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PHYSICAL PHENOMENA RELATED TO CRYSTAL GROWTH IN THE SPACE ENVIRONMENT

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16. Abstract

The mechanism of crystal growth which may be affected by the space environment were studied and conclusions as to the relative technical and scientific advantages of crystal growth in space over earth bound growth without regard to economic advantage were deduced. It was concluded that the crucibleless technique will most directly demonstrate the unique effects of the greatly reduced gravity in the space environment. Several experiments, including crucibleless crystal growth using solar energy and determination of diffusion coefficients of common dopants in liquid silicon were recommended.

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SUMMARY

The objectives of this program are to study the mechanism of crystal growth which may be affected by the space environment and to deduce conclusions as to the relative technical and scientific advantages of crystal growth in space over earth bound growth without regard to economic advantage. To meet these objectives, the literature on crystal growth from the melt, solution, and vapor phases was reviewed, and the physical phenomena important for crystal growth in a zero-gravity environment were analyzed.

The melt-growth is the most important technique for the production of large crystals of electronic materials. In the Czochralski pulling technique with the melt contained in a crucible, forced convection is necessary to overcome the random thermal fluctuations due to natural convection and to minimize the impurity inhomogeneity in the melt due to segregation. The absence of free convection in the space environment will only mean that the forced convection can be of smaller magnitude. In the float zone and crucibleless techniques, the surface tension of the melt and the levitating electromagnetic field overcome the gravitational force to support the molten zone. The crucibleless technique will therefore most directly demonstrate the unique effects of the greatly reduced gravity in the space environment.

Several experiments, including crucibleless crystal growth using solar energy, determination of diffusion coefficients of common dopants in liquid silicon, etc., were recommended for the Space Shuttle, and continued effort to carry out preliminary experiments on earth was suggested.

I. Introduction

This is the final report of a study program "Physical Phenomena Related to Crystal Growth in the Space Environment" sponsored by the Langley Research Center of the National Aeronautics and Space Administration, Hampton, Virginia, under contract NAS1-11869. The objective of this contract is to study the mechanism of crystal growth which may be affected by the space environment and to deduce conclusions as to the relative technical and scientific advantages of crystal growth in space over earth bound growth without regard to economic advantage.

To meet the above objective, the literature on crystal growth techniques was reviewed, the physical phenomena important for crystal growth in a zero-gravity environment were analyzed, and three meetings were held at the Electronic Sciences Center of Southern Methodist University to discuss various aspects of this program. Participants at these meetings included Mr. Wendell G. Ayers of the Langley Research Center, Drs. Ting L. Chu and Ronald K. Smeltzer of Southern Methodist University, and three eminent consultants -- Dr. Jack P. Holman, Professor of Thermal and Fluid Sciences at Southern Methodist University, Dr. Francois Padovani, Manager of Silicon Research and Development at Texas Instruments, Incorporated, and Dr. Walter R. Runyan, Manager of Materials Processing at Texas Instruments, Inc. It was concluded from detailed analyses of crystal growth from the melt, solution, and vapor phases that crucibleless growth in the space environment has distinct technical and scientific advantages and merits investigations in space. Furthermore, the study of gas phase crystal growth in space can contribute significantly to the basic understanding of this most important technique in modern electronics. Several suggestions were also made concerning earth bound experiments which will facilitate the design of crystal growth experiments in the space environment.

In this report, the commonly used crystal growth techniques are reviewed, the effects of zero gravity on various growth processes and the scientific and technical merits of crystal growth in the space environment are discussed, and recommendations on space and earth bound experiments are described.

II. Crystal Growth of Electronic Materials

The crystal growth of solid state materials from the melt, the solution, and the vapor phase is an art of many years (Ref. 1). With the advent of semi-conductors in the late forties, the crystal growth techniques have advanced rapidly, and considerable progress has also been made in the understanding of the crystal growth processes. The growth of large, nearly perfect single crystals of germanium and silicon has contributed significantly to the understanding of their properties. The properties of electronic materials are strongly dependent on the structural perfection. For example, grain boundaries act as carrier recombination centers and mobility scattering centers. Also, the boundary may act as an insulating layer, and the measured properties of polycrystalline material may be more indicative of the properties of grain boundaries than of the true properties of individual crystal grains. Thus, the growth of single crystals is essential for the characterization of electronic materials and the fabrication of many electronic devices. The techniques used successfully for the crystal growth of electronic materials are reviewed in the following sections.

II.1. Growth from the Melt

The crystal growth from a melt has been the most successful technique for the preparation of single crystals of electronic materials. This technique offers the advantages of high growth rates and the preparation of large single crystals. However, the material under consideration must melt congruently without irreversible decomposition, and there is no solid state phase transformation between the melting point and the temperature to which the crystal will later be cooled. Also, the temperature required for melt-growth is higher than that required by the solution and vapor growth techniques, and contamination from the container may be a problem.

II.1.1. Principles of Melt-Growth

When a crystal is grown from a melt, the solidification process must be controlled to avoid random nucleation. Usually, a single crystal seed is used, and the solidification is allowed to take place on the surface of the seed by adjusting the thermal geometry. Under proper conditions, the growth continues the crystallographic orientation of the seed to form a single crystal. The thermal conditions at the growing liquid-solid interface are the most important factors governing the crystal growth process and are influenced by many factors. In practice, the liquid is heated at a temperature above the melting point by conduction and radiation from a thermal source. The heat of fusion is generated at the interface at a rate directly proportional to the rate of solidification. Heat is lost from the interface by conduction through the grown crystal and by conduction and radiation from the crystal to thermal sinks provided by the container walls and any gaseous atmosphere. If there is a net accumulation of heat to the interface, the crystal will melt. If there is a net loss of heat at the interface, the crystal will grow at a rate determined by the rate of dissipation of heat of fusion. Thermal gradients in the liquid and solid determine the rate at which heat arrives at and leaves the interface, thus determining the rate of crystal growth. The control of temperature and temperature gradients are therefore of utmost importance in melt-growth techniques.

The thermal gradients in the growing crystal also determine the shape of the solidifying interface. Figure 1 shows the isothermal surfaces for concave, planar, and convex interfaces. In the planar cases, there are only longitudinal gradients. The curved interfaces are associated with transverse temperature gradients as well as longitudinal ones. The transverse gradients can be especially troublesome. For expample, when the interface concaves into the liquid, Fig. 1 (a), the cooler surface of the crystal acts as a constricting tube which tends to squeeze the hotter interior and could cause plastic deformation of the interior of the crystal. A planar interface can be achieved by minimizing thermal loss from the surfaces of the crystal by using afterheaters (Ref. 2).

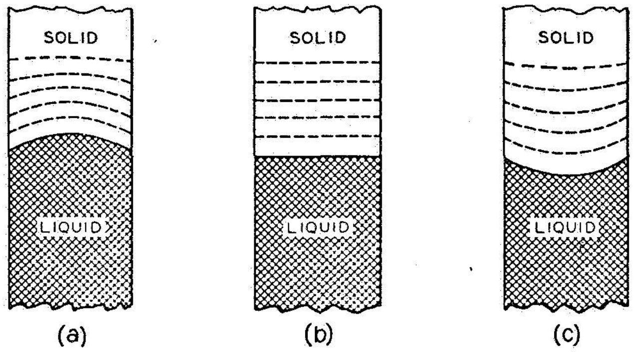


Fig. 1. Isothermal surfaces in a growing crystal when the liquid-solid interface is (a) concave into the liquid, (b) planar, and (c) convex into the liquid.

During the crystal growth by the solidification of a melt, the crystal does not have exactly the same composition as the melt because of the segregation of impurities. In the case where only one impurity with a segregation coefficient k is present, the impurity distribution along the length of the crystal is given by (Ref. 3):

$$C(x) = k\, C_o\, (1-x)^{k-1}$$

where C(x) is the concentration of impurity in the crystal as a function of the fraction, x, of the melt solidified, and C_o is the initial concentration of impurity in the melt. Unless the segregation coefficient is near unity, the impurity content changes along the length of the crystal making it impossible to produce a crystal of uniform impurity concentration.

II.1.2. Growth in a Containing Crucible

The Bridgman-Stockbarger technique is the oldest and widely used technique for growing single crystals from the melt. In this technique, both the melt and the growing crystal are contained in the same crucible, and Fig. 2 shows the crucibles used for the growth process. When a vertical crucible is used, it is filled with the polycrystalline material, placed in a furnace, and heated to a temperature above the melting point to melt the

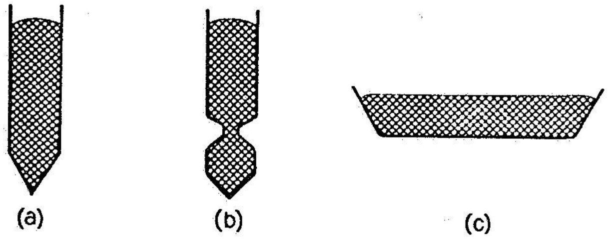


Fig. 2. Crucibles used in the Bridgman-Stockbarger technique.

entire charge. The crucible is then slowly cooled in such a manner that solidification begins at the tapered end of the crucible. Because of the small volume of the tapered region, the probability of forming only a single nucleus is enhanced. Further cooling is carried out so that an isothermal surface near the melting point passes progressively from the constricted region through the melt until the entire melt has solidified. In this manner, the single nucleus which first forms in the tip of the crucible can be made to grow and fill the entire crucible, yielding a single crystal of the size and shape of the crucible itself. Using the crucible configuration in 2 (b), a single crystal may be grown even if it is not possible to form one single nucleus in the first constricted region. If several nuclei are formed yielding several grains which reach the second constriction, it is highly probable that only one of the growing grains will be properly oriented to grow through this constriction. The surviving grain then serves as the seed for the growth process. The process of self-seeding by spontaneous nucleation is usually employed when a vertical crucible is used. It is very difficult to control the crystal growth with a seed crystal because of the inability to see the liquid-solid interface. The seeding may be readily carried out by using a horizontal crucible, Fig. 2(C), and this technique has been used widely in the growth of germanium single crystals (Ref. 2).

