spectrometer viewing the source directly.

The observed deposition rate on the steel 2 cm from the source at normal incidence was $0.4\,\mu\,hr^{-1}$. Extrapolating this to 1 cm distance gives a predicted deposition rate of $1.6\,\mu\,hr^{-1}$. Closer source to substrate distances are possible at the highest substrate temperatures where radiative heating from the source is tolerable.

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APPENDIX A

The following, excerpted from the informal Phase B Plan previously submitted to NASA, describes the most important aspect of the planned Phase B work in terms of choice of substrate types for study. Depositions are to be carried out at various temperatures and resulting films characterized metallographically and, where large enough crystals are obtained, electrically, for potential application as thin film photovoltaic material.

SUBSTRATE SELECTION CRITERIA

Substrates chosen for study in this program should satisfy most or all of the following criteria.

1. Materials which have exhibited epitaxial growth of silicon in previous experiments. Some of these materials should be studied in the present program as a basis of comparison and in an attempt to extend the existing data, particularly with regard to measurement of reactive gases present.

2. A priori likelihood of obtaining good epitaxy with sufficient grain size based on theoretical or other evidence.

3. Technical interest relative to ultimate applications in solar cells or in bipolar devices on insulating substrates.

4. Availability of practical in situ cleaning and heating techniques.

5. Thermal expansion coefficient and compatibility of substrate with respect to chemical reactions and diffusions into silicon.

These criteria will be discussed individually. In the process it will be seen that relatively few substrate candidates survive screening by all or even most of these criteria.

1. Extension of Existing Work

Here we may refer to the homoepitaxial growth experiments of Widmer and Jona, the silicon recrystallization experiments of Mayer, and the chemical vapor deposition work of Chu[16]. The work of Widmer is limited in that his studies of silicon on (1, 0, 0) silicon did not extend over the temperature range just below 600°C. Such an extension would be important to compare with the work of Jona who observed homoepitaxy at room temperature for this orientation and for comparison with the recrystallization studies of Mayer who observed more rapid crystallization in the (1, 0, 0) direction. An even more compelling reason for studies of silicon on silicon is that this is the process which is encountered beyond the first few layers of deposition onto any substrate.

With regard to Chu's work with chemical vapor deposition of silicon on tungsten, it would be of interest to see if his 5 micron grain size could be increased by the use of vacuum vapor deposition in an ultra-clean system. Tungsten is also a prime substrate candidate in terms of its close match in thermal expansion coefficient with silicon and the fact that tungsten has been proposed by several investigators as a prime candidate diffuse barrier on other less expensive substrates. Recent work in development of high vacuum vapor deposition of dense tungsten films by use of superheated levitated tungsten melts indicates that deposition of such thin layers on practicable substrate materials may be practical, particularly if the possibilities for such manufacturing processes in the space environment are considered.

The work of Chu at Bell Telephone Laboratories succeeded in growing silicon heteroepitaxially on sapphire at a temperature of only 650°C. Further investigation

of this process both as a basis for comparison in the present program as well as to pursue further possibilities for this important process would be useful. The role of reactive gases, as well as total system pressure in these experiments, should be investigated as well as the possibilities for achieving single crystal or polycrystalline films of device quality. Such a development would have important implications for integrated circuit technology by providing bipolar device on insulating substrates.

2. Probability of Obtaining Good Epitaxy

Of course, the principal candidates satisfying this criterion are oriented silicon (particularly (1, 0, 0)), sapphire, spinel and tungsten. In addition to the work by Chang on sapphire, Gassman achieved, as noted, heteroepitaxial growth on spinel. Also as noted, 5 micron grains of silicon have been grown on tungsten substrates by Chu.

Two general approaches are visualized for selection of other substrates with a reasonable probability for promoting epitaxial growth. The first would emphasize glassy materials such as fused quartz or glassy carbon. The rationale for such a choice is that by providing relatively weak binding between silicon and substrate, rotation of islands of silicon in the initial phases of growth is promoted as these islands come into contact. A second line of attack, begun by Jona, is to select metal substrates which would provide "good registry," namely close packed metal systems such as Al, Ni and Be. Here large grain substrates would be chosen. Jona has already observed ordered growth of silicon on these substrates at room temperature but his evaporation rates were insufficient to keep up with diffusion of silicon into the substrate at temperatures required for epitaxial growth of silicon. Other close packed metals should be studied at evaporation rates hundreds of times those used by Jona. These evaporation rates, to provide 10 to 20 microns film thickness in a few hours time, are to be compared with Jona's rates of 1/3 monolayer per minute.

3. Technical Interest for Ultimate Applications

For solar cell applications, conducting substrates are required for this approach. This application would favor either a metal or glassy carbon substrate. Success in developing a vacuum epitaxial growth process on a conducting substrate for thin silicon films of sufficient quality would have important implications for developing a simple continuous mass production process for solar cells and arrays. This is because the presence of a back contact on a continuous strip of the silicon material would allow for subsequent shingle-like overlays for series connections. For this application polycrystalline material may be suitable, provided grain width exceeds film thickness and the grains exhibit bulk-like mobility and sufficient minority carrier lifetime.

