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SINGLE CRYSTAL EPITAXY AND CHARACTERIZATION OF BETA-SILICON CAR--ETC(U)
JAN 80 R F DAVIS N00014-79-C-0121

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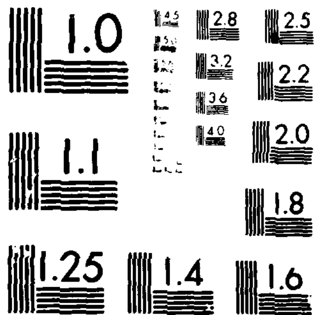
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The project involves the development of low pressure chemical vapor deposition and r-f sputtering techniques for the synthesis of single crystal thin films of β-SiC. The CVD apparatus is being produced in-house and a detailed description of the design is provided herein. Theoretical CVD phase diagrams of the Si-C-H system are also being produced as a function of Si/Si+C and total pressure. Both reactive sputtering of Si in CH_4 and normal sputtering of a SiC target are being readied.

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Annual Technical Report #243-027-001

on

SINGLE CRYSTAL EPITAXY AND CHARACTERIZATION OF BETA SILICON CARBIDE

Supported by ONR under

Contract N00014-79-C-0121

January, 1980

Submitted by

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Engineering Research Services Division
North Carolina State University
Raleigh, North Carolina 27650

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I. Introduction

Silicon carbide is the only compound species that exists in the solid state in the Si-C system and can occur in the cubic (C), hexagonal (H) or rhombohedral (R) structures. It is also classified as existing in the beta and alpha modifications. The beta, or cubic, form crystallizes in the zincblende or sphalerite structure; whereas, a large number (approximately 140) of the alpha occur in the hexagonal or rhombohedral forms known as polytypes. At one time it was thought that the beta modification was thermodynamically stable at low temperatures and that it transformed irreversibly to one or several of the alpha forms by a solid state phase transformation at about 2100°C.[1] Above this temperature the alpha modification was considered stable. However, later efforts by Ryan, et al.[2] and other international groups involved in thin film growth have shown that a relatively moderate excess pressure (~ 10 atm.), especially of N_2, favors the growth of β at all temperatures. Indeed, under certain conditions, the transformation is completely reversible. Impurities, defects, temperature, Si evaporation and ambient gas appear to influence not only the transformation but the resulting polytype as well. This, coupled with small differences in stacking fault energies among the various forms, makes reproducible growth of thin films difficult unless considerable precautions are taken.

Because of the emerging need for high temperature, high frequency and high power electric devices, blue L.E.D.s, Schottky diodes, U.V. radiation detectors, high temperature photocells and heterojunction devices, silicon carbide is being increasingly examined throughout the world for employment as a candidate material in these specialized applications. The electron Hall mobility of high purity undoped β-SiC is approximately a factor of three larger (~ 1000 cm^2/v-sec) than that of the α-form over the temperature range of 300-1000K because of the smaller amount of phonon scattering in the cubic material. The energy gap is also less in the β form (2.3 eV) compared to the α-forms (e.g., 6H = 2.86 eV). Thus, the β-form is now considered more desirable for electronic device applications, and, therefore, the growth of thin films of this material constitutes the principle

objective of this research program. Unfortunately, the earlier push in the 1956-1970 time span to develop SiC as an electronic material concentrated heavily on high temperature growth processes such as the Lely sublimation-condensation technique which produced a variety of α polytypes in experiments which were rarely reproducible. Toward the end of this initial thrust, techniques such as chemical vapor deposition (CVD), sputtering, traveling solvent and solution growth showed promise not only as techniques per se but as experimental avenues wherein the growth of β-SiC could be achieved.

The objective of the present research program is to capitalize on and extend the knowledge of the CVD and sputtering processes that were discerned not only in the brief initial efforts with SiC, but that have also been developed for these processes in the intervening years in research on other semiconductor materials. Although the actual experimental portion of the effort is still awaiting delivery of several components,* considerable progress has been made in terms of design of the CVD equipment and the computer-aided production of CVD phase diagrams. A sputtering unit has arrived just prior to this writing and the peripheral equipment for this unit is being installed as it is received. The details of these efforts are reported below.

II. Chemical Vapor Deposition

A. Background

Chemical vapor deposition is a material synthesis method in which the constitutents of the vapor phase react to form a solid film at some surface. Typical gas combinations which have been employed in the growth of SiC are CCl_4 and $SiCl_4$, SiH_4 and C_3H_8, $SiCl_4$ and C_6H_{14} and Ch_3SiCl_3 alone. In private communications, Ryan[3] has informed the principal investigator that a small amount of HCl is desired to etch away the areas of poor growth which begin on the substrate.

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*The recent tremendous surge in semiconductor manufacturing by all common techniques has generated order backlogs for equipment and parts having waiting periods of up to six months, even for most favored customers.

The reaction in the vicinity of the heated substrate has been shown to vary according to the type of source species and ambient gas.[4, 5] Gatos and co-workers[6] have analyzed the equilibrium partial pressures in the hydrogen-silicon-carbon system and concluded that the efficiency of SiC formation decreases with 1) increasing temperature ($\geq$ 1650°C) which causes decomposition and loss of Si and 2) a decreasing silicon-to-carbon ratio in the gas mixture. The epitaxial growth from a silane and propane mixture was found by these researchers[6] to be linearly dependent on the silane pressure for a given temperature and propane input which suggests that Si mobility and concentration at the substrate controls growth. As noted above, Mogab and Leamy[7] found similar results in their studies of the reactions of hydrocarbons with silicon single crystal surfaces. The kinetics research of the present writer has also shown that Si is a much slower diffusing species than C and should control growth where mobility across surfaces is of importance. Finally Gatos et al.[6] have reported that the SiC growth process is best described by an adsorption-desorption process and must be carried out in an atmosphere having a Si/C ratio of 1/1 or larger if the simultaneous deposition of graphite and SiC is to be avoided. These findings are similar to those of Brander.[4, 8]

In order to understand CVD processes, one should know which chemical reactions occur in the reactor and to what extent. Furthermore, the effects of process variables such as temperature, input concentrations and flow rates on these reactions must be understood. The approaches taken to date to discern the aforementioned variables have been 1) visits and discussions with various former and present investigators in the CVD field, 2) design of the experimental apparatus to be used in the present work and 3) development via computer of CVD phase diagrams. Visits to C. Ryan and co-workers at Rome Air Defense Command, Berkman and co-workers at RCA, several laboratories in California and the International CVD Conference in October of 1979 have been invaluable in the development of the design of the CVD process, the determination of the pertinent equipment for each major section and the handling of toxic and flammable gases. Also, these visits have reinforced the ideas espoused much earlier by workers in the SiC growth field concerning the importance of careful control of temperature, gas composition and flow rate and the maintenance of very low levels of impurities.

B. CVD Phase Diagram

As the design of the CVD system evolved, it became obvious that more information was needed in terms of the solid reaction products which would occur under prescribed conditions of concentrations of certain reactant gases, pressure and temperature. Our research has revealed that numerous methods have been reported for computing thermodynamic equilibrium compositions and that essentially all the techniques have been based on the methods of either Brinkley (9, 10) or White, et al. (11). The former requires the writing of a series of chemical reactions and the computation of their respective equilibrium constants; whereas, the latter involves minimizing the summation of the free energies of all species. Eriksson (12) has extended White et al.'s method to include systems containing more than one condensed phase and has developed a computer program, SOLGAS, for performing the calculations. He has modified the program (13, 14) to be SOLGASMIX so that condensed solution phases could also be considered. To prevent the omission of an important species, the programs can consider all conceivable gaseous species and condensed phases of invariant or variable stoichiometry and mixtures at constant total pressure and temperature in a single calculation. Unstable condensed phases are rejected from the calculation. This program can also handle non-ideal phases, provided activity coeffieient relationships are available. Finally, Bessman and Spear[15a, b] have produced a new version of the program (SOLGASMIX-PV) incorporating the ideal gas law. This last version is now capable of calculating equilibra at a constant total gas volume with variable total pressure. These investigators have kindly provided these programs and helpful suggestions for use in developing CVD phase diagrams in this SiC research. A listing of the programs as used in our research are given in Appendix I.

In developing CVD phase diagrams, thermodynamic calculations using CVD variables can be used to show the ranges of input conditions for a CVD system which will produce a specific condensed phase(s) and phase boundaries at equilibrium. In our particular employment of these CVD programs, all conceivable gaseous species are included with the condensed phases in calculating the equilibrium composition of the system as a systematic function of the CVD variables of temperature, total pressure and reactant concentrations.