The Bridgman technique is simple and especially useful for the crystal growth of materials which decompose at the melting point. Since no relative motion is required between the liquid and growing crystal, the Bridgman technique may be carried out in a sealed tube to establish the desired vapor pressure of the volatile component. The disadvantages of the Bridgman technique include the inability to control the dopant concentration and distribution in the grown crystal, the difficulty of selecting an inert crucible for many materials, and the relatively poor structural perfection of the grown crystal due to the prevailing thermal conditions.

II.1.3. Crystal Pulling

The most common melt-growth technique is the pulling technique developed by Czochralski in 1917. The Czochralski technique was refined by

Teal and Little for the growth of germanium and silicon single crystals (Ref. 4). The basic elements of a crystal puller are shown in Fig. 3. The melt is contained in a suitable crucible, A, heated by an energy source, B. The single crystal seed, C, is held in a shaft, D, which can be raised and rotated at controlled rates. To grow the crystal, the melt is first held at a temperature slightly above the melting point of the material. The seed is lowered into the melt, and the temperature of the melt is raised slightly to melt a small portion of the seed to insure the melting of the seed by the melt. The temperature of the melt is then lowered until the melt begins to freeze onto the seed, and the seed is slowly pulled away from the melt. The grown portion of the crystal is cooled by conduction along the seed and seed holder and also by conduction and radiation to its surroundings, thus dissipating the heat of fusion.

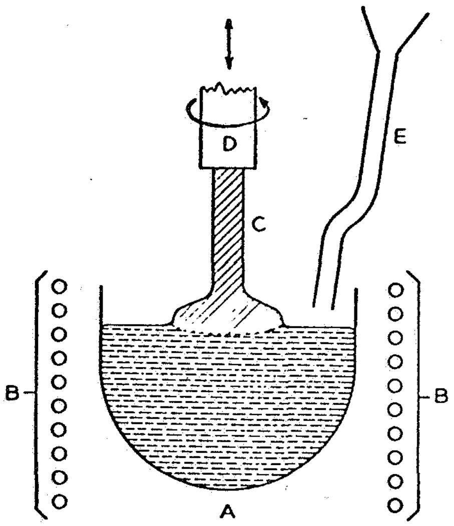


Fig. 3. Schematic of the basic elements of a crystal puller.

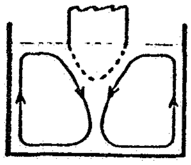
The shape of the cross section of the pulled crystal perpendicular to the growth axis is determined by two competing factors. The development of equilibrium faces of lowest surface energy tends to produce a polygonal cross section while the surface tension of the melt tends to produce a circular liquid-solid interface. The resulting cross section is a compromise between these two forces. For example, the surface tension of molten silicon is considerably higher than that of molten germanium, and the pulled silicon crystals have essentially circular cross sections and germanium crystals pulled along a <100> crystallographic direction has four flats of {110} orientations (the carats designate a group of crystallographically equivalent directions and the braces designate a group of crystallographically equivalent planes).

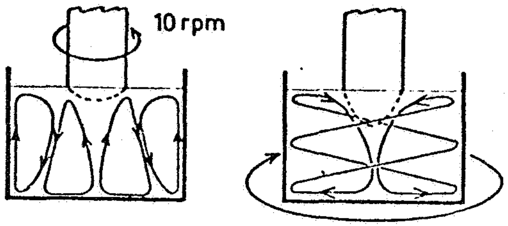
The important parameters affecting the chemical perfection (such as the uniformity of dopant distribution) and structural perfection of the pulled crystals include the thermal gradients in the melt and in the crystal, the fluid motion in the melt, and the shape of the solid-liquid interface during the crystal growth. The temperature gradients are essential for the crystal growth process. The temperature of the crucible wall is kept above the melting point of the material, and the thermal gradients are such that heat flows from the crucible into the crystal-melt interface, and from there into the grown portion of the crystal. The difference between these two thermal fluxes determines the rate of crystal growth.

The fluid motion during Czochralski growth is very complicated and is strongly influenced by the thermal and forced convection (Ref. 5). Thermal convection flow will be generated as steady circulation in any liquid where the temperature gradient is not aligned with the direction of gravity and no other external forces are present. In many geometric configurations, this flow is the steady streamline circulation generated between vertical boundaries by horizontal temperature gradients and occurs in Czochralski growth as hot liquid rising at the stationary crucible walls and falling in the center. The forced convection results from the rotation of the crystal and the crucible. In the case of a rotating disk in an infinite isothermal medium, the velocity boundary layer thickness has been shown to be uniform across the surface of the disk and is approximately equal to $(\mu/\omega)^{\frac{1}{2}}$, where μ is the kinematic liquid viscosity and ω the crystal rotation rate. During the crystal growth process, the liquid forced outward by centrifugal acceleration is replaced by a central flow up to the disk surface. When the crucible or melt rotates around a vertical axis, the boundary layer at the upper liquid surface cannot remain uniform because the rotation of an isothermal fluid in a cylindrical container results in a parabolic depression at the upper free surface due to the velocity and pressure changes. Consequently, the boundary layer produced when a stationary disk is placed on the top surface should show a maximum thickness at the rotation axis where the radial velocity has its lowest value.

Experiments have been designed to simulate fluid flow existing during crystal growth using a water-glycerine mixture. The observed flow patterns are shown schematically in Fig. 4. Treating the crystal and crucible rotation rates separately, the following observations may be summarized. Figure 4 (a) shows the liquid flow configuration for thermal convection alone, i.e., no crystal rotation. The hot liquid rose at the outer crucible wall and descended gradually near the center. At low crystal rotation rates, thermal convection flow was diminished close to the interface because the fluid flow from the rotating crystal was countercurrent to that caused by the thermal convection. The deflection of streamlines is shown schematically in Fig. 4 (b). At higher crucible rotation rates, the crystal acted like a fan, drawing liquid up at the center and spinning it out at the sides. Thermal convection is relatively unimportant in this case. At low crucible rotation rates, the liquid flow close to the crucible wall moved in a long closed streamline path, and the extent of thermal convection was diminished. For faster crucible rotation rates, flow separation occurred at the periphery of the crystal, and eddies developed in the outer region of the liquid. The region close to the crystal-melt interface still possessed the same basic non-uniform flow. Also, combinations of crystal and crucible rotation in the same direction produced only a modification of the simple crucible rotation flow, and the crystal rotation did not exert its previous influence on the bulk fluid flow, except at low crucible rotation rates. For counter rotations, the central convection cell shown in Fig. 4 (e) became quite stable.

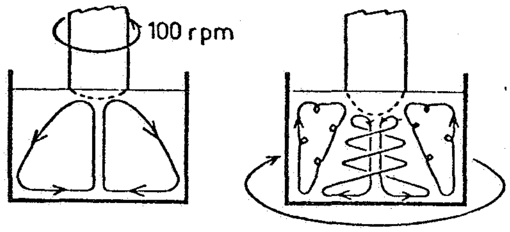
The convection patterns arising from simultaneous crystal and crucible rotation during Czochralski growth has been further analyzed (Ref. 6).


(a) thermal convection only



(b) low crystal rotation rate

(d) 25 rpm low crucible rotation rate



(c) high crystal rotation rate

(e) 100 rpm high crucible rotation rate

Fig. 4. Schematic flow patterns in transparent liquid model.
(a) thermal convection only, (b) low crystal rotation rate, (c) high crystal rotation rate, (d) low crucible rotation rate, (e) high crucible rotation rate.

Convection in a rotating high-temperature melt with a crystal growing at the upper free surface and rotating at a different velocity has been shown to consist of two distinct types. In the outer region of the liquid, where almost solid-body rotation occurs, flows due to the rotation only are strictly two dimensional with respect to an axis rotating with the crucible and the relative observer effects tend to obscure the streamlined convection patterns. In the region of liquid beneath the crystal, three-dimensional flows occur in directions determined by the vertical variations of the radial centrifugal pressure gradient. Thermal convection flows from nonvertical temperature gradients are shown to be enhanced by crucible rotation in the outer liquid region and reduced in the inner region by the strong inner flows.

