Arnold Schwarzenegger
Governor

SINGLE CRYSTAL SILICON SHEET GROWTH

INDEPENDENT ASSESSMENT AND FINAL EISG REPORT

Prepared For:
California Energy Commission
Energy Innovations Small Grant Program

Prepared By:
Energy Materials Research

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ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

INDEPENDENT ASSESSMENT REPORT (IAR)

SINGLE CRYSTAL SILICON SHEET GROWTH

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LEGAL NOTICE

PREFACE

The Public Interest Energy Research (PIER) Program supports public interest energy research and development that will help improve the quality of life in California by bringing environmentally safe, affordable and reliable energy services and products to the marketplace. The PIER Program, managed by the California Energy Commission (Commission), annually awards up to $62 million of which 5% is allocated to the Energy Innovation Small Grant (EISG) Program. The EISG Program is administered by the San Diego State University Foundation through the California State University, which is under contract to the Commission.

The EISG Program conducts up to four solicitations a year and awards grants for promising proof-of-concept energy research.

PIER funding efforts are focused on the following seven RD&D program areas:

- Residential and Commercial Building End-Use Energy Efficiency
- Energy Innovations Small Grant Program
- Energy-Related Environmental Research
- Energy Systems Integration
- Environmentally-Preferred Advanced Generation
- Industrial/Agricultural/Water End-Use Energy Efficiency
- Renewable Energy Technologies

The EISG Program Administrator is required by contract to generate and deliver to the Commission an Independent Assessment Report (IAR) on all completed grant projects. The purpose of the IAR is to provide a concise summary and independent assessment of the grant project in order to provide the Commission and the general public with information that would assist in making follow-on funding decisions. The IAR is organized into the following sections:

- Introduction
- Objectives
- Outcomes (relative to objectives)
- Conclusions
- Recommendations
- Benefits to California
- Overall Technology Assessment
- Appendices
    - Appendix A: Final Report (under separate cover)
    - Appendix B: Awardee Rebuttal to Independent Assessment (awardee option)

For more information on the EISG Program or to download a copy of the IAR, please visit the EISG program page on the Commission's Web site at:
http://www.energy.ca.gov/research/innovations

or contact the EISG Program Administrator at (619) 594-1049, or email at:
eisgp@energy.state.ca.us.

For more information on the overall PIER Program, please visit the Commission's Web site at http://www.energy.ca.gov/research/index.html.

Single Crystal Silicon Sheet Growth

EISG Grant # 00-02

Awardee: Energy Materials Research
Principal Investigator: Carl E. Bleil
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Grant Funding: $75,000
Grant Term: September 2000 – August 2002

Introduction

Public and private parties are rapidly accepting solar voltaic technology to produce grid-connected electricity. Adopters of this technology see the advantages of clean on-site power and net metering[1]. Capital cost, sometimes known as first cost, for solar technology remains high. This is a deterrent to wider use.

To reduce capital cost, the research community could develop solar cells with increased efficiency, reduced process costs, or reduced the cells' material costs. This project focused on the production of low cost, high quality silicon sheets.

The researcher constructed a device (See Figure 1) to produce single-crystal sheets of semiconductor-quality silicon directly from a polycrystalline source. If successful, this technology could produce high-quality silicon sheets at a competitive price. The researcher expected a two-fold reduction in the energy consumed per square meter of electronic-grade silicon sheet and a consequent halving of the production cost. These improvements could reduce the cost of silicon solar cells up to 50%, and increase the use of solar energy.