Both α-SiC and β-SiC are included in our calculations. In each calculation, one of the variables is changed while all other variables are held constant at an arbitrary set of "standard values." These standard values are typically chosen near the mid-range of the experimental controls, so the desired condensed phase is deposited when all variables are fixed at their respective standard value.

In our present calculations, the elements Si, C and H_2 are the principal species, since SiH_4 and CH_4 are the reactant gases and H_2 is the carrier gas. The type of substrate becomes important only if it emits a gaseous species or enters the reaction upon the formation of the condensed phase or causes structural rearrangement of the solid products. Although this aspect of the research is in its initial stages, one of the important diagrams developed thus far for the Si-C-H system at one atmosphere pressure is presented in Figure 1. An inert substrate is assumed. The Si/Si+C mole ratio depends on not only the fixed input gas ratio, but also on how much SiC is deposited. The same is true for the amount of H_2 in the system. Therefore, a maximum of three phases (a gas phase and two condensed phases) can exist in equilibrium at any given temperature.

The resulting diagram of Figure 1 reveals that above 1000K (the lowest temperature yet examined, β-SiC has a negative standard free energy of formation and the amount that forms as a single phase to the left of the Si/Si + C = 0.5 point occurs over a varying range of these ratios which is a direct function of the amount of H_2 present. At all other ratios or temperatures, solid free C or Si also deposit or Si becomes a liquid. It should be kept in mind that a positive ΔG_f for α-SiC does not mean that it will not form (especially if α-SiC single crystals were used as a substrate) only that it is slightly less thermodynamically preferable than β-SiC under the given conditions. Since the thermal decomposition of SiH_4 is essentially complete at temperatures greater than 1000°K, the effect of adding H_2 to the system is to promote the reaction with excess carbon atoms to produce various gaseous hydrocarbon species and thus provide for the formation of β-SiC over a wide range of Si/Si+C ratios less than 0.5.

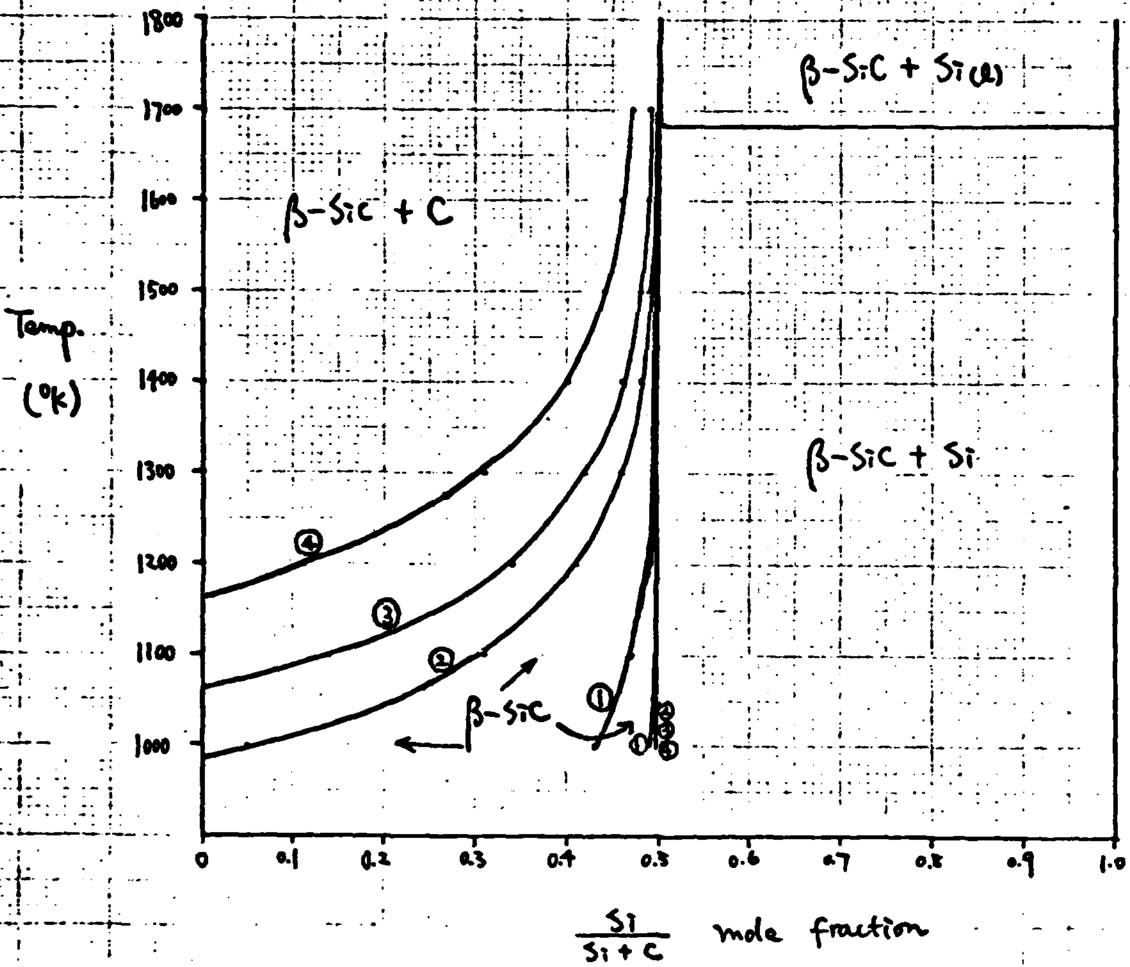

Figure 1. CVD Phase Diagram of Si-C-H System at one Atmosphere Pressure

It has been reported by Ban[16] that more than 80% of the SiH_4 in a 2% SiH_4 mixture in H_2 is decomposed at T > 1073K. Thus, at lower concentrations of H_2, even greater decomposition is to be expected, Based on our calculations, almost all SiH_4 should be decomposed under equilibrium conditions. Furthermore, the higher the temperature, the greater will be the decomposition of CH_4. As noted above, the pressure of H_2 will react with the C and thus provide considerable process control.

Finally it should be noted that diagrams were also derived using Ar at one atmosphere in lieu of H_2 from the foregoing discussion, the phase field of β-SiC is essentially that labeled (1) in Figure 1, as there is no species to react with the free carbon.

The next calculations will entail going to reduced pressures in order to determine any changes in amount of β-SiC that will form. Preliminary research at 10^{-3} atm without the presence of H_2 indicates the formation of β-SiC only at a ratio of Si/Si+C of 0.5 until approximately 1550K where the region widens rapidly toward the lower ratios as temperature is increased. These investigations will continue throughout the next year.

C. Design of the CVD System

At normal atmospheric pressure, the rates of mass transfer to the gaseous reactant and by product species and the surface reactant rate to form the film deposit are generally of the same order of magnitude. Therefore, in order to attain the objective of uniform film thickness and properties over a surface, it is necessary to ensure that careful consideration be given to both types of rate determining steps. Mass transfer rates depend mainly upon reactant concentration, diffusivity and boundary layer thickness which is related to reactor configuration, flow velocity, distances from edges, etc. Surface reaction rates, however, depend mainly upon reactant concentration and temperature.

The diffusivity of a gas is inversely related to pressure. Therefore, as pressure inside the reactor is lowered from one atmosphere to 0.5-1.0 torr, the diffusivity increases by a factor of 1000. This is only partially offset by the fact that the laminar boundary layer (distance across which the reactants must diffuse) increases at less than the square root of the pressure.

The net effect is more than one order of magnitude increase of the gas phase transfer of reactants to and by-products from the substrate surface, and the rate-determining step in the sequence is the surface reaction. Therefore, in such a low-pressure operation (LPCVD), much less attention need be paid to the mass transfer variables that are so critical at atmospheric pressure.

An additional advantage of LPCVD is the considerable reduction in autodoping from gaseous species derived from the substrate material. In CVD processes at one atmosphere, the laminar portion of the boundary layer next to the sample is very narrow. As such, any species diffusing out of the substrate enters this narrow layer and has a relatively high probability of returning to surface of the material, being deposited and becoming incorporated into this deposit. For these reasons, an LPCVD system has been designed as shown in Figures 2-5 and described below. Because this system is and will be continually in the process of evolution even after the completion of the initial "best" arrangement, the author has chosen to present the figures in an unfinished form rather than to take several days to make engineering drawings. The latter will be produced for that arrangement which will be found to be optimum.