The shape of the solid-liquid interface is closely related to the fluid motion and temperature profile in the melt. The fluid motion and the solid-liquid interface shape during the Czochrakski crystal growth have been computed from the numerical solution of the Laplace equation (Ref. 7,8). A cylindrical crystal of a constant radius is grown from a melt in a cylindrical crucible as shown in Fig. 5. It is assumed that the heat transfer in the melt

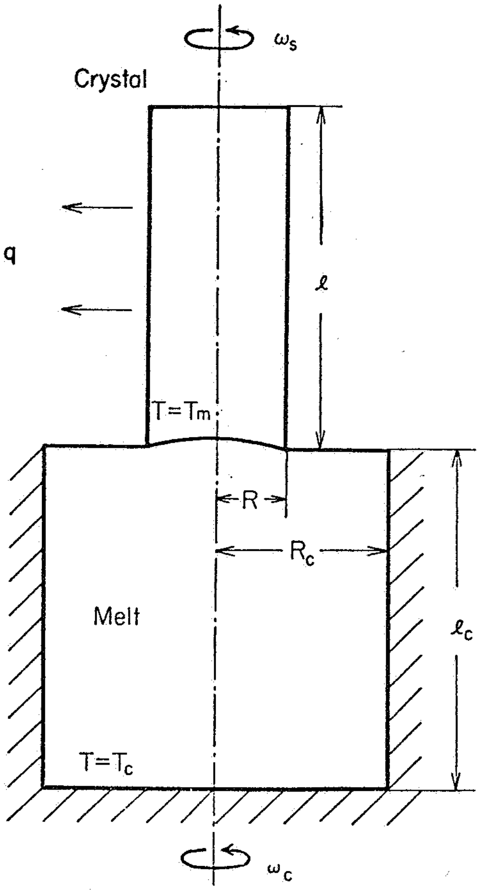


Fig. 5. The growth of a cylindrical crystal.

is governed only by conduction and that the radiation and gas convection losses from the crystal and melt surfaces are given by $\epsilon\sigma(T+273)^4$ and $\alpha(T+273)^{1.25}$, respectively (where ϵ and α are emissivity and thermal conductivity, respectively). The fluid motion has been calculated using various crystal rotation rate, ω_s, in the range 0-40 rpm and crucible rotation rate, ω_c, in the range 0-10 rpm. The results are shown in Fig. 6. The results are in qualitative agreement with those shown in Fig. 4. The shape of the solid-liquid interface has been studied under various crucible and crystal rotation rates. The effect of the crucible rotation on the interface shape is shown in Fig. 7. At low crucible rotation rates, the interface shape is almost unchanged, although the flow pattern is changed from the natural convection flow to the crucible-rotation-dominating flow. At higher crucible rotation rates, the downward flow becomes strong, and the temperature profile is altered in such a manner that the isotherms are slightly displaced downwards. Fig. 8 shows the effect of crystal rotation on the interface shape with no crucible rotation and with a crucible rotation rate of 10 rpm.

The homogeneity of dopant distribution is an important property of semi-conductor crystals. The radial distribution of dopant in a plane

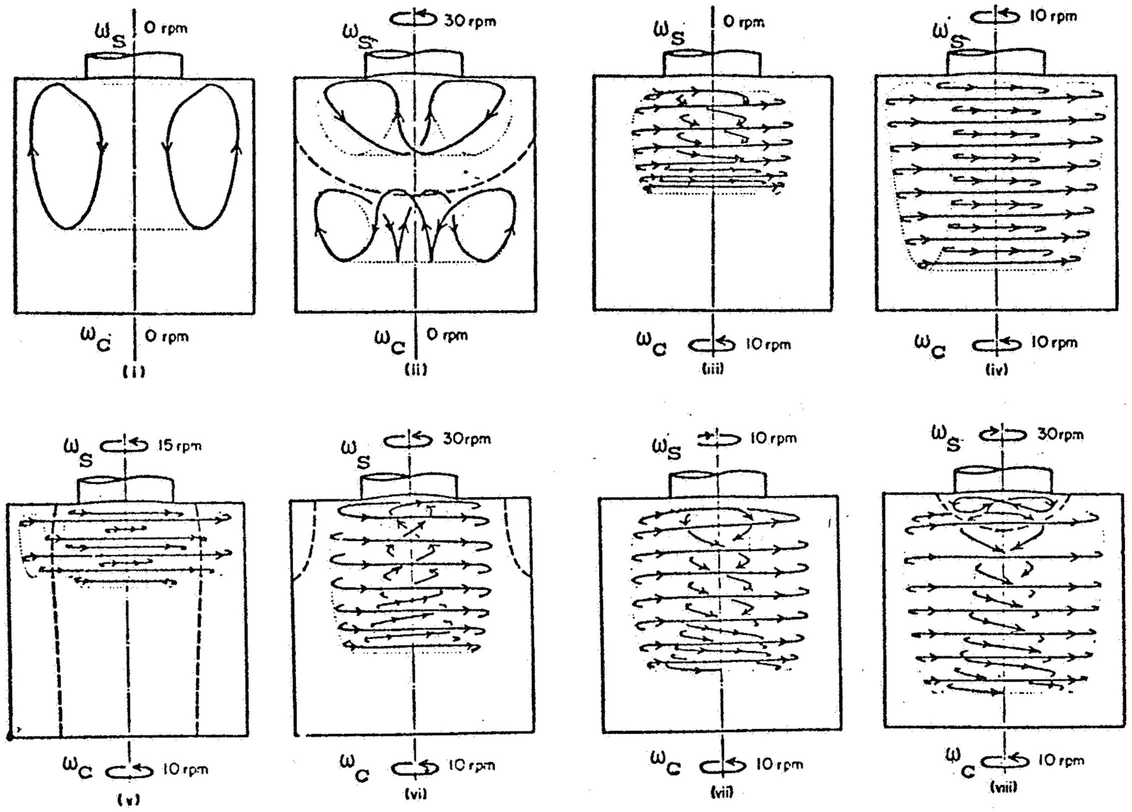


Fig. 6. Fluid flow patterns under various crystal and crucible rotation rates.

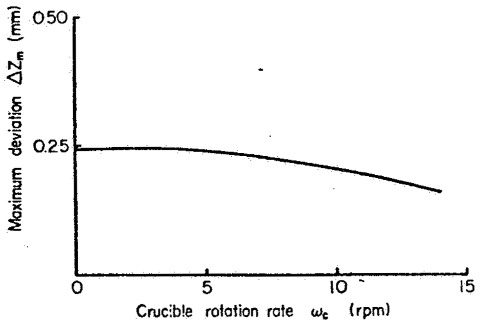


Fig. 7. Effect of crucible rotation on the interface shape.

perpendicular to the growth direction is determined principally by the shape of the solid-liquid interface and the fluid flow patterns in the liquid.

These parameters can be controlled experimentally by varying the direction and magnitude of rotation rates, temperature gradients in the melt, etc.

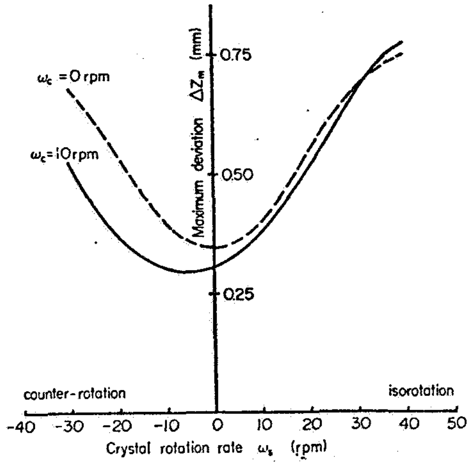


Fig. 8. Effect of crystal rotation on the interface shape with and without crucible rotation.

Figures 9-11 show the effects of crucible rotation and seed rotation on radial resistivity of <111> Czochralski-grown silicon crystals (Ref. 9).

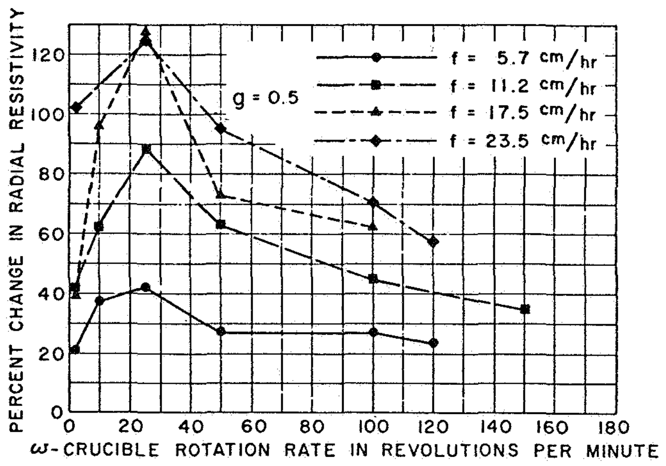


Fig. 9. Effect of crucible rotation on radial resistivity.

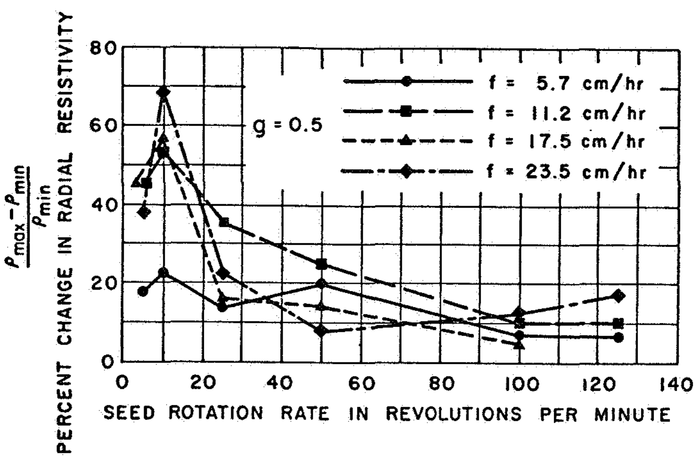


Fig. 10 Effect of see rotation on radial resistivity.