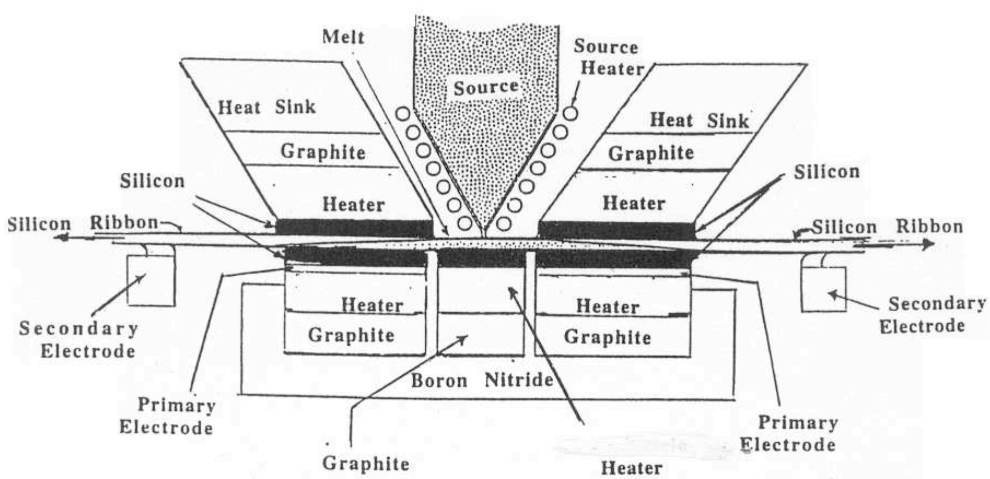

Figure 1. A Schematic of the Commercial Prototype processor appears above. This drawing illustrates the complexity of the proposed system. Even so, it is somewhat misleading, as it does not show the suite of sensors, the pulling system, or the control logic. The last is embedded in a microprocessor.

[1] Net Metering – A billing method for grid-connected consumers producing electricity enabling them to pay only for the electricity used in excess of that which they generate. It does not require the utility to pay for excess electricity.

Objectives

The goal of this project was to determine the feasibility of producing single-crystal sheets of semiconductor-quality silicon directly from a polycrystalline source. The researcher established the following project objectives:

1. Assemble a controlled-atmosphere process chamber for crystal growth. Design the chamber to allow regulation of both the temperature field and its gradients.
2. Develop process-control algorithms for the following: pulling speed of the crystalline sheet; regulating the mass rate of the silicon source to match that of the growing sheet; maintaining the position of the nucleating tip and the melt level; and maintaining the position of the final element of the solid-liquid interface.
3. Implement computer monitoring and control of the process.
4. Produce prototype silicon sheets for testing. Energy consumed per square meter of material should be one half that of today's best practices.
5. Verify that the properties of silicon sheets meet those required for commercial solar cells. Cost per square meter of electronic grade silicon material should be one half of today's competitive price.
6. Identify failure modes of the process.

Outcomes

1. The researcher assembled a stainless-steel vacuum chamber. Initially, it functioned properly in all pressure and temperature ranges of the process. Subsequently, three of five expensive commercial electric heaters failed. Low-cost replacement heaters were devised, built, and incorporated into the system within project budget.
2. The researcher developed several sensors and successfully integrated most of them into the control system. Some manual adjustments were necessary.
3. The researcher devised a combination of hardware, software, and manual methods to control the process.
4. Heater failures delayed significantly the initiation of silicon production. The researcher made extensive modifications to accommodate the replacement heaters. Because of the changes in the process chamber, the researcher was not able to produce silicon sheets or measure energy consumption per square meter.
5. As a result of outcome 4, the researcher was not able to verify the properties or cost of silicon sheets.
6. When multiple heater failures occurred, the researcher added an objective to identify failure modes of the process. He also began an investigation of all components.

Conclusions

The researcher did not prove the feasibility of producing single-crystal sheets of semiconductor-quality silicon directly from a polycrystalline source. He achieved three of six project objectives. The failure of the original heaters nearly ended the project in the 16th month. A heater redesign, coupled with a successful construction technique, made replacement heaters possible. However, to fit the larger new heaters within the chamber, the researcher made many modifications to other components. These modifications consumed project time. At the conclusion of this project the researcher believed all of his equipment was functioning and available to produce single-crystal silicon sheets.

Recommendations

The PA recommends that the researcher complete the objectives proposed for this project. Once those objectives have been completed the researcher should perform detailed analysis of the resulting data. Based on those analyses, a funding agency could evaluate the probability of commercial success and decide whether to grant further development funding. For subsequent work the PA recommends that the researcher establish absolute energy use and sheet costs targets based on best available technology.

Benefits to California

Public benefits derived from PIER research and development are assessed within the following context:

- Reduced environmental impacts of the California electricity supply or transmission or distribution system
- Increased public safety of the California electricity system
- Increased reliability of the California electricity system
- Increased affordability of electricity in California

The primary benefit to the ratepayer from this research is reduced environmental impacts of the California electricity system. A significant reduction in the cost of photovoltaic cells could promote increased production of solar energy. Reduced need for power production from fossil fuels could have a stabilizing effect on electricity prices while benefiting the environment.

Overall Technology Transition Assessment

As the basis for this assessment, the Program Administrator reviewed the researcher's overall development effort, which includes all activities related to a coordinated development effort, not just the work performed with EISG grant funds.