As shown in Figure 2, the principal reactant gases are methane (CH_4) and silane (SiH_4) with a carrier gas of H_2. Although all gases will be of highest available purity (H_2 will be purified "in-house" using a Pd/Ag cell), CH_4 and H_2 will also be "scrubed" to remove any residual oxygen and H_2O which could react with SiH_4 to form SiO_2. In addition, crosspurge assemblies will be employed to eliminate impurity capture during tank exchange. HCl will be used to clean the single crystal Si substrates and to etch away any excess Si from the SiC during growth. Stainless steel tubing, specially cleaned for chromatographic experiments, will be used throughout the system. An MKS electronic system will be used to control the flow of each of the gases in the system. The flow of the carrier gas (when used) will be set at a particular value and SiH_4 ahd CH_4 slaved to this value in a particular ratio. HCl will have an independent flow controller, since 1) the operator may desire to vary the amount of etch used for the Si and SiC, respectively, and 2) the MKS unit can handle only three gases. The flow rate of each gas (except HCl) will be measured by a Tylan flow meter which returns a signal to the MKS unit which, in turn, compares

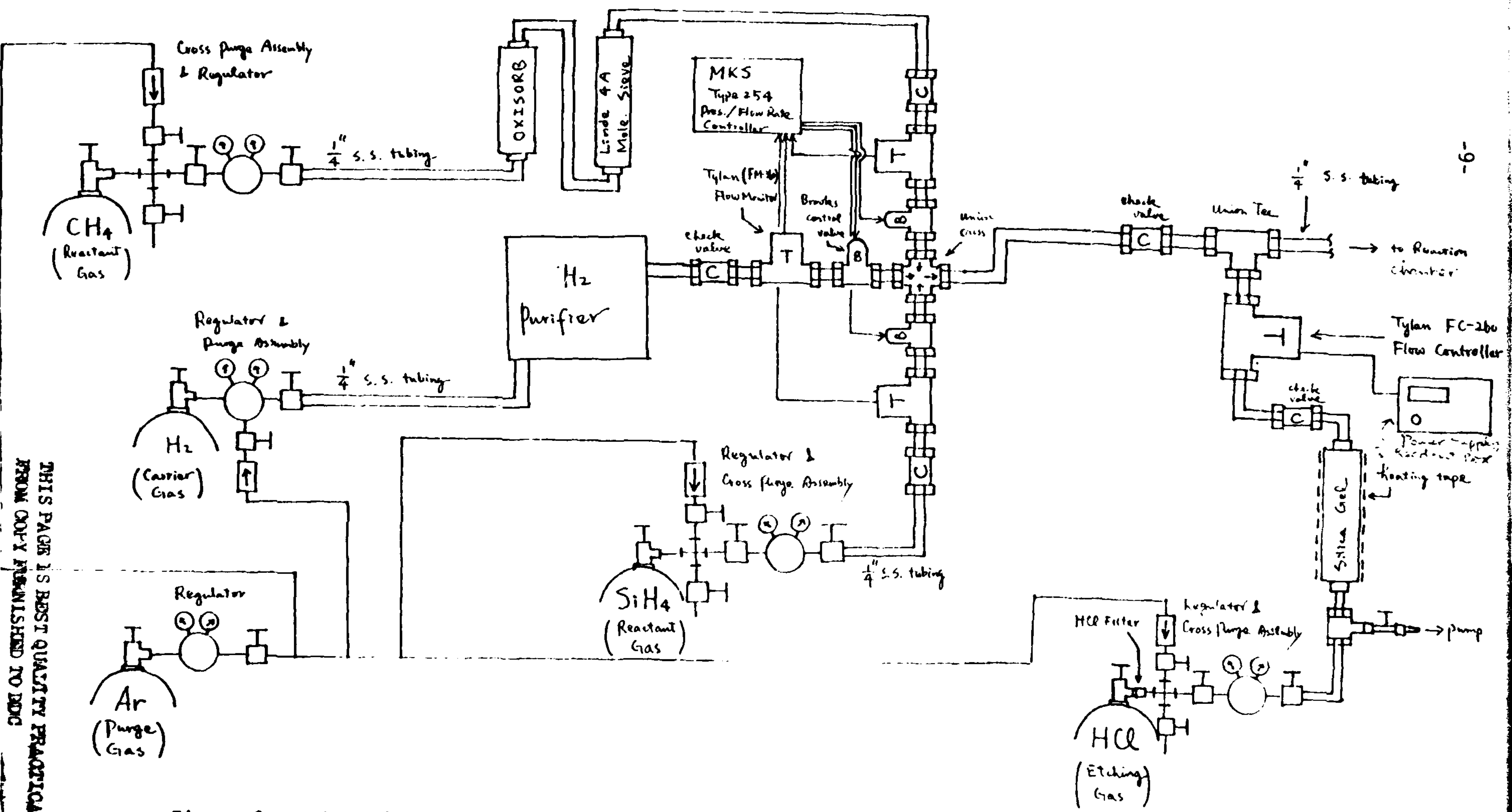

Figure 2. Schematic of Gas Flow, Monitoring and Regulation for CVD System

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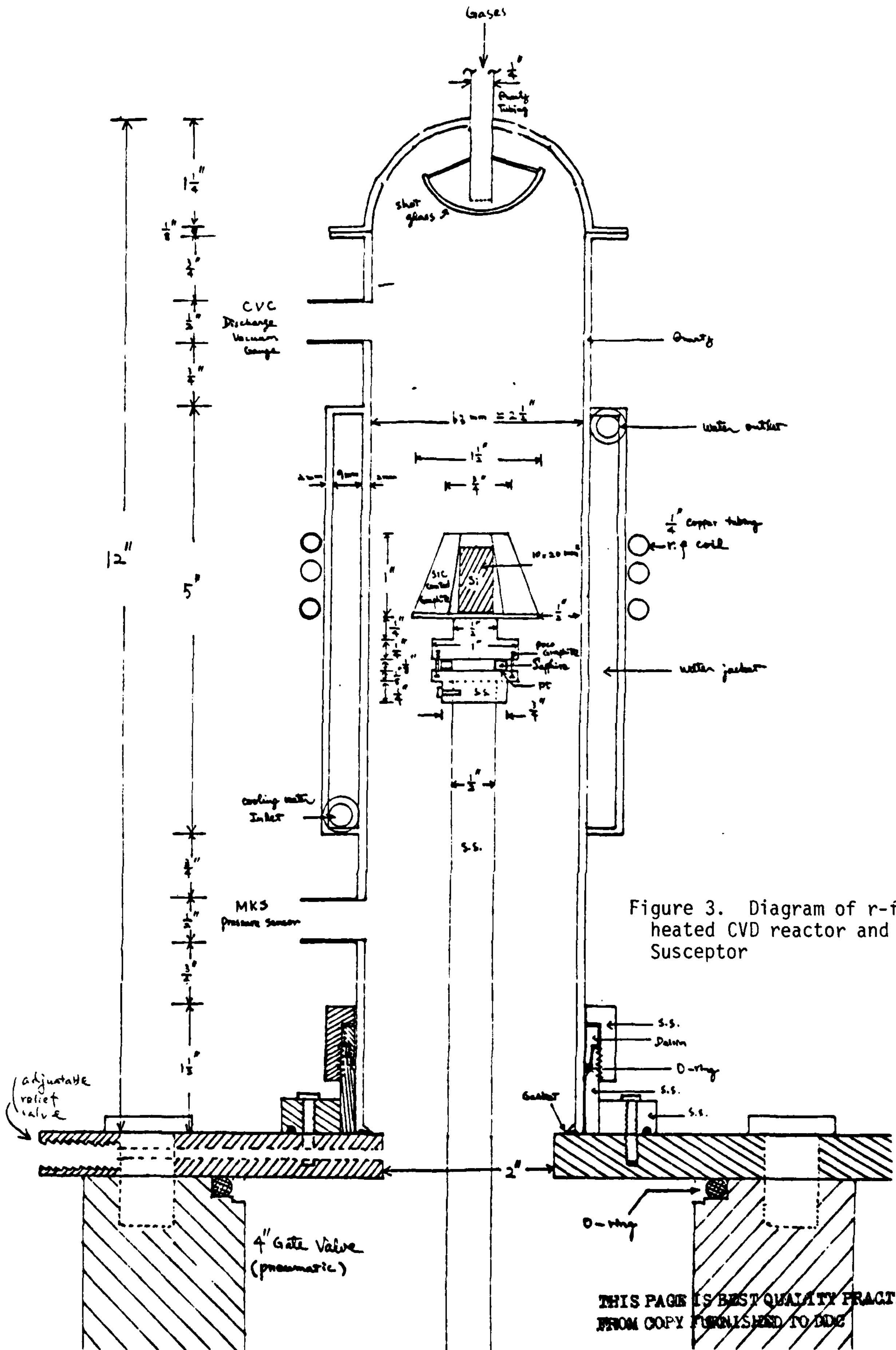