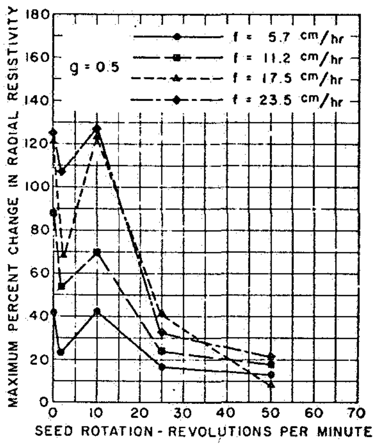


Fig. 11 Combined effects of seed rotation and 25 rpm crucible rotation on radial resistivity.

The maximum variation in the radial solute distribution occurred at a crystal rotation of 10 rpm and a crucible rotation of 25 rpm and these effects were independent of each other. These variations may be explained by the effects of thermal convection on fluid flow. The flow normal to the interface due to rotation is uniform over the radius, where that flow due to thermal convection will follow gradual curved streamlines and possess a definite stagnation point near the center of the interface. Thus, at low crystal rotation rates, the boundary layer thickness near the stagnation point remains unchanged, while at the outer regions of the interface the thickness is reduced by the additive effects of the tangential velocity component and the thermal convection velocity. This combined effect will then cause an increase in the radial gradient of solute concentration as the crystal rotation increases in the low range. The effect of crucible rotation is to inhibit thermal convection, but it does not change the stagnation point. The streamline flow at the crystal interface is quite similar to that of thermal convection, but the longitudinal flow component should be enhanced at the outer portion of the interface and the degree of radial solute segregation is increased. Crystal rotation rates above 10 rpm were observed to be more effective in reducing radial solute segregation than high crucible rotation rates. This effect is associated with a more rapid decrease in the laminar layer at the interface center than at the outside, so the effects of secondary flow at the outer periphery are minimized. In summary, the maximum solute uniformity is possible only when the boundary layer at the growing interface is controlled by crystal rotation.

II.1.4. Crucibleless Methods

While good quality single crystals of many electronic materials have been produced by the Czochralski pulling technique from a melt contained in a crucible, the chemical reactivity of some molten materials has made it difficult to find a satisfactory crucible to contain the melt. For example, fused silica is the most commonly used crucible material for the pulling of silicon crystals. However, molten silicon reacts with fused silica to yield silicon monoxide according to the equation:

$$\mathrm{Si}\ (\ell) + \mathrm{SiO_2}(s) \rightleftarrows 2\ \mathrm{SiO}(g)$$

The equilibrium vapor pressure of silicon monixide at the melting point of silicon is approximately 10 Torr. Thus, the silicon monoxide can vaporize from the molten silicon at an appreciable rate, and the reaction continues throughout the crystal growth process. The purity of the silica container therefore limits the ultimate purity of silicon. Furthermore, oxygen also dissolves in molten silicon to an atomic concentration of higher than $10^{18}\mathrm{cm}^{-3}$. Oxygen is an electrically significant impurity in silicon and produces complicated electrical changes after various heat treatments (Ref. 10). To avoid the problem of crucible contamination, crucibleless techniques developed for the crystal growth of semiconductors are described below.

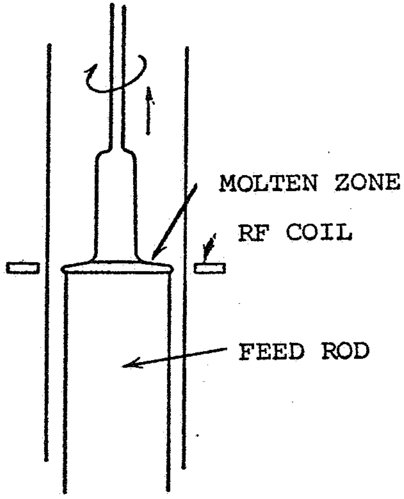


Fig. 12. Pulling of silicon crystals from a partially melted polycrystalline boule.

Silicon crystals of good chemical and structural perfection have been pulled from a partially melted boule, as shown schematically in Fig. 12 (Ref. 11). In this technique, a large diameter silicon ingot is supported vertically in a silica envelope. The top of this ingot is melted by a suitably designed radio frequency induction coil. A seed crystal is then used for the pulling of a single crystal from the molten top of the silicon boule just as in ordinary single crystal pulling. As the crystal is pulled, the boule is moved slowly upward into the radio frequency coil so that the crystal-melt interface remains essentially fixed relative to the coil. The process is continued until the boule is depleted. This process utilizes the advantages of crystal pulling without the disadvantage of crucible contamination, and crystals up to 5 cm in diameter essentially free of dislocations have been produced.

Another widely used technique for the crystal growth of electronic materials is the floating zone process, a zone melting technique. Zone melting was first used by Pfann for the purification of electronic materials (Ref. 3). In this technique, a narrow zone of a relatively long charge is melted, and the molten zone is traversed through the charge as shown schematically in Fig. 13. The solute distribution in the zone-melted bar (except in the last zone) after single-pass is given by

$$C/C_o = 1 - (1-k)\ e^{-kx/\ell}$$

where C_o is the initial concentration, k is the segregation coefficient,

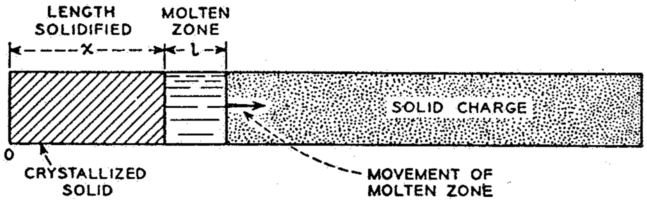


Fig. 13. Schematic diagram of the zone-melting process.

ℓ is the zone length, and x is the length solidified. The solute concentration after single-pass zone melting is shown in Fig. 14. In the floating zone process (Ref. 12), an ingot of silicon is supported at its end by two chucks, and a small section of the rod is melted (Fig. 15). If the molten section is not too long, it will be supported between the two solid portions of the rod by the surface tension of liquid silicon. The two sections of the rod can be moved independently, and the relative speed of their movements determine the diameter of the resulting rod. The molten region can be made to traverse the entire length of the rod, and zone refining can be achieved. Furthermore, by starting with a single crystal seed at one end of the rod, a single crystal can be grown. Self-seed techniques, such as the constriction used in the Bridgman technique, may also be used. The primary advantage of the floating zone technique is the absence of many contamination sources present in other crystal growth process, and nearly intrinsic silicon has been prepared in this manner (Ref. 13).

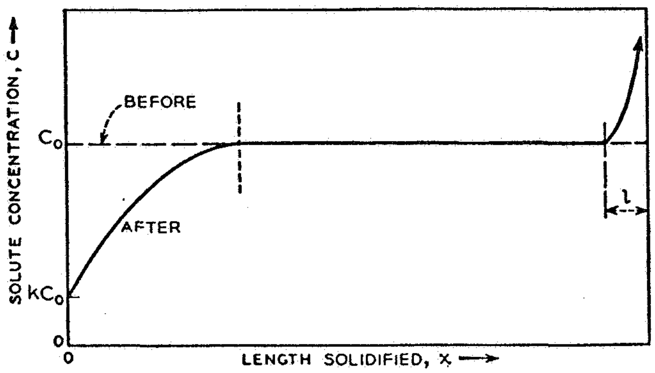


Fig. 14. Solute concentrations before and after single-pass zone-melting.

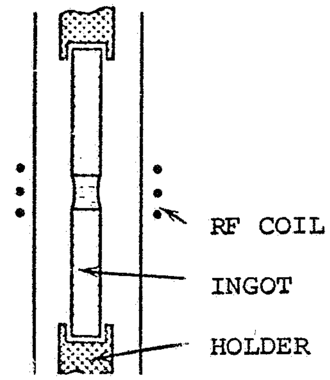


Fig. 15. Schematic diagram of the floating zone technique.

In the floating zone technique, the surface tension is primarily responsible for the stability of the molten zone between the two solid portions of the ingot. However, the gravitational field acts on the molten zone and tends to make the zone collapse. The hydrostatic pressure increases with the length of the molten zone, and at some point, this pressure will be large enough to overcome the surface tension, causing the molten zone to collapse. Assuming that the only active forces are surface tension and the gravitational field, the maximum stable zone length has been shown to be about $2.7(\rho/dg)^{\frac{1}{2}}$, where ρ, d, and g are the surface tension of the liquid, the density of the liquid, and the gravitational constant, respectively. Although there appears to be no theoretical limitation on the diameter of the crystal that can be grown by the floating zone technique, it is difficult in practice to melt completely through a rod and maintain a zone length much smaller than the rod diameter. This would indicate that crystals could be grown with diameters only slightly larger than $2.7(\sigma/dg)^{\frac{1}{2}}$, i.e., about 2 cm for silicon.

II.2. Growth from Solution

Solution growth is simple in principle and has many applications. This technique is particularly suited for the growth of materials which have high vapor pressure or decompose irreversibly at the melting point. The solution growth can be accomplished at temperatures considerably below the melting point of the material, and the use of lower temperature alleviates many of the problems associated with the melt growth process. However, solvent substitution and inclusion could occur.

II.2.1. Principles of Solution Growth

The solution growth method is based on the temperature dependence of solubility according to the relation:

$$\frac{d \ln s}{dT} = \frac{\Delta H}{RT^2}$$

where s is solubility, ΔH is the heat of solution, and R is the gas constant. Most dissolution reactions are endothermic, i.e., the solubility increases with increasing temperature. For example, the solubility of gallium arsenide in gallium increases with increasing temperature. Thus, during the slow cooling of a solution of gallium saturated with gallium arsenide at a given temperature, 900°C for example, the solution becomes supersaturated and nucleation will begin. In the presence of a seed crystal, nucleation and growth will occur preferentially on the seed.