Marketing/Connection to the Market

The U.S. Department of Energy has completed two independent marketing surveys on related technology. The results of these surveys suggest that commercialization of this technology, when successfully proven, will occur in the solar energy industry first. The researcher should develop a marketing plan to take his technology to the equipment manufacturers who supply the makers of solar cells. Independent investors, aware of this work, have expressed interest in the successful outcome of this development

Engineering/Technical

Due to equipment failures, the researcher did not demonstrate feasibility during the period of this project. The researcher did make good progress in developing the equipment and controls necessary for the production of single-crystal silicon sheet. Once he uses this equipment to produce the sheets, he needs to demonstrate energy and cost savings. The next stage will be construction and testing of prototype machinery.

Legal/Contractual

The principal investigator holds six patents for this technology. He plans to form a corporation, when the product development stage is reached. There are no legal barriers to the next stage.

Environmental, Safety, Risk Assessments/ Quality Plans

Quality Plans include Reliability Analysis, Failure Mode Analysis, Manufacturability, Cost and Maintainability Analyses, Hazard Analysis, Coordinated Test Plan, and Product Safety and Environmental**.** The researcher has evaluated many forms of risk. He has performed analyses of possible fundamental failure of the technology and concluded that risks are very low. The market risk for the technology is constantly changing as competing technology developments are developed. Other quality plans must be developed in future activities.

Production Readiness/Commercialization

Production readiness remains in the research stage. There are several process and production problems, mostly in the handling of material. The researcher has potential solutions, but he must prove them effective. The PA suggests collaboration with consultants or companies experienced in the design and manufacture of semiconductor equipment.

Appendix A: Final Report (under separate cover)

Appendix B: Awardee Rebuttal to Independent Assessment (none submitted)

Appendix A to IAR 00-02
CEC-500-2006-005

ENERGY INNOVATIONS SMALL GRANT (EISG) PROGRAM

EISG FINAL REPORT

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Legal Notice

Acknowledgements

It is a great pleasure to acknowledge the very helpful assistance from several colleagues at Oakland University. During the pursuit of this project, Dr Rau and Professor Srinivasan from the Physics Department and Professor Rusek of the Engineering Department were particularly helpful. I would also like to thank Oakland University for making many facilities and services available. Finally, I would like to thank the Commission for the funding of this project, administered through the San Diego State University Foundation.

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Abstract

One serious concern in the United States is our expanding dependence on the world supply of fossil fuels. One approach to allay these concerns is to develop renewable sources of energy such as solar energy. Cost is the primary deterrent to the commercial use of solar energy. Increased collector efficiency and reduced energy and material costs provide a solution. An innovative technology development for the production of single crystal sheets of semiconductor quality silicon directly from a polycrystalline source is the objective of this proposal. To realize this goal, a very uniform temperature field was produced within the new growth area and thermal gradient control was provided. A direct coupling between the crystal growth rate and the pulling rate was introduced. Sensors were developed to provide melt level stabilization and replenishment control. Computer monitoring and control provided a stable response. Failure of the special heaters delayed the final performance of the project. Specific performance goals of this project were a two-fold reduction in the energy consumed, and halving the cost/sq. meter of electronic grade silicon sheet. When proven successful at a practical production rate, this technology will demonstrate the highest production rate and provide the competitive advantage of the lowest cost, high quality silicon of any process currently known.

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Executive Summary

Introduction:

A serious concern in the United States is our expanding dependence on the world supply of fossil fuels. The only approach to allay these concerns is to develop renewable sources of energy. Renewable solar energy is one promising source. Hence, research on solar energy is an important part of the PIER Subject Area: Renewable Energy Technologies. Cost is the primary deterrent to the commercial use of solar energy. The initial capital costs for solar modules and the solar system infrastructures are the major expenses. The need is to increase the collector efficiency and reduce the energy and material costs for solar applications. This may be realized through innovative technology development.

The commercial production of low cost, high quality silicon sheet is one solution to this problem. The specific impetus for this proposal was a new technological approach for the production of single crystal sheets of semiconductor quality silicon directly from a polycrystalline source. The research and development leading to a controlled and fully automated process is the critical path to commercialization. When proven successful at a practical production rate, this technology will demonstrate the highest production rate and provide the competitive advantage of the lowest cost, high quality silicon of any process currently known. Specific performance goals of this project are a two-fold reduction in the energy consumed, and halving the cost/sq. meter of electronic grade silicon sheet. These improvements alone can reduce the cost of silicon solar modules by more than 50%. Both results will have a positive impact on the economic growth of California and the US. The return on investment in California will be potentially realized through the reduction of the cost of electrical power, the stabilizing effect on the power industry and the possible availability of hydrogen for mobile fuels not derived from fossil fuel sources.