Figure 3. Diagram of r-f heated CVD reactor and Susceptor

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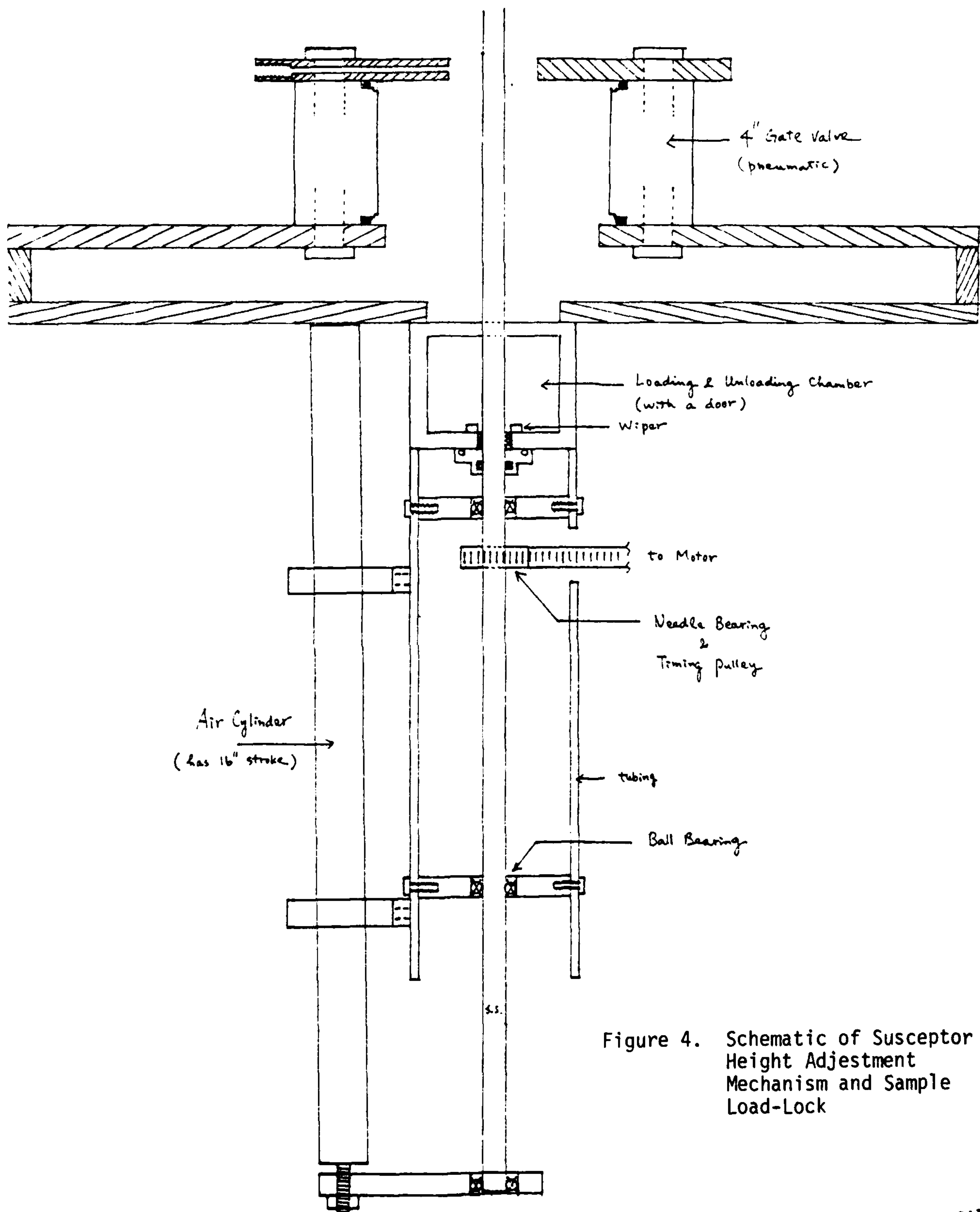

Figure 4. Schematic of Susceptor Height Adjestment Mechanism and Sample Load-Lock

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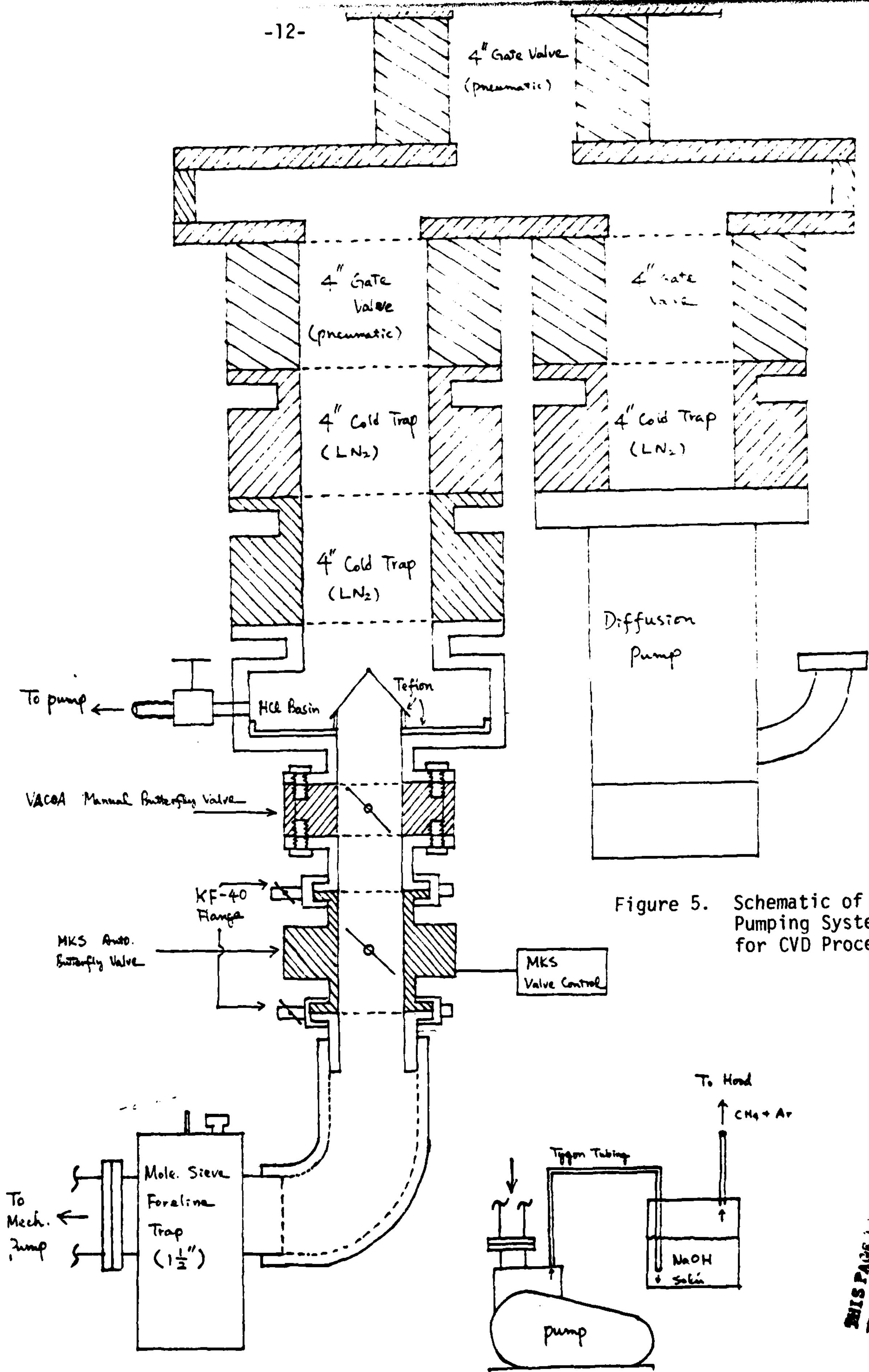

Figure 5. Schematic of Pumping Systems for CVD Process

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this signal with the electrical setpoints established by the operator and adjusts the Brooks electronic valves, if the desired and the actual flow rates are different. Check valves will be employed in each line to prevent contamination of the lines and gas bottles. In addition, argon-operated bellows sealed valves (not shown) will be employed as an insurance measure against the possible closure failure of the Brooks valves and to establish the initial flow conditions of all gases before thet enter the main chamber. In the latter process the gases are first vented to the mechanically pumped side of the reaction chamber; when set flow rates are established, the supply is immediately switched to the already heated chamber.