The solution growth process involves three steps: (1) the diffusion of solute to the crystal-solution interface, (2) the deposition of the solute on the growing interface, and (3) the dissipation of the heat of crystallization. Step (1) or (2) is usually rate-determining. As a result, growth rates from solution are usually only a few percent of those from pure melt, where the rate-determining step is the dissipation of the heat of fusion from the solid-liquid interface. Thus, solvents of low viscosity are preferred to facilitate the transport of solute by diffusion. A single crystal seed is generally used because of the difficulties involved in controlling the spontaneous nucleation.

II.2.2. Solution Growth Techniques.

Several techniques have been developed for the crystal growth of semiconductors from solution. These techniques are widely used for the growth of III-V compounds required for various device applications.

The epitaxial growth of gallium arsenide has been accomplished by a tilting boat method as shown in Fig. 16 (Ref. 14). Initially, the substrate is held tightly against the flat bottom at the upper end of a graphite boat. A tin-gallium arsenide mixture is placed at the lower end. The graphite boat is fixed in position at the center of a constant temperature zone of the furnace tube, and the boat is heated to about 640°C in a hydrogen atmosphere. As the temperature increases, gallium arsenide dissolves in the tin at the lower end of the boat. The power is then turned off and the furnace is tipped so that the tin solution covers the substrate surface. As the

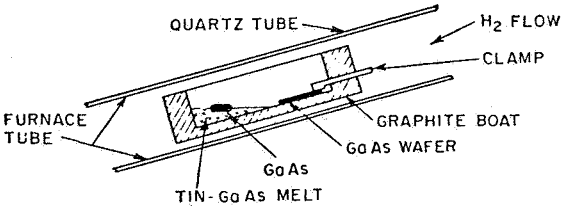


Fig. 16. Schematic diagram of the apparatus for the epitaxial growth of gallium arsenide from a tin solution.

furnace cools, gallium arsenide recrystallizes from the solution and deposits epitaxially onto the substrate surface.

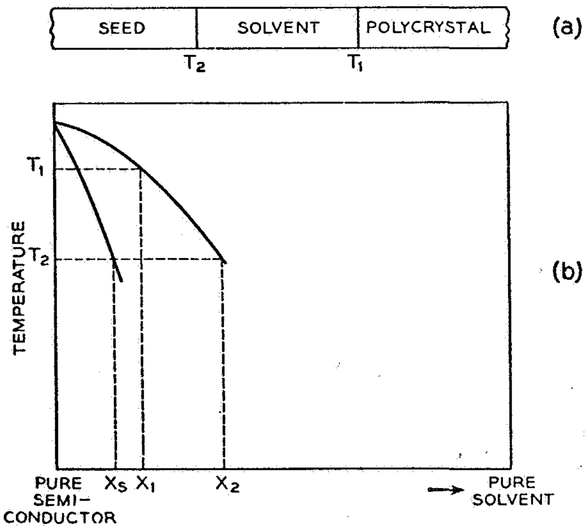


Fig. 17. The temperature gradient recrystallization technique (a) schematic presentation of the system, (b) phase relations between the semiconductor and the solvent.

The temperature gradient recrystallization technique shown in Fig. 17 has produced relatively large single crystals of semiconductors. The seed crystal is heated to temperature T_2, and a polycrystalline ingot of the semiconductor is heated to temperature T_1. A solution of composition X_2 serves as the solvent and is placed between the seed and the polycrystalline source. The solvent dissolves practically none of the seed since it is saturated with semiconductor at T_2. However, it does dissolve a portion of the polycrystalline material until the concentration at the solution-polycrystalline source interface has reached the value X_1. Thus, the solution at the source interface is of higher concentration than that at the seed interface. Because of this concentration gradient, the semiconductor diffuses through the solution producing a supersaturated solution at the seed surface. The semiconductor will precipitate on the seed, and the seed will grow. The traveling solvent method is based on the temperature gradient recrystallization and has been used for the growth of refractory semiconductors such as silicon carbide (Ref. 15).

II.3. Growth from the Vapor Phase

Many semiconductors do not melt at temperatures and pressures conveniently obtained in the laboratory and have, in some cases, been successfully grown from the vapor phase. For this technique to be applicable, the material of interest must either vaporize without undergoing irreversible decomposition or be preparable by chemical reactions of gaseous reactants. The direct growth methods include sublimation, vacuum evaporation, etc. The chemical vapor growth technique has been used extensively during the past twenty years for the preparation and crystal growth of electronic materials either in the bulk form or as thin layers on substrate surfaces. This technique has the distinct advantages that refractory materials can be prepared at temperatures considerably below their melting point or decomposition temperature, and that the impurity concentration and distribution in the product can be controlled to an extent not obtainable by other techniques. Also, a wide range in the thickness from a fraction of a micron to a few centimeters or more can be achieved and controlled. These advantages have been utilized in the preparation of a broad spectrum of conductors, semiconductors, and insulators in the single crystalline, polycrystalline, or amorphous form. In chemical vapor growth, all species except the desired product are volatile at the processing temperature. The growth process may be carried out by two distinct approaches: the transport of the desired substance by chemical reactions in a temperature gradient, and the reaction of gaseous compounds containing the constituents of the desired material at high temperatures. A substrate is usually used particularly in the growth of single crystalline materials where the nucleation and growth processes must be controlled. To achieve epitaxial growth, the chemical reaction must be predominately heterogeneous taking place on the substrate surface, since volume reaction results in the formation of atomic or molecular clusters of random orientation in the space surrounding the substrate and the deposition of these clusters on the substrate will produce non-oriented growth.

II.3.1. Direct growth methods.

Similar to solution growth, direct growth from the vapor phase also involves three steps: (1) the transport of the vapor to the growing surface, (2) the nucleation and growth of a new layer, and (3) the dissipation of the heat of vaporization. However, the molecular diffusivity is generally more rapid in a vapor than in a liquid and is no longer so strongly rate controlling. The most important variables are the vapor pressure of the material in the growing chamber and the temperature of the growing surface. Since the vapor pressure is usually controlled by the temperature of the source material, the difference between the source temperature and the substrate temperature determines the supersaturation of the vapor, and therefore the growth rate, at the growing surface.

Epitaxial layers of elemental semiconductors, such as germanium and silicon, have been prepared by vacuum evaporation. Using an ultrahigh vacuum, about 10^{-10} Torr, homoepitaxial silicon layers free of structural defects can be grown at temperatures as low as 650°C on {111} surfaces and 350°C on {100} surfaces of silicon substrates (Ref. 16).

When the growth is carried out under atmospheric pressure, high temperatures are often required to obtain sufficient vapor pressure of the source material, and a suitable container must be selected to minimize contaminations. For example, a silicon carbide container has been used to grow silicon carbide single crystals (Ref. 17). Granular silicon carbide was placed in a graphite crucible, and a cylindrical mandrel was pressed into the granules to form a cylindrical hole. A cover was formed from another piece of silicon carbide. To grow crystals, the silicon carbide-lined graphite crucible was heated at 2500 to 2600°C under an atmosphere of hydrogen or argon. The furnace was designed so that temperature gradients are produced in the crucible, and the crystals grow along these gradients.

II.3.2. Chemical Transport Technique

The chemical transport technique is applicable to solid substances which will react reversibly with a gaseous reagent (the transport agent) to form volatile products (Ref. 18). When the equilibrium constant of this reaction is temperature-dependent, the solid substance can be transported by the presence of a temperature gradient. In practice, the chemical transport technique can be carried out in a closed or gas-flow system. The solid substance to be transported (A), a transport agent (B), and a substrate (S) are placed in a reaction system with A and S in temperature regions T_A and T_S, respectively. The reaction between A and B in the source region T_A yields volatile products C, D, etc., according to the equation:

$$aA(s) + bB(g) = cC(g) + dD(g) + \text{-----}$$

The products are transported to the substrate region T_S as a result of the pressure gradient. Because of the change in temperature in this region, the reverse reaction takes place, depositing A on the substrate. The transport agent regenerated in the substrate region serves to repeat the process in a closed system and is not reused in a gas-flow system. The relative magnitude of T_A and T_B required for the transport process depends on the variation of the equilibrium constant of the reaction with temperature. When the equilibrium is shifted toward the formation of A as the temperature is decreased, then $T_A > T_S$ is a necessary condition for the transport, and vice versa. Thus, the feasibility of using the transport technique for the chemical vapor growth of a given material can be readily deduced from thermochemical considerations. The rate of transport depends on the temperature of the source and the substrate, the concentration of the transport agent, and the gaseous diffusion and convection. Thermal convection is believed to be significant at pressures higher than about 3 atm. The deposition rate increases with increasing temperature difference, and increasing concentration of the transport agent.

The closed-tube chemical transport technique may be used for the growth of bulk crystals by controlling the nucleation and growth of the transported material on the wall of the reaction tube. This is possible because the transport variables in a closed system can be so adjusted that the entire system is essentially at equilibrium. When a closed tube containing the source material and a transport agent is maintained at a uniform, constant temperature, no net transport occurs. Nucleation may be initiated by introducing a heat sink on a small region of the tube so that the temperature of this region is a few degrees lower than the remainder of the system. Since this cooler region cannot be made infinitely small, many nuclei are formed at random. However, by reversing periodically the direction of the temperature gradient, intervals of deposition are alternated with intervals of etching to reduce the number of nuclei, thereby leading to the formation of larger crystals.