Objectives:

The goal of this project was to determine the feasibility of new technology for practical production of semiconductor quality silicon sheet. The following project objectives were established:

1. Assemble a Working Process Chamber: A clean working environmental chamber will be developed to achieve the desired crystal growth. In this chamber a very uniform thermal field will be produced with control of both the field and the gradients. Additionally, the atmosphere surrounding the active process will be controlled to reduce evaporation of the molten silicon and avoid the inclusion of unwanted impurities.

2. Develop the Process Controls: The previous attempts to accomplish the overall goal of this project did not succeed because the necessary process controls were unavailable. The following will be accomplished:

- a) The pulling speed of the crystalline sheet will be uniformly controlled.
- b) The mass rate of flow from the silicon source will be controlled to equal to that of the growing sheet.
- c) The position of the nucleating tip and the melt level will be kept within a narrow range to assure continuous processing.

d) The position of the final element of the solid-liquid interface (exit meniscus will not be allowed to attach to the primary electrode.

e) These control elements will be synchronized to realize the desired growth process.

3. Implement the Computer Monitoring and Control of the Process: A computer interface, incorporating Lab View software will be developed to handle the multiplicity of sensors and the control precision required for this process.

4. Initiate Silicon Sheet Production: The production of single crystal silicon sheet will begin. Polycrystalline silicon sheet has been produced by horizontal ribbon growth (HRG), a related process. However, only when single crystal silicon sheet growth is achieved will the new process be verified. Then, subsequent production will be used as a tool for parametrically determining the quality of the sheet silicon that may be produced with this technology.

5. Verify Silicon Sheet Properties: The physical and electronic properties of the as grown silicon will be determined independently through the services of government and private testing laboratories. The National Renewable Energy Laboratory (NREL) has agreed to perform these tests. Some tests can be made in-house. The following list represents the properties to be evaluated and their target values to determine technological success of the process.

	Test	Target Quality
a)	Structure:	Dislocation free single crystal
b)	Impurity levels	Unaltered from the source
c)	Surface:	Unpolished commercial grade--+/- 3 microns
d)	Flatness	Commercial Specification +1- 4 microns
e)	Solar Cell Efficiency:	> 18%

6. Establish the failure modes of the Processor: Important failure modes of the process will be identified. Any process that is to become a commercial enterprise should be reviewed with regard to the potential failure modes of the critical components and process function. Failure modes of critical components may alter the forecast of production costs. A prevailing failure of process function could terminate the project. Potential failure modes of the following components and functions will be reviewed: Environmental chamber, sensors, heaters, source feed, the crystal pulling system, stable the thermal field or gradients, impurity control and dislocation free single crystal growth.

Outcomes: Not all of the objectives listed above have been reached. The following presents the status in each area.

Process Chamber: A stainless steel vacuum chamber has been assembled and functions properly in all process pressure and temperature ranges. Three of five expensive commercial Boroelectric heaters previously purchased from Advanced Ceramics failed. Low cost replacement heaters were devised, built and incorporated in the system within budget. The two heat sinks, which were each designed and built to remove 900 watts uniformly through a temperature difference of 13 80K, performed successfully.

Process Controls: A sensor was developed to locate the position of the nucleating tip of the growing silicon sheet. The element (graphite), selected to make contact with the solid silicon, does not bond with the silicon.

The signal from the nucleating tip sensor activates the pulling mechanism uniformly except at startup. The position of the nucleating tip depends only on the rate of tip growth (i.e. the rate of removal of the heat of fusion). A special braking system was introduced to correct for the pulling motor step function behavior at startup. It was originally intended to also use the signal activating the pulling mechanism to control the drive moving the source material toward the melt zone. The irregular response of the motor drive at startup and the risk of ramming the system below the melt made this approach impractical. Periodic manual adjustment was used instead.

A sensor based on a capacitor response was designed and constructed to monitor and control the level of the melt. To avoid the possible RF interference, a simple capacitor comparison system was employed. The output of the device was used to remotely control the power level of the replenishment power source.