The chamber, Figure 3, is composed of a water (or He) cooled, vacuum tight quartz chamber mounted on a stainless steel plate. Gas entering the chamber will be deflected to the hemispherical cap to produce a more evenly distributed flow, additional mixing and additional path length for the establishment of equilibrium flow patterns. The r-f heated, barrel type susceptor will be a nominally hexagonal, high purity SiC-coated carbon device supported by a high purity Poco graphite assembly and a stainless steel rod attached to a hydraulic and motorized assembly, Figure 4, which will provide the capability of rotation and vertical movement of the susceptor. The latter motion will allow a change of samples in a loading chamber, Figure 4, without exposing the fused quartz chamber to air. Pressure in the chamber will be measured by a capacitance manometer which has a feedback and control loop through a second MKS controller to an automatic butterfly valve, Figure 5; thus, control of flow and pressure will be independent of each other. Temperature will be measured initially by an optical prometer; however, other methods are being explored. As indicated above, the initial substrates will be high purity float zone, n-type Si single crystal wafers having resistivities in the range of 240-400 Ω-cm. Both (100) and (111) wafers, previously etched and polished, in order to compare the effect of substrate orientation on the efficacy of deposition will be employed.

As shown in Figures 3, 4 and 5, a set of three gate valves will be used to isolate the various parts of the reaction and pumping sections.

The diffusion-pumped side will be used to evacuate the total system and to differentially pump an RGA (not shown). The other pumping assembly includes two cold traps to freeze HCl before it reaches the automatic valve and mechanical pump. (There is some concern that SiH_4 may also be frozen out to dangerous concentrations; thus, this aspect of the procedure will be closely monitored.) The HCl basin has been replaced by a particle trap located above the first cold trap. The upper manual butterfly valve allows a larger opening in the automatic valve and therefore closer control of the pressure. A molecular sieve is also included to prevent mechanical pump oil from backstreaming into the valves and traps.

In conclusion, this system has evolved around the investigators' needs for very tight control on flow rates, pressure, temperature and purity. Numerous people at laboratories around the world have discussed their experiences and offered suggestions on CVD design; many of these ideas are included in these drawings. It will continue to evolve until the objective of the reproducible production of single crystal β-SiC thin films is attained.

III. R. F. Sputtering

An alternative method of depositing SiC is via r-f glow discharge sputtering. In this process the target plate of material to be deposited directly or reacted with a gas to produce a synthesized film is connected to a negative r-f voltage supply. The substrate and holder face the target and the former may be biased, heated, cooled or some combination of these. A gas, usually Ar, is subsequently introduced as a medium in which a glow discharge can be initiated and maintained. As a result of the plasma, positive ions strike the target plate and remove principally neutral target atoms by momentum transfer, and these condense into thin films.

Two approaches are planned at this point: 1) reactive sputtering wherein a high purity Si substrate is sputtered in a reactive gas of methane and Si and C species combine on a heated substrate to form SiC and 2) direct diode sputtering of a high purity SiC target onto a cooled or heated substrate. It should be noted that in the first approach the Si target may become conditioned with C such that a thin layer of SiC is produced and the process approach that of the second method.

Reactive sputtering[17-20] or sputtering of a target of the composition of the desired epitaxially grown crystal have produced reasonably good films of β-SiC. Wasa et al,[17] have prepared both amorphous and polycrystalline α-SiC films by sputtering one inch pressed disks of α and β-SiC of approximately 99.7% purity onto substrates of glass, sapphire and (111) silicon. The polycrystalline films were only formed when the substrates (except glass) were heated to ≥ 700°C. The most interesting aspect of this research was that the deposited α-SiC transformed to β-SiC during annealing in vacuum at 1100°C for one hour. Berman et al,[18] have also reported a method of converting amorphous SiC into crystalline SiC by annealing at high temperature. They also used pressed disks of α-SiC as the target for sputtering. The reported electron diffraction patterns taken in reflection appeared to include polycrystalline rings. Learn and Haq[19] investigated the preparation of single-crystalline films of β-SiC on α-SiC substrates by reactive sputtering in acetylene gas using elemental Si as the target material. Finally, Nishino et al.[20] have produced their own β-SiC target from crystals etched from a silicon solution and ground into powder. A (111) silicon wafer was again used as the substrate and heated to 1000°C and above. These investigators concluded that the substrate temperature should be kept at around 1200°C to obtain good single crystal coatings. The sputtered films were oriented in the same [111] direction as the silicon face.

In our own work, we are currently modifying rather extensively and upgrading an older sputtering unit. Feedback flow and pressure controls similar to that employed in the LPCVD work will also be used in the remodeled sputtering system. We are currently awaiting arrival of spare parts, new equipment and targets.

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APPENDIX I. SOLGASMIX-PV LISTING

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**FTN,L,E,M,C.
C
C          ***   SOLGASMIX-PV   ***
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C  CALCULATES EQUILIBRIA AT CONSTANT PRESSURE OR VOLUME.  THE PROGRAM IS A
C  MODIFICATION OF SOLGASMIX (G. ERIKSSON, CHEMICA SCRIPTA., 8 (1975) 100).
C
C
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A(99,10), AO(99,10), AKT(99), AKTF(99), B(10,99), BO(10),
     $G(99), KH(20), L, M, M1, MA, MB, MF(20), ML(20), MP, MS, NO(99),
     $NP, PI(20), PTOT, T, TEXT(99), Y(99), YF(99), YTOT(20),V,NV,NVV
      DIMENSION FEF(99), GE(99,6), HF(99), IEL(10), IFM(15), IGT(6),
     $IOK(99), XI(99),TITLE(10),EL(10),GT(99,6)
      H = DLOG(10.)
      IN=5
      IOUT=6
      MF(1) = 1
   26 PTOT = 1.
      DO 48 K = 1, 20
   48 KH(K) = 0
      READ (IN,240) (TITLE(I),I=1,10)
  240 FORMAT (10A8)
      WRITE (IOUT,230) (TITLE(I), I=1,10)
  230 FORMAT ('1',20X,10A8)
      READ (IN,102) L, MP, MR, (ML(M), M = 1, MP)
  102 FORMAT (40I2)
      WRITE (IOUT,250) L,MP,MR,(ML(M),M=1,MP)
  250 FORMAT ('0NO. OF ELEMENTS = ',I2,5X,'NO. OF MIXTURES = ',I2,5X,
     1'NO. OF INVARIANT SOLIDS = ',I2/,'0NO. OF SPECIES PER MIXTURE = ',
     210(I2,','))
      IF (MP .EQ. 1) GO TO 146
      DO 132 M = 2, MP
      MF(M) = ML(M-1) + 1
  132 ML(M) = ML(M-1) + ML(M)
  146 M1 = ML(MP) + 1
      MS = ML(MP) + MR
      READ (IN,260) (EL(I),I=1,L)
  260 FORMAT (10A8)
      DO 33 I = 1, MS
      XI(I) = 0.
      READ (IN,280) (A(I,J),J=1,L)
  280 FORMAT (16F5.0)
      DO 33 J = 1, L
   33 AO(I,J) = A(I,J)
      READ (IN,200) NV,V
  200 FORMAT (I1,9X,E10.0)
      READ (IN,102) (IEL(J), J = 1, L)
      READ (IN,102) MGT, MOK
      IF (MGT .GT. 0) GO TO 14
```