The growth of silicon crystals by the chemical transport technique in a closed tube will be used as an example. Silicon reacts reversibly with silicon tetraiodide to form silicon diiodide according to the reaction

$$\mathrm{Si(s)} + \mathrm{SiI_4(g)} \rightleftarrows 2\ \mathrm{SiI_2(g)}$$

Since the equilibrium of this reaction is shifted toward the formation of silicon as the temperature is decreased, silicon tetraiodide is able to transport silicon from a source at about 1100°C to a lower temperature region. Single crystals and epitaxial layers of silicon have been prepared in this manner (Ref. 19). A schematic diagram of the epitaxial growth apparatus is shown in Fig. 18.

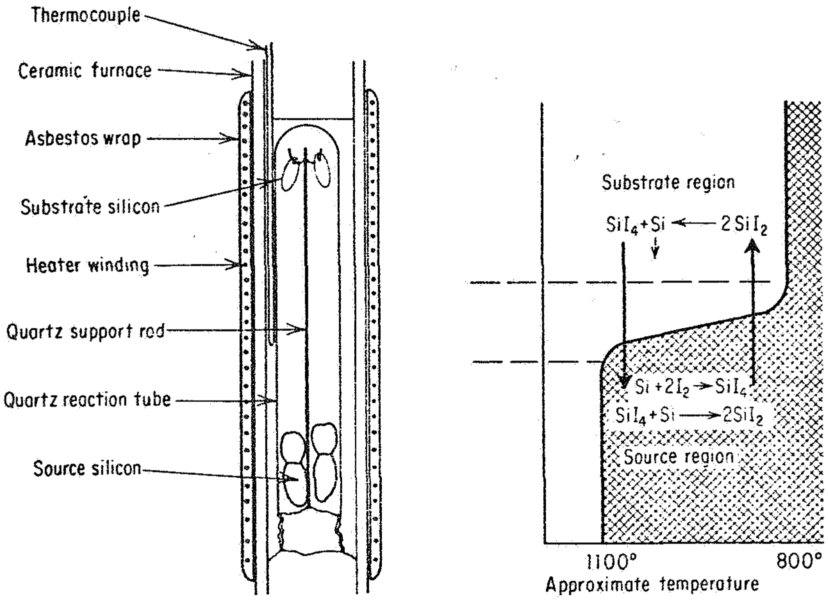


Fig. 18. Apparatus for the epitaxial growth of silicon by chemical transport.

II.3.3. Chemical Reactions in a Flow System

Chemical vapor growth by conventional chemical reactions in a gas-flow system is the most commonly used technique in the electronic industry. A variety of chemical reactions with widely different free energy changes and activation energies are usually available for the growth of a given material. The commonly used reactions include thermal decomposition, thermal reduction, hydrolysis, ammonolysis, etc. The chemical reaction chosen for the growth process should be thermochemically and kinetically favorable, and the experimental conditions must be adjusted so that the heterogeneous reaction dominates. For example, the use of low partial pressure of the reacting species tends to suppress volume reactions. The gas-flow system is flexible in that the purity or dopant concentration in the grown material is readily controlled. In practice, the substrate is maintained at a suitable temperature in a reaction tube provided with a gas inlet and exhaust tubes. The substrate may be heated in a resistance furnace or supported on a suitable susceptor and heated externally by an rf generator. The rf heating is most commonly used, since the walls of the reaction tube are at relatively low temperatures and the volume reactions and random nucleations are minimized. The reactant mixture is introduced into the reaction tube; under proper conditions, the reaction takes place on the substrate surface depositing the desired material.

Chemical vapor epitaxial growth in a gas flow system has made real significant contributions to solid state electronics. The epitaxial growth of silicon accomplished in the late fifties has had a real impact on the development of new and improved devices. The thermal decomposition of silane, the most promising low temperature process, takes place according to the reaction

$$SiH_4(g) \rightarrow Si(s) + 2\ H_2(g)$$

This process has been studied in more detail in a horizontal reactor shown schematically in Fig. 19. It has been demonstrated that a thin stagnant layer with a large temperature gradient ($>100°C\ mm^{-1}$) is present above the heated susceptor, and the main gas flow is vertically mixed by thermal convection above the stagnant layer (Ref. 20). Experimentally measured growth rates were in good agreement with the assumption that the deposition of silicon is determined only by the diffusion of silane through the stagnant layer. A small angle of tilting of the susceptor is necessary for obtaining thickness uniformity along the susceptor. When hydrogen chloride is added to silane, the growth rate can be interpreted in terms of a mutually independent growth of silicon from silane and an etching of silicon by hydrogen chloride (Ref. 21). Comparison of growth rates from mixtures of silane-hydrogen chloride and hydrogen-silicon tetrachloride indicates that gas phase reactions are slow and that equilibrium between solid silicon and the gas phase is established. Kinetic data point to a diffusion controlled reaction rate, and it is shown that thermodiffusion in the stagnant layer retards the growth rate of silicon and enhances the etching reaction.

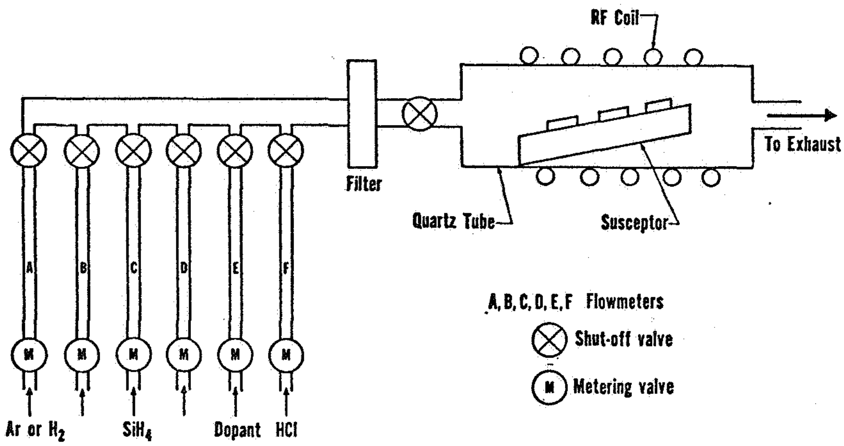


Fig. 19. Schematic diagram of the apparatus for the epitaxial growth of silicon by the pyrolysis of silane.

III. Physical Phenomena Related to Crystal Growth in Zero Gravity

Nearly all crystal growth processes involve both a solid and a fluid (liquid or vapor) component. Since internal bonding forces in solids are much greater than one-g forces, only the properties of the fluid are influenced by gravity. In the liquid state, intrinsic forces such as cohesion and surface tension are of the same order as one-g forces, and the familiar properties of liquids are the result of the interaction of intermolecular forces and the gravitational force. If the gravitational force disappears, the behavior of fluids will be determined by molecular forces alone. Thus the near-zero gravity condition will have a significant influence on the fluid behavior which may affect the crystal growth process.

Fluid properties of interest to crystal growth include: melting point, vapor pressure, diffusion, viscosity, thermal conductivity, surface tension, and chemical reactivity. The effects of some of these properties on crystal growth will be greatly modified by a zero-gravity environment. For instance, gravity-driven thermal convection is the most important natural convection process in all but thin fluid layers on earth and is strongly influenced by fluid viscosity and thermal conductivity. Viscosity and thermal conductivity may therefore be less important in zero-gravity crystal growth. However, the magnitude of the surface tension force may become more important. Also, in the absence of convection, diffusion will be much more significant for the mass transport process.

Crystal growth involves many processes of great complexity including mass transport, nucleation, interface interaction, fluid flow, etc. Mass transport occurs via convection and diffusion. If mass transport could be studied separately from other factors, the analysis of the crystal growth process would not be intractable. However, mass transport is intimately coupled with heat transfer which occurs by convection, conduction, and radiation. For example if the heat input to a system in a steady state is changed, new mass and thermal convection currents will occur until a new steady state is established. The final conditions are not just determined by superimposing the heat input onto the initial thermal condition. Rather, the new or altered convection patterns due to the heat input must be considered. Emphasis in this report, however, is directed to mass transport which can be influenced by natural and forced convections. Mass transport by diffusion is not considered since diffusion is independent of gravity. Diffusion, however, may be a dominant mass transport mechanism in a zero-gravity environment. In this case, crystal growth may be considered as a Stefan problem (Ref. 22), which is one class of transport problems involving the diffusion equation with a moving or free boundary. It should be noted that the Stefan analysis is not useful in the presence of other effects such as convection. Since crystal growth on earth is frequently influenced by convection in the fluid, the mechanisms of convection, the role of convection in crystal growth, and the expected results of crystal growth in zero-gravity are discussed in this section.

III.1. Convection

Fluid flow can be motivated by many types of convective driving forces, and the effects of convective flow are to break up long-range diffusion fields and to alter temperature and concentration gradients. The convective flow effects are often more important than diffusive transfer in crystal growth processes. The most important convection mechanisms are discussed below.

III.1.1. Gravity Driven Convection

Gravity driven convection occurs as the result of gravity acting on density differences within a fluid and is the most well-known form of free convection. Density variations in a fluid can be created by temperature gradients and by concentration gradients, both of which are expected to be present in crystal growing systems. When crystals are grown from a melt with a low impurity concentration, a situation frequently encountered in the growth of silicon, the temperature gradient mechanism will dominate.