Work with insulating substrates, besides furnishing comparison data with previous ultra-vacuum work, could also have important applications if films of sufficient quality can be produced. If films of sufficient mobility and lifetime can be deposited on insulating substrates, this could eliminate the requirement for diffusion isolation currently used with silicon epitaxially deposited on doped silicon substrates in integrated circuit applications.

Ranking of substrate candidates for these applications would, of course, emphasize low cost. For integrated circuit applications, cost is less important than for solar cell applications.

4. Availability of Practical in situ Cleaning

The most extensive data on thermal desorption cleaning is available on tungsten and a few other refractory metals. These techniques are also available for silicon. Work by Jona has shown that in situ vapor deposition of aluminum in ultra-vacuum gives atomically clean surfaces. This technique will be considered provided grains of sufficient size can be formed.

5. Chemical and Diffusion Compatibility with Silicon

Here the equilibrium phase diagrams are only a general guide. Low lying eutectics are, of course, to be avoided. W, sapphire, spinel quartz, Be and of course Si satisfy this criterion. Solid state reactions appear to be a problem, such as the formation of silicides which may interfere with initial epitaxial growth. Also of importance is the diffusion constant of these materials into silicon. These have been measured for Al, Ni, Fe[18] and many other materials.

Also of relevance is the tolerance of crystalline Si to various impurities in regards to the effect on practical device efficiency. For solar cell applications studies by both Monsanto[18] and Westinghouse[19] have indicated concentrations of Ti and V in the 10^{-12} cm^{-3} range are sufficient to appreciably degrade solar cell performance. A number of other metal impurities have been ranked in terms of the critical concentration which degrades device performance to 90% of nominal efficiency. Elements for which a high sensitivity has been measured are to be avoided. Along these lines it should be noted that the use of titanium either as substrate material or in vacuum sublimation pumps for the chamber itself is particularly to be avoided.

CHOICE OF SUBSTRATE CANDIDATES SATISFYING REQUIRED CRITERIA

In several conferences with experts at the General Electric Corporate Research and Development Center and with Professor David Turnbull, the above criteria were discussed and a relative ranking given to a number of possible substrate candidates. The present status of such a ranking is given below. Beyond the first few listed, further detailed consideration of solid state chemistry and diffusion, crystal lattice registry and in situ cleaning techniques will be made and some changes in ordering may be anticipated later in the Phase B program. The latest iteration of this list is as follows.

1. Tungsten. Easiest for in situ cleaning, no eutectics with silicon below 1400°C, close lattice registry for (1, 0, 0) growth direction, close thermal

expansion match with Si, previous CVD success in growing 5 micron grains, candidate as diffusion barrier for other substrate materials.

2. Silicon. This is the main process involved in any event beyond the first few layers deposited. It is also important to establish a connection with previous studies of Widmer and Jona. (1, 1, 1) and (1, 0, 0) orientations should be studied as a function of deposition temperature. Substrate heating and in situ cleaning technique already available in this laboratory.

3. Sapphire. The work of Chang should be replicated and extended if possible. This substrate has important applications potential for integrated circuits.

4. Glassy Carbon. A conducting substrate which will allow test of the easy island rotation approach. Allows relatively high temperature deposition without reaction with silicon. This also represents a potentially inexpensive substrate material and can be considered with a backing of other material to furnish sufficient strength.

5. Close Packed Metals. In this category Al, Ni and Be should be considered because of the pioneering work of Jona at low deposition rates. Of these, Al would be technically most interesting if substrate cleaning techniques developed by Jona could be extended to mass production processes. Other close packed metals should also be considered in terms of basic compatibility with silicon (1, 1, 1) growth and technical feasibility. Pre-deposition characterization of orientation and morphology of the substrates are required.

CLEANING AND HEATING TECHNIQUES

As noted, these are already available in this laboratory for tungsten and silicon substrates. For insulating substrates, the technique of Chang will be adopted. This involves sputtering of a conducting metal layer on the back of the substrate wafer and the use of two such wafers back to back. Consultation with

Chang indicates that this technique is reliable and allows for good pyrometry in the case of transparent substrates. The close packed metal candidates capable of being cleaned by etching and thermal desorption will be favored (e.g. Ni).

FILM CHARACTERIZATION

The main film characterization for the early phases of the program is to be in terms of grain size achieved as a function of deposition conditions. It is expected that substrate temperature and deposition rate will be the main variables. For polycrystalline deposits with sufficiently large grain size additional film characterization is to be carried out. This may include electron microscopy and X-ray diffraction to study orientation and crystalline perfection. Dislocation etch pits may be counted for grains of sufficient size.

For substrates showing adequate grain size and sufficient freedom from defects for possible device applications, thin metal films will be deposited on the front surface for measurement of voltage current relationships in the Schottky devices thus formed.

In the event that Schottky devices are produced showing that sufficiently large grain silicon has been produced which appears to be of device quality, solar cell devices will be fabricated using the Schottky approach or possibly by evaporation of a layer of opposite polarity silicon on the front surface of films so studied. It is anticipated that solar cell device characterization work being pursued under an Independent Research and Development program will be available in sufficient time to be applicable to this portion of the Phase B program.