```
      IF (MOK .GT. 0) READ (IN,102) (IOK(N), N = 1, MOK)
      DO 255 I=1,MS
  255 READ (IN,270) TEXT(I),HF(I)
  270 FORMAT (A8,2X,7E10.3)
      GO TO 310
   14 READ (IN,102) (IGT(N), N = 1, MGT)
   85 DO 265 I=1,MS
  265 READ (IN,270) TEXT(I), (GE(I,N),N=1,MGT)
      DO 266 I=1,MS
      DO 267 N=1,6
  267 GY(I,N)=0.
      DO 266 N=1,MGT
  266 GY(I,IGT(N))=GE(I,N)
      WRITE (IOUT,300) (TEXT(I),(GY(I,N),N=1,6  ),I=1,MS)
  300 FORMAT ('0SPECIES',6X,'A',14X,'B',14X,'C',14X,'D',14X,'E',14X,'F',
     1/,99('0',A8,3X,6(E12.5,3X),/))
  310 WRITE (IOUT,230) (TITLE(I),I=1,10)
      WRITE (IOUT,340) (EL(I),I=1,L)
  340 FORMAT ('0',20X,'SUBSCRIPTS ON ELEMENTAL SYMBOLS OF EACH SPECIES',
     1/,'0',18X,10(A8,2X))
      DO 350 I=1,MS
  350 WRITE (IOUT,360) TEXT(I),(A(I,J), J=1,L)
  360 FORMAT ('0',A8,8X,10(F5.2,5X))
   42 READ (IN,103) T
      WRITE (IOUT,122) T
  122 FORMAT (4H0T =, F8.2, 2H K/)
      IF (MGT .EQ. 0) GO TO 82
      DO 84 I = 1, MS
   84 G(I) = 0.
      DO 81 N = 1, MGT
      IF (IGT(N) .LT. 6) TP = T**(IGT(N) - 3)/8.31433
      IF (IGT(N) .EQ. 6) TP = DLOG(T)/8.31433
      DO 81 I = 1, MS
   81 G(I) = G(I) + GE(I,N)*TP
      GO TO 8
   82 DO 49 I = 1, MS
      READ (IN,103) FEF(I)
   49 G(I) = (FEF(I) + 1000.*HF(I)/T)/8.31433
      IF (MOK .EQ. 0) GO TO 4
      DO 23 N = 1, MOK
      I = IOK(N)
      G(I) = -N*FEF(I)
      DO 23 J = 1, L
      K = IEL(J)
   23 G(I) = G(I) + A(I,J)/A(K,J)*G(K)
    4 WRITE (IOUT,230) (TITLE(I),I=1,10)
      WRITE (IOUT,106) (TEXT(I), HF(I), FEF(I), G(I), I = 1, MS)
  106 FORMAT (15X, 5HHF298, 8X, 3HFEF, 9X, 4HG/RT/(' ',A8,F12.0,2F12.3))
      GO TO 8
   37 READ (IN,103) PTOT
  103 FORMAT (8E10.0)
    8 READ (IN,102) KVAL1
      GO TO (40,40,40,7,34,42,37,85,26,1), KVAL1
   40 READ (IN,102) NPKT
      READ (IN,102) (KH(J), J = 1, L)
    7 DO 164 J = 1, L
      N = KH(J)
```

```
      GO TO (161,162,163,161,162,163), N
  161 READ (IN,103) (B(J,N), N = 1, NPKT)
      GO TO 164
  162 READ (IN,103) B(J,1)
      IF (NPKT .EQ. 1) GO TO 164
      DO 160 N = 2, NPKT
  160 B(J,N) = B(J,1)
      GO TO 164
  163 READ (IN,103) B(J,1), STEP
      DO 165 N = 2, NPKT
  165 B(J,N) = B(J,N-1) + STEP
  164 CONTINUE
      GO TO (35,39,34,34), KVAL1
   35 DO 370 I=1 MS
  370 READ (IN,103) Y(I)
      GO TO 166
   39 BEST = 0.
      DO 169 J = 1, L
      IF (B(J,1) .GT. BEST .AND. KH(J) .LT. 4) BEST = B(J,1)
  169 CONTINUE
      BEST = BEST/DFLOAT(MS)
      DO 167 I = 1, MS
  167 Y(I) = BEST
  166 DO 135 M = 1, MP
      YTOT(M) = 0.
      MA = MF(M)
      MB = ML(M)
      DO 135 I = MA, MB
  135 YTOT(M) = YTOT(M) + Y(I)
   34 NP = 0
   27 NP = NP + 1
      DO 75 I = 1, MS
   75 NO(I) = 1
      DO 22 J = 1, L
      BO(J) = B(J,NP)
      I = IEL(J)
      IF (KH(J) .LT. 4) GO TO 170
      PI(J) = (G(I) + H*BO(J))/A(I,J)
      GO TO 22
  170 XI(I) = BO(J)/A(I,J)
      IF (BO(J) .NE. 0.) GO TO 22
      DO 30 I = 1, MS
      IF (A(I,J) .EQ. 0.) GO TO 30
      NO(I) = 0
      Y(I) = 0.
   30 CONTINUE
   22 CONTINUE
      CALL GASOL
      WRITE (IOUT,230) (TITLE(I), I=1,10)
      WRITE (IOUT,111) T, PTOT
  111 FORMAT (4HOT =, F8.2, 2H K/ 4H P =, 1PE10.3, 4H ATM/)
      IF (NV.EQ.0) GO TO 210
      WRITE (IOUT,220) V
  220 FORMAT (4H V =, 1PE10.3, 2H L/)
  210 CONTINUE
      IF (N .LE. NP) GO TO 64
      WRITE (IOUT,118)
```

```
118 FORMAT (/50H THE EQUILIBRIUM COMPOSITION HAS NOT BEEN OBTAINED)
    GO TC 28
 64 IF (M .EQ. 0) WRITE (IOUT,121)
121 FORMAT (33H THE SMALL Y-VALUES ARE NOT EXACT/)
    DO 17 J = 1, L
    IF (KM(J) .LT. 4) GO TO 17
    K = IEL(J)
    XI(K) = 0.
    DO 50 I = 1, NS
 50 XI(K) = XI(K) + AO(I,J)*Y(I)
 17 CONTINUE
    WRITE (IOUT,105)
105 FORMAT (15X,7HX*/MOLE,8X,6HY/MOLE,10X,5HP/ATM,8X,8HACTIVITY)
    DO 140 N = 1, NP
    IF (N .GT. 1) WRITE (IOUT,125)
125 FORMAT (41X, 13HMOLE FRACTION)
    NA = MF(N)
    NB = ML(N)
    DO 140 I = NA, NB
140 WRITE (IOUT,124) TEXT(I), XI(I), Y(I), YP(I), AKT(I)
124 FORMAT (' ',A8,4(3X,E12.5))
    IF (MR .GT. 0) WRITE (IOUT,120) (TEXT(I), XI(I), Y(I), I = N1, NS)
120 FORMAT (/(' ',A8,2(3X,E12.5)))
    CALL SPEQUA
 28 IF (NP - NPKT) 27,8,8
  1 STOP
    END
```

```
      SUBROUTINE GASOL
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A(99,10), AO(99,10), AKT(99), AKTF(99), B(10,99), BO(10),
     $G(99), KH(20), L, M, M1, MA, MB, MF(20), ML(20), MP, MS, NO(99),
     $NP, PI(20), PTOT, T, TEXT(99), Y(99), YF(99), YTOT(20),V,NV,NVV
      DIMENSION F(99), IFAS(20), ISOL(20), LX(99), NSUM(500), OPI(10),
     $B(20,21), YFTOT(20), YX(99)
      MX = 0
  171 IS = -1
      NSUM = 0
      NG = 0
   55 ISUM = 0
      MSA = 0
      IF (MS .LT. M1) GO TO 47
      DO 52 I = M1, MS
      IF (Y(I) .EQ. 0.) GO TO 52
      MSA = MSA + 1
      ISOL(MSA) = I
      ISUM = ISUM + 2**(I + MP - M1)
   52 CONTINUE
   47 MPA = 0
      NG = NG + 1
      IF (NG .EQ. 501) NG = 1
      NSUM(NG) = ISUM
      YSUM = 0.
      DO 152 M = 1, MP
      IF (YTOT(M) .EQ. 0.) GO TO 152
      MPA = MPA + 1
      IFAS(MPA) = M
      NSUM(NG) = NSUM(NG) + 2**(M - 1)
      YSUM = YSUM + YTOT(M)
  152 CONTINUE
      IF (NSUM(NG) .GE. IS .AND. MPA + MSA .LE. L) GO TO 69
   59 IS = IS + 2
      DO 154 N = 1, MPA
      M = IFAS(N)
  154 YTOT(M) = 0.
      ISUM = 0
      MPA = 1
      YTOT(1) = 1.
      IF (MSA .EQ. 0) GO TO 73
      DO 68 N = 1, MSA
      I = ISOL(N)
   68 Y(I) = 0.
      MSA = 0
   73 IF (IS .EQ. 1) GO TO 74
      IT = IS
   61 M = 0
   71 M = M + 1
      IF (2**M .LE. IT) GO TO 71
      IF (M .GT. MP) GO TO 57
      MPA = MPA + 1
      IFAS(MPA) = M
      YTOT(M) = 1.
      MA = MF(M)
```