Classical fluid mechanics has been used to analyze the stability of a pure fluid in a gravitational field (Ref. 23). A fluid can be in mechanical equilibrium with no macroscopic motion without being in thermal equilibrium. However, a rigid condition is put upon the temperature distribution: it can only depend on the vertical dimension. Furthermore, when a temperature gradient is directed downwards, mechanical equilibrium is only possible if

$$\frac{dT}{dZ} > -g \frac{T}{C_p V} \left(\frac{\partial V}{\partial T}\right)_P$$

where g is the acceleration due to gravity, C_p is the heat capacity at constant pressure, and V is the volume. Otherwise, internal currents will appear in the fluid, and this internal motion, referred to as free convection, tends to mix the fluid and to minimize the temperature gradient.

The thermal convection may be characterized by two dimensionless numbers: the Prandtl number and the Grashof number (Ref. 24). The Prandtl number is defined as $Pr = \nu/\chi$, where ν and χ are respectively the kinematic viscosity and thermometric conductivity of the fluid. The kinematic viscosity is related to viscosity, η, and density, ρ, by the relation $\nu = \eta/\rho$. It can be shown that $\chi = \kappa/C_p\rho$, where κ is the thermal conductivity. The Prandtl number can be expressed in terms of measureable parameters as

$$Pr = \eta\, C_p/\kappa.$$

This dimensionless number is a measure of the relative importance of the viscosity to the thermal conductivity in effecting the convective flow.

The Grashof number is defined as

$$Gr = g\beta L^3 \Delta T/\nu^2$$

where β is the thermal expansion coefficient, L is the characteristic length, and ΔT is the temperature difference. The product of the Prandtl number and the Grashof number is defined as the Rayleigh number: Ra = PrGr. This quantity is most often used to characterize the fluid stability. Since the gravitational acceleration appears to the first power in the Rayleigh number, Ra is reduced proportionally when g is reduced. It should also be noted that the system dimension is to the third power in the Rayleigh number. Thus no drastic increase in the size of the fluid body over the size used on earth can be made in the space experiment if small accelerations occur. Two analytical solutions for Ra are well know. In the case of a fluid situated between two infinite horizontal planes with the lower plane at a higher temperature, the onset of convection occurs for $Ra > 1710$. If the upper surface is free, the critical Rayleigh number is 1100. For a fluid bound by vertical walls, critical Rayleigh numbers are also on the order of 1000 (Ref. 25). For very large values of the Grashof number, on the order of 50,000 for the first case, fluid flow becomes turbulent.

In typical crystal growth arrangements, the Rayleigh number usually exceeds the critical values for the onset of convective flow. For example, if L = 5 cm and $\Delta T = 10°C$, Ra exceeds 10^5 for metals such as aluminum and tin (Ref. 26, 27). It is not established, however, if this value is large enough to indicate turbulent flow (Ref. 28).

Convection studies have been carried out in many melt-growth experiments. In horizontal crystal growth in an open boat, convection arises from the horizontal temperature gradient and the accompanying density gradient. The liquid near the solid-liquid interface, being cooler, is relatively dense and tends to sink, while that at the hot end of the boat tends to rise. Circulation of the liquid results in flow along the top of the boat towards the interface and flow along the bottom away from the interface. However, the actual flow patterns are more complicated (Ref. 26). The major effect of thermal convection is to cause temperature fluctuations at the liquid-solid interface, and these fluctuations lead to non-uniform growth rates and consequent impurity striations in the crystal. For conducting melts such as indium antimonide, the fluctuations can be damped by the application of a magnetic field normal to the horizontal growth axis, and striations in the crystal are also eliminated (Ref 27, 29). The thermal convection in rectangular volumes of liquid gallium has been shown to produce sinusoidal temperature oscillations of large amplitude in both "heated from below" and "heated from the side" configurations, and the period of the oscillation depends on the melt dimensions (Ref. 30). Convection phenomena are particularly important in the growth of large diameter crystals by the Czochralski technique. For example, silicon crystals of 3" diameter are currently pulled from a crucible containing several kilograms of melt. Thermal convection fluid flow has been studied in a calcium flouride melt (m.p., 1360°C) using a typical silicon puller (Ref. 31), and a motion picture was made to illustrate the results of this study (Ref. 32). Large temperature fluctuations in the melt were measured, and the effects of crystal and crucible rotation on the fluid flow were observed. Large crystal rotation rates reduced the temperature fluctuations, and crucible rotation also tended to reduce turbulence in the melt. The geometry of the heat sources and shields was found to be very important in reducing turbulent flow in the melt. Gross solute inhomogeneities in Czochralski grown germanium have been observed when only thermal convection mixing was used (Ref. 33). The simulation of Czochralski growth with a water-glycerine mixture as the melt and a metal cylinder as the crystal has been used to study the fluid flow patterns, as described in Section II.1.3 (Ref. 5,6). However, these experiments were carried out near room temperature, and the magnitude of thermal convection effects were much less than what occurs in a high-melting liquid.

Convective temperature fluctuations in vapor growth are presumably of less importance than those in melt growth because of the higher frequencies obtained in gases (Ref. 34), and the lower growth rates reduce the striation spacing to sub-diffusion distances.

III.1.2. Surface Tension-Driven Convection

The temperature dependence of surface tension forces can cause convection in thin fluid layers (Ref. 35). Surface tension forces exist at the interface between a liquid and a solid, at the interface between two immiscible liquids, and at a free liquid surface. These convection driving forces are significant in crystal growth; however, they have not been considered since gravity driven convection dominates in most cases. The Apollo 14 heat flow and convection experiments have firmly established the existence of surface tension convection in thin fluid layers under zero-gravity conditions (Ref. 36). It is therefore possible that surface tension-driven free convection is the most significant fluid mixing force in zero gravity.

There are very few established theoretical results regarding surface tension-driven convection. No analyses or experimental observations on the liquid-solid interface are known (Ref. 37). In the case of the liquid-liquid interface, the Marangoni effect is associated with the convection motion due to variations in interfacial tension and has been used to explain turbulent phenomena at the interface between two unequilibrated liquids. Surface tension-driven convection in thin fluid layers with a free surface is also referred to as the Marangoni effect. In this case, any temperature gradient along the surface will create a surface tension gradient at the interface. Liquid flow will then occur from hotter to colder regions since the surface tension decreases with increasing temperature. It has also been observed that a uniform vertical temperature gradient will cause convective motion in a hexagonal cellular pattern, called Benard Cells. The situation is more complicated if the liquid is evaporating, and the convection is then less regular. It is apparent that surface tension-driven convection can be observed on earth only in films up to a few millimeters thick since gravity-driven convection will tend to mask surface tension convection. In a zero-gravity environment, however, surface tension-driven convection may occur on the surface of a large volume of liquid.

The theoretical foundations of surface tension-driven convection are not well established, although several significant theoretical papers have appeared (Ref. 38 - 41). Analogous to the case of gravity-driven convection, the Marangoni number is defined to describe surface tension-driven convection (Ref. 35):

$$B = \sigma \frac{dT}{dy} d^2/\rho\nu\chi$$

where σ is the temperature coefficient of surface tension, d is the thickness of the liquid layer, $\frac{dT}{dy}$ is the temperature gradient in the thickness dimension, ρ is the density of the liquid, ν is the kinematic viscosity, and χ is the thermometric conductivity. Physically, the dimensionless number B expresses the relative importance of surface tension and viscosity forces. It has been concluded that a critical value of the Marangoni number is required for the onset of convective flow. Since the Marangoni number depends upon the square of the liquid depth, surface tension-driven convection will be significant in zero-gravity melt growth.

In addition to convection, surface tension forces are also responsible for capillary action. The dimensionless Bond number is used as a comparison between gravitational and capillary forces (Ref. 42):

$$Bo = g\ \rho\ r^2/\sigma$$

where g is the gravitational acceleration, ρ is the density, r is the radius of capillary, and σ is the surface tension. For Bo >> 1, the gravitational force dominates, and for Bo << 1, capillary force dominates. In the latter case, which could be easily achieved for any material in zero-gravity, a long column of liquid would rise in a capillary. The capillary constant has been defined as $a = (2\sigma/\rho g)^{\frac{1}{2}}$.

III.1.3. Other Convection Mechanisms

In addition to gravity and surface tension, other natural convection mechanisms may exist; however, no analytical studies have been carried out. For example, convection may occur near the interface of a solidifying crystal due to the volume change accompanying solidification. Convection has also been observed in layers when a liquid contains a non-linear vertical profile of impurities (Ref. 43). This phenomenon can probably be ignored in melt-growth; however, it may be significant in the solution growth process. Also, evidence for a low-g surface tension-driven convection near edges due to radial temperature gradients was inferred from the Appollo 14 experiments.

III.2. Crystal Growth in Zero Gravity

On the basis of previous discussions, the effect of zero gravity on crystal growth processes are summarized in Table I. For most applications, the reduced strain brought about by zero gravity appears to have negligible effect. If extra large crystals were to be grown from very small seeds it could be an advantage, but crystal inertia, coupled with a jerky pull or rotation system could still induce damage or complete fracture of the seed. Zero gravity, however, should allow undistorted whiskers (Ref. 44) to be grown up to the maximum length dictated by either container, diffusion length, or initial size of liquid cap (assuming the vapor-liquid-solid growth mechanism), depending on which one is the limiting factor. Growth of rather large equilibrium shaped crystals in fluxes or other solutions could be advantageous, although an immediate use for such crystals is not obvious.