```
      MB = ML(M)
      DO 150 I = MA, MB
      IF (NO(I) .EQ. 1) Y(I) = YSUM
  150 CONTINUE
      GO TO 136
   57 I = M + ML(MF) - MP
      IF (I .GT. MS) RETURN
      IF (NO(I) .EQ. 0) GO TO 59
      MSA = MSA + 1
      ISOL(MSA) = I
      ISUM = ISUM + 2**(M - 1)
      Y(I) = YSUM
  136 IT = IT - 2**(M - 1)
      IF (IT .GT. 1) GO TO 61
      IF (MPA + MSA .GT. L) GO TO 59
   74 IPAS(1) = 1
      IF (NSUB(NG) .GT. IS) NG = NG + 1
      IF (NG.EQ.501) NG=1
      NSUB(NG) = IS
   69 IF (NG .EQ. 1) GO TO 129
      DO 148 K = 2, NG
      IF (NSUM(NG) .EQ. NSUM(K-1)) GO TO 59
  148 CONTINUE
      IF (NSUM(NG-1) .EQ. MSUM) NSUM(NG-1) = -NSUM(NG-1)
      IF (NG.LT.3.OR.NSUM(NG-2).NE.-NSUB.OR.NSUM(NG).EQ.MSUM) GO TO 129
      NSUM(NG-2) = -NSUM(NG-2)
  129 DO 142 M = 1, MP
      MA = MF(M)
      MB = ML(M)
      IF (YTOT(M) .GT. 0.) GO TO 130
      DO 126 I = MA, MB
      AKT(I) = 0.
      AKTP(I) = 1.
      Y(I) = 0.
  126 YP(I) = 0.
      GO TO 142
  130 DO 45 I = MA, MB
      IF (NO(I) .EQ. 1 .AND. Y(K) .LT. 1.E-8) Y(I) = 1.E-8
      AKTP(I) = 1.
   45 LX(I) = 0
      CALL ABER
      IF (YTOT(M) .EQ. 0.) GO TO 47
  142 CONTINUE
      LS1 = L + MPA + MSA
      LS = LS1 - 1
      LS2 = LS + 2
  134 DMIN = 1.E-6
      IVAR = 0
      IVARJ = ML(1) - MS
   16 DO 6 J = 1, LS1
      DO 6 K = J, LS2
    6 R(J,K) = 0.
      DO 9 N = 1, MPA
      L1 = L + N
      M = IPAS(N)
      MA = MF(M)
      MB = ML(M)
```

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```
      DO 5 I = MA, MB
      IF (Y(I) .EQ. 0.) GO TO 5
      F(I) = G(I) + DLOG(AKT(I))
      R(L1,LS2) = R(L1,LS2) + F(I)*Y(I)
      DO 77 J = 1, L
      IF (A(I,J) .EQ. 0.) GO TO 77
      AY = A(I,J)*Y(I)
      R(J,L1) = R(J,L1) + AY
      R(J,LS2) = R(J,LS2) + AY*F(I)
      DO 80 K = J, L
   80 R(J,K) = R(J,K) + AY*A(I,K)
   77 CONTINUE
    5 CONTINUE
      DO 9 J = 1, L
    9 R(J,LS2) = R(J,LS2) - R(J,L1)
      IF (MSA .EQ. 0) GO TO 63
      DO 67 N = 1, MSA
      I = ISOL(N)
      K = L + MPA + N
      R(K,LS2) = G(I)
      DO 67 J = 1, L
   67 R(J,K) = A(I,J)
   63 DO 31 J = 2, LS1
      N = J - 1
      DO 31 K = 1, N
   31 R(J,K) = R(K,J)
      IF (MX .EQ. 0) GO TO 156
      DO 131 J = 1, L
  131 BO(J) = B(J,NP)
      DO 172 N = 1, MPA
      M = IPAS(N)
      IF (MF(M) .NE. ML(M)) GO TO 172
      MA = MF(M)
      DO 89 J = 1, L
      IF (A(MA,J) .EQ. AO(MA,J)) GO TO 89
      AKVOT = (1. - A(MA,J)/AO(MA,J))*Y(MA)
      DO 91 K = 1, L
      IF (A(MA,K) .EQ. AO(MA,K)) BO(K) = BO(K) + AKVOT*A(MA,K)
   91 CONTINUE
      GO TO 172
   89 CONTINUE
  172 CONTINUE
  156 DO 44 K = 1, L
      IF (KH(K) .LT. 4) GO TO 44
      DO 83 J = 1, LS1
   83 R(J,LS2) = R(J,LS2) - PI(K)*R(J,K)
   44 R(K,LS2) = R(K,LS2) + BO(K)
      DO 10 K = 1, LS
      IF (KH(K) .GT. 3) GO TO 10
      ELMAX = 0.
      DO 11 J = K, LS1
      IF (ABS(R(J,K)) .LE. ELMAX .OR. KH(J) .GT. 3) GO TO 11
      MROW = J
      ELMAX =DABS(R(J,K))
   11 CONTINUE
      IF (ELMAX .GT. 0.) GO TO 36
      IF (K .GT. L .OR. BO(K) .EQ. 0.) GO TO 10
```

```
      GO TO 59
   36 IF (MROW .EQ. K) GO TO 13
      DO 15 N = K, LS2
      RADBYT = R(MROW,N)
      R(MROW,N) = R(K,N)
   15 R(K,N) = RADBYT
   13 KA = K + 1
      DO 46 J = KA, LS1
      RKVOT = R(J,K)/R(K,K)
      DO 46 N = KA, LS2
   46 R(J,N) = R(J,N) - RKVOT*R(K,N)
   10 CONTINUE
      DO 20 N = 1, LS1
      K = LS2 - N
      IF (KH(K) .GT. 3) GO TO 20
      IF (R(K,K) .NE. 0. .AND. R(K,LS2) .NE. 0.) GO TO 62
      PI(K) = 0.
      K = K - L - MPA
      IF (K .LE. 0) GO TO 20
      I = ISOL(K)
      Y(I) = 0.
      GO TO 55
   62 PI(K) = R(K,LS2)/R(K,K)
      KA = K - 1
      IF (KA .EQ. 0) GO TO 20
      DO 58 J = 1, KA
   58 R(J,LS2) = R(J,LS2) - PI(K)*R(J,K)
   20 CONTINUE
      IF (IVAR .EQ. 0 .OR. IVARJ .GE. 0 .OR. SLAM .LT. 0.1) GO TO 66
      DO 70 J = 1, L
      IF (DABS(PI(J)).GT.1.E-8.AND.DABS(OPI(J)/PI(J)-1.).GT.DMIN)
     1GO TO 65
   70 CONTINUE
      NR = 0
      IF (NG .EQ. 1) GO TO 155
      DO 157 K = 2, NG
      IF (NSUM(NG) .EQ. -NSUM(K-1)) NR = NR + 1
  157 CONTINUE
  155 DO 143 M = 1, MP
      IF (YTOT(M) .GT. 0.) GO TO 143
      CALL XBEN
      YFTOT(M) = 0.
      DO 144 I = MA, MB
      YFTOT(M) = YFTOT(M) + YF(I)
      YX(I) = YF(I)
      AKT(I) = 0.
  144 YF(I) = 0.
      IF (NV.EQ.0) GO TO 326
      YA=0.
      DO 325 I=1,NL(1)
  325 YA=Y(I)+YA
      PTOT=YA*.0821*T/V
  326 CONTINUE
      IF (M .EQ. 1) YFTOT(M) = YFTOT(M)/PTOT
  143 CONTINUE
  145 DIFM = 1.
      DO 158 M = 1, MP
```

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      IF (YTOT(M) .GT. 0. .OR. YFTOT(M) .LE. DIFM) GO TO 158
      KA = M
      DIFM = YFTOT(M)
  158 CONTINUE
      IF (DIFM .EQ. 1.) GO TO 138
      IF (NR .EQ. 0) GO TO 159
      NR = NR - 1
      YFTOT(KA) = 1.
      GO TO 145
  159 MSUM = MSUM(NG)
      YTOT(KA) = 1.
      MA = MF(KA)
      MB = ML(KA)
      DO 153 I = MA, MB
  153 Y(I) = YSUM*YX(I)/YFTOT(KA)
      GO TO 47
  138 IF (MS .LT. M1) GO TO 51
      DIFM = 0.
      DO 54 I = M1, MS
      IF (NO(I) .EQ. 0 .OR. Y(I) .GT. 0.) GO TO 54
      PIA = -G(I)
      DO 56 J = 1, L
   56 PIA = PIA + A(I,J)*PI(J)
      IF (PIA .LT. DIFM) GO TO 54
      KA = I
      DIFM = PIA
   54 CONTINUE
      IF (DIFM .EQ. 0.) GO TO 51
      Y(KA) = YSUM
      GO TO 55
   51 IF (MX .EQ. 1) GO TO 93
      DO 168 N = 1, MPA
      M = IPAS(N)
      IF (MF(M) .NE. ML(M)) GO TO 168
      MA = MF(M)
      DO 173 J = 1, L
      IF (A(MA,J) .EQ. AO(MA,J)) GO TO 173
      MX = 1
      GO TO 171
  173 CONTINUE
  168 CONTINUE
   93 IVARJ = 0
      GO TO 66
   65 DO 60 J = 1, L
   60 OPI(J) = PI(J)
   66 SLAM = 1.
      DO 12 N = 1, MPA
      L1 = L + N
      M = IPAS(N)
      MA = MF(M)
      MB = ML(M)
      DO 12 I = MA, MB
      IF (Y(I) .EQ. 0.) GO TO 12
      PIA = F(I) - PI(L1)
      DO 19 J = 1, L
   19 PIA = PIA - A(I,J)*PI(J)
      YX(I) = PIA*Y(I)
```