Table I. Effects of Zero Gravity on Crystal Growth Processes

Effect	Impact on Crystal Growth
Reduced weight of crystal	Eliminate any high temperature deformation caused by excessive crystal weight.
Reduce likelihood of unattached crystals "falling" to "bottom" of container	Allow more nearly equilibrium shaped crystals to be grown from solutions or fluxes since crystals would not pile up on bottom.
Virtually eliminate convection currents	Probably very little on Czochralski and float zone techniques since most practical growth systems require forced convection to homogenize the composition of the melt. For those materials normally grown in horizontal boats, no extra stirring is usec however, it is not clear whether elimination of natural convection is desirable. For those cases where forced convection is not necessary, impurity striations caused by natural convection induced temperature fluctuations would be eliminated.
Allow molten portion to assume shape dictated by surface tension	Allow larger molten zones in the float zone process. Allow spherical shaped crystals to be grown. (Actually different surface energies for various crystal faces will probably preclude the latter).

The elimination of natural convection currents has been suggested as the most important aspect of crystal growth in space, and one which would allow crystals of higher perfection to be grown. This usefullness does not appear founded. The thermal gradients to which the crystal is exposed and the mechanical constraints imposed on it while still hot enough to be in the plastic flow region in general determine the crystallographic perfection, and it is not clear that the elimination of convection will in any way make these gradients less severe.

The Czochralski pulling technique with the melt contained in a crucible is the most important technique for the production of large seimiconductor crystals at present. The role of natural and forced convections in this technique has been analyzed both theoretically and experimentally (cf. II.1.3. and III.1.1.), and the importance of forced convection is well recognized. One purpose of the forced convection is to overcome the random thermal fluctuations due to natural convection. More importantly, the forced convection is necessary to minimize the impurity inhomogeneity in the melt due to segregation. Also, the forced convection is used to tailor the temperature gradients inthe melt. It is thus evident that forced convection will be needed in a zero-gravity environment. The absence of free convection will only mean that the forced convection can be of smaller magnitude.

The floating zone and crucibleless techniques (cf II.1.4.) are currently used for the production of ultrahigh purity silicon crystals. The molten zone is supported by the surface tension of molten silicon and the levitating electromagnetic field provided by a properly shaped rf coil. The volume of the melt is limited by the gravitational force which tends to make the zone collapse. Thus, the crucibleless techniques will most directly demonstrate the unique effects of the greatly reduced gravity in the space environment. However, forced convection is still necessary to minimize impurity inhomogeneities in the grown crystal. For example, the source rod and the crystal may be rotated asymmetrically in opposite directions as shown in Fig. 20.

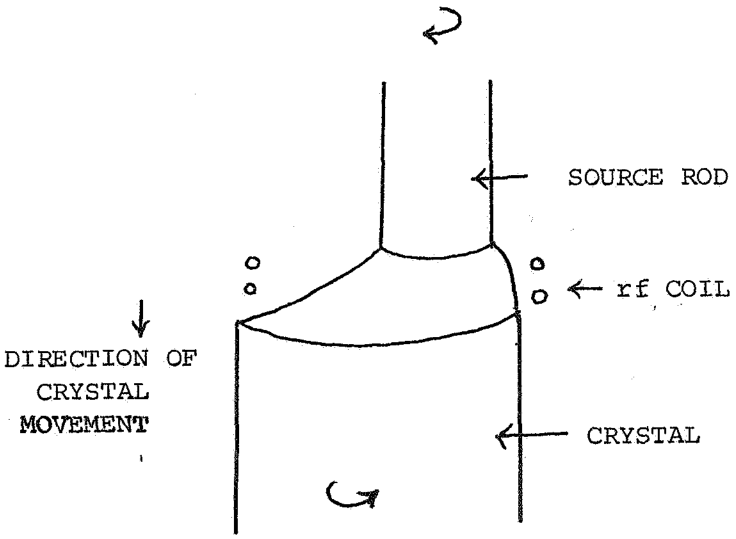


Fig. 20. An asymmetric technique for crucibleless crystal growth.

This arrangement is known to provide a planar solid-liquid interface and uniform distribution of dopants in the grown crystal. The rotation of the crystal will of course generate an acceleration which will tend to make the molten zone unstable. However, the acceleration generated is small at rotation rates required for homogenizing the melt, about 0.01 g when a crystal of 5 cm diameter is rotated at a rate of 20 rpm. The molten zone can be at least six times longer than that obtainable on earth since the maximum stable zone length is inversely proportional to the square root of gravitational acceleration.

It should be mentioned that floating liquid zones in simulated zero gravity have been studied by the suspension of one liquid in another of equal density (Ref. 45, 46). The stability of the floating zone was studied as a function of wetting conditions, zone shape, and rotation. Float zones have also been simulated with soap films which are essentially weightless (Ref. 47).

In the solution and vapor growth techniques, the transport of solute or reactants to the substrate surface by diffusion and convection is usually the rate-determining step of the growth process. Thus, the use of these techniques in space offers no direct technical advantages. However, investigations of chemical vapor epitaxial growth in space will provide an insight into the role of convective transfer in this most important process of modern electronics, and the manufacturing technology can be better optimized.

The Skylab manned orbital laboratory to be launched in April 1973 will carry apparatus for a variety of solidification and crystal growth experiments sponsored by NASA's Materials Science and Manufacturing in Space Program (Ref. 48). The experiments related to crystal growth include gallium arsenide crystal growth, vapor growth of II-VI compounds, radioactive tracer diffusion, microsegregation in germanium, growth of spherical crystals, indium antimonide crystals, and mixed III-V crystal growth.

IV. Recommendations

There are no obvious revolutionary changes (either scientific or economic) in crystal growth procedures or results which would be brought about by growing in space. However, several process refinements might prove useful under some circumstances, and a number of experiments related to crystal growth would be very desirable to perform. The high vacuum associated with space, although convenient in some respects, is not considered to be a great consequence since relatively good vacuums are available on earth at modest cost. Therefore all recommendations revolve around the low gravity environment. The possibility also exists that a requirement for some new materials may arise which would make space growth very attractive. In order to be justifiably grown in space such materials should probably fulfill one or more of the requirements of Table II.

Table II. Criteria for Crystal Growth Experiments in Space

Materials deform easily and yet must be grown unsupported

Materials should be float zone refined but have very low surface tensions and cannot be electromagnetically stabilized so that only small diameters can be grown under normal conditions.

Deliberate growth of a single crystal matrix around randomly dispersed inclusions of different density.

Any growth process which requires complete convection current suppression for successful operation. (Diffusion control for example could be most easily accomplished in this manner.)

The following discussion describes several of those experiments, excluding those already planned for earlier missions, which appear worthwhile. While it might appear unimaginative, the suggestion of some carefully documented straight-forward crystal growth operations is based on the observation that the actual performance of an experiment under radically different conditions (as this would be) often produces a variety of unexpected results.

1. Floating-Zone Crucibleless Crystal Growth Using Solar Energy. As discussed in Section II.2., the low gravity environment is particularly suited for the crystal growth of refractory electronic materials by the floating zone crucibleless technique. The easy access of a good vacuum, about 10^{-6} Torr, with an infinite pumping speed is also an advantage. However, the large power requirements for the growth of refractory crystals may be a serious limitation. Electrical energy aboard a spacecraft is usually derived from solar cell arrays which have conversion efficiencies on the order of 10%, and the use of direct sunlight is more attractive. The solar energy required to maintain a molten silicon zone can be readily estimated from the radiation and conduction losses. Assuming that the emissivity of molten silicon is 0.8 and that the conduction loss is of the same order of the radiation loss, an incident power of 70 W cm^{-2} is needed to maintain the molten zone. Since the solar power density is 1 kW m^{-2}, a reasonable sized optical system is sufficient to provide the energy required for the pulling of silicon crystals of a few centimeters diameter. The temperature gradient in the melt can be controlled by rotating the crystal and the polycrystalline rod in opposite directions.

2. Determination of Diffusion Coefficients of Common Dopants in Silicon. The state of the art silicon crystals of large diameter invariably exhibit microsegregation of dopants, and a basic understanding of the dopant behavior in the melt, such as the diffusion coefficients, will be extremely useful for the optimization of the growth process. The determination of the diffusion coefficients of common dopants, such as boron, phosphorus, arsenic, carbon, aluminum, and gallium, in liquid silicon can be best determined in the space environment where the convective flow is negligible.

3. Study of Vapor Growth in a Horizontal Reactor. The role of convection in the conventional chemical vapor epitaxial growth process can be determined by carring out the growth process in space. For example, the growth rate of silicon or other electronic materials can be measured as a function of composition and flow rates of the reactant mixture, and these results are expected to be extremely valuable in the optimization of the epitaxial growth process on earth.

4. Conventional Melt-Growth Experiment. To better understand the conventional crystal pulling from melt contained in a crucible, a crystal pulling experiment should be carried out in which all phases of growth are carefully documented with recorded data and movies. The extent of convection may be studied by using Wilcox's approach (Ref. 31, 32).

It is also felt that prior to the execution of the above experiments in the Space Shuttle, preliminary experiments should be carried out on earth to test the concept of crucibleless crystal growth with solar energy and to develop the apparatus for all experiments. Specifically, a lower melting semiconductor, such as indium antimonide, should be used to investigate the various parameters of the crucibleless crystal growth process. The determination of the diffusion coefficients of common dopants in liquid silicon may be carried out by using an isothermal environment.

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