```
      IF (PIA .GT. SLAM) SLAM = PIA
   12 CONTINUE
      IF (SLAM .GT. 1.) SLAM = 0.999*(SLAM - 0.5)/(SLAM*SLAM)
      IF (MSA .EQ. 0) GO TO 72
      DO 53 N = 1, MSA
      I = ISOL(N)
      K = L + MPA + N
      IF (PI(K) .LT. 0.) L1 = 0
      IF (IVAR .EQ. 0 .OR. PI(K) .GT. -Y(I)) GO TO 53
      IF (SLAM .LT. 1. .AND. -PI(K)/YSUM .LT. 1.E8) GO TO 53
      Y(I) = 0.
      GO TC 55
   53 Y(I) =DABS(PI(K))
   72 YSUM = 0.
      DO 128 N = 1, MPA
      M = IFAS(N)
      MA = MF(M)
      MB = ML(M)
      DO 29 I = MA, MB
      IF (Y(I) .EQ. 0.) GO TO 29
      Y(I) = Y(I) - SLAM*YX(I)
      IF (Y(I) .LT. 1.E-20) Y(I) = 0.
   29 CONTINUE
      CALL ABER
      IF (YTOT(M) .EQ. 0.) GO TO 47
  128 YSUM = YSUM + YTOT(M)
      IVAR = IVAR + 1
      IF (IVAR .EQ. 25 .OR. IVAR .EQ. 50) DMIN = 100.*DMIN
      IF (IVAR .EQ. 75) GO TO 59
      IF (IVARJ .LT. 0 .OR. L1 .EQ. 0 .OR. SLAM .LT. 1.) GO TO 16
      IVARJ = IVARJ + 1
      IF (IVARJ .EQ. 10) GO TO 88
      DO 3 N = 1, MPA
      M = IFAS(N)
      MA = MF(M)
      MB = ML(M)
      DO 3 I = MA, MB
      IF (Y(I) .GT. 0. .AND.DABS(YX(I))/Y(I) .GT. 1.E-6) GO TO 16
    3 CONTINUE
   88 DO 149 N = 1, MPA
      M = IFAS(N)
      CALL XBER
      IF (MA .NE. MB) GO TO 133
      DO 92 J = 1, L
      IF (A(MA,J) .NE. AO(MA,J)) Y(MA) = A(MA,J)/AO(MA,J)*Y(MA)
   92 CONTINUE
  133 DO 149 I = MA, MB
      IF (NO(I) .EQ. 0 .OR. Y(I) .GT. 0.) GO TO 149
      Y(I) = YTOT(M)*YP(I)
      IF (Y(I) .LT. 1.E-20 .OR. LX(I) .EQ. 1) GO TO 149
      LX(I) = 1
      GO TO 13±
  149 CONTINUE
      IF (IVARJ .EQ. 10) N = 0
      RETURN
      END
```

```
      SUBROUTINE ABER
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A(99,10), A0(99,10), AKT(99), AKTF(99), B(10,99), B0(10),
     $G(99), KH(20), L, M, M1, MA, MB, MF(20), ML(20), MP, MS, N0(99),
     $NP, PI(20), PTOT, T, TEXT(99), Y(99), YP(99), YTOT(20),V,NV,NVV
      YTOT(M) = 0.
      DO 2 I = MA, MB
    2 YTOT(M) = YTOT(M) + Y(I)
      IF (YTOT(M) .GE. 1.E-8) GO TO 151
      YTOT(M) = 0.
      RETURN
  151 CONTINUE
      IF (NV.EQ.0) GO TO 326
      YA=0.
      DO 325 I=1,ML(1)
  325 YA=Y(I)+YA
      PTOT=YA*.0821*T/V
  326 CONTINUE
      IF (M .EQ. 1) YTOT(1) = YTOT(1)/PTOT
      DO 127 I = MA, MB
  127 YP(I) = Y(I)/YTOT(M)
      CALL FACTOR
      DO 141 I = MA, MB
  141 AKT(I) = AKTF(I)*YP(I)
      RETURN
      END
```

```
      SUBROUTINE ITER
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A(99,10), AO(99,10), AKT(99), AKTF(99), B(10,99), BO(10),
     $G(99), KH(20), L, M, M1, MA, MB, MP(20), ML(20), MP, MS, NO(99),
     $NP, PI(20), PTOT, T, TEXT(99), Y(99), YP(99), YTOT(20),V,NV,NVV
      DIMENSION OYP(99)
      PLOG = DMAX1(DLOG(PTOT),10.)
      MA = MP(M)
      MB = ML(M)
      DO 38 I = MA, MB
      IF (NO(I) .EQ. 0 .OR. Y(I) .GT. 0.) GO TO 38
      PIA = -G(I)
      DO 87 J = 1, L
   87 PIA = PIA + A(I,J)*PI(J)
      IF (PIA .GT. PLOG) PIA = PLOG
      AKT(I) =DEXP(PIA)
      YP(I) = AKT(I)
   38 CONTINUE
      IVAR = 0
  147 IVAR = IVAR + 1
      IF (IVAR .LT. 25) CALL FACTOR
      DO 139 I = MA, MB
      OYP(I) = YP(I)
  139 YP(I) = AKT(I)/AKTF(I)
      DO 137 I = MA, MB
      IF (YP(I).GT.0..AND.DABS(OYP(I)/YP(I)-1.).GT.1.E-4)GO TO 147
  137 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE FACTOR
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A(99,10), A0(99,10), AKT(99), AKTF(99), B(10,99), B0(10),
     $G(99), KH(20), L, M, M1, MA, MB, MF(20), ML(20), MP, MS, N0(99),
     $NP, PI(20), FTOT, T, TEXT(99), Y(99), YF(99), YTOT(20),V,NV,NVV
C
C         THE ACTIVITY COEFFICIENT EXPRESSIONS FOR THE SPECIES IN THE NONIDEAL
C         MIXTURES ARE INSERTED AFTER THE STATEMENT NUMBER THAT CORRESPONDS TO
C         THE MIXTURE NUMBER. FOR A SOLID WITH VARIABLE STOICHIOMETRY WHICH IS
C         REGARDED AS A SEPARATE MIXTURE, THE COMPOSITION MUST ALSO BE SPECIFIED
C         (MAXIMUM ONE STOICHIOMETRIC COEFFICIENT IS ALLOWED TO DEVIATE).
C
C         NOTICE THAT AN AMOUNT OF A SPECIES WHICH IS LESS THAN 1.E-20 MOLES
C         IS SET EQUAL TO ZERO.
C
C         A0 = A DEVIATING STOICHIOMETRIC COEFFICIENT
C         AKT = ACTIVITY
C         AKTF = ACTIVITY COEFFICIENT
C         Y = AMOUNT OF SUBSTANCE
C         YF = MOLE FRACTION OR PARTIAL PRESSURE
C
      GO TO (1,2,3,4,5,6,7,8,9,10), M
    1 CONTINUE
      RETURN
    2 CONTINUE
      RETURN
    3 CONTINUE
      RETURN
    4 CONTINUE
      RETURN
    5 CONTINUE
      RETURN
    6 CONTINUE
      RETURN
    7 CONTINUE
      RETURN
    8 CONTINUE
      RETURN
    9 CONTINUE
      RETURN
   10 CONTINUE
      RETURN
      END
```

```
      SUBROUTINE SPEQUA
      IMPLICIT REAL*8 (A-H,O-Z)
      COMMON A(99,10), A0(99,10), AKT(99), AKTP(99), B(10,99), B0(10),
     $G(99), KH(20), L, M, M1, MA, MB, MF(20), ML(20), MP, MS, N0(99),
     $NP, PI(20), PTOT, T, TEXT(99), Y(99), YF(99), YTOT(20),V,NV,NVV
C
C        SPEQUA IS A SUBROUTINE FOR CALCULATION OF QUANTITIES WHICH ARE
C        DERIVABLE FROM THE EQUILIBRIUM COMPOSITION.
C
      RETURN
      END
```

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