A system related to the positioning of the nucleating tip was used to monitor the position of the exit meniscus. Control here is less stringent.

Initiation of Silicon Sheet Production: Heater failures seriously delayed the initiation of silicon production. Extensive modifications have been made to accommodate the replacement heaters. Work will continue with the existing equipment to verify the success of the technology.

Conclusions: Three of the five project objectives have been achieved under simulated conditions. The unfortunate failure of the original heaters potentially ended the project in the 16 month. However, a workable heater design coupled with a unique and successful construction technique made replacement heaters possible. The cost to produce the new heaters was only 20% of the cost to purchase replacement heaters from Advanced Ceramics and fell within the budget. However, in order to fit the larger size of the new heaters within the chamber, many modifications of other components were required. This consumed much time but has reactivated the project. All of the sensors are now available so that the critical test to produce new crystalline silicon sheet may continue.

Recommendations: Continue development with existing equipment to support next phase. Seek sufficient funding to implement commercial quality equipment.

Public Benefits: Success in achieving project objectives will:

Permit lower energy and material costs for solar collectors,
Increase the solar energy market,
Educe an important source for mobile electric power (hydrogen).
Reduce the dependence on fossil fuels,

Main Report

Introduction:

A serious concern in the United States is our expanding dependence on the world supply of fossil fuels. The only approach to allay these concerns is to develop renewable sources of energy. However, the implementation of alternative energy sources to prolong or replace the use of fossil fuels remains a significant national problem. This problem is very broad in scope, involving both fixed and mobile energy demands. Hence, research on this topic is an important part of the PIER Subject Area: Renewable Energy Technologies.

Renewable solar energy is one promising energy resource. Commercial photovoltaic solar generation of electrical power presents an enormous opportunity to reduce the use of fossil fuels. Cost is the primary deterrent to the commercial use of solar energy. The initial capital costs for solar modules and the solar system infrastructures are the major capital expenses. The most important constraint in the development of solar power generation is the lack of low cost, high quality materials for high efficiency solar collectors. This constraint may be removed through innovative technology development. The commercial production of continuous, single crystal silicon sheet is one means to increase the solar module efficiency while reducing material and energy costs.

Photovoltaic applications for single crystal silicon require thin sheet stock with good dimensional and impurity control. The current world market for wafers is over

Photovoltaic applications for single crystal silicon require thin sheet stock with good dimensional and impurity control. The current world market for wafers is over seven billion dollars/year (1). Traditional Czochralski (CZO) methods produce cylinders of single crystal silicon that must be sliced, lapped and polished to produce wafers for this market. This CZO process produces 40% to 70% loss of the as-grown crystal (2). While the modern CZO process does produce high quality, dislocation free silicon, the use of a crucible of foreign material and the processing to produce wafers, may introduce contaminants. These can significantly reduce the yield of the subsequent devices. Moreover, while the energy and lost crystal material of the CZO process is large, the processing cost for cutting, lapping and polishing to produce the wafers is also significant. A process, such as ours, which avoids this loss, can have a meaningful impact on the economics and competitiveness of the semiconductor industry.

The approach recommended here is the development of an innovative practical processor furthering the Horizontal Ribbon Growth (HRG) method. The HRG process relates to a novel processing technology to produce sheet materials from bulk solids. The process is applicable to a wide range of materials, including germanium and gallium arsenide, but the current development is restricted to silicon. Since its invention by Dr. Bleil in the 1960's (3), the HRG method has been recognized as a potential means of growing high quality silicon sheets at very high production rates (4). Attempts by others to achieve these goals did demonstrate polycrystalline sheet growth at 106 cm/min (5). However, control of the process necessary to produce continuous single crystal growth was not achieved (6). The patented approach presented here and validated in the laboratory addresses the critical control features of a modified HRG process necessary to realize the continuous growth of single crystal silicon sheets (7).

Concept Feasibility: The essence of the new approach, to resolve the difficulties cited above, is to address the entire system as one complex thermodynamic entity. This permits one to take advantage of the special properties of silicon listed in Appendix A. The process proposed is shown in Figure 1. In this system, a thin silicon sheet is withdrawn from a small melt zone, which is primarily constrained between crystal/melt interfaces. The new crystal sheet growth below the heat sink overrides the melt pool above the primary electrodes, forming sloping solid-melt interfaces, which constrain the melt pool. Note that the solid is less dense than the melt adding stability of the sloping interface. The primary electrodes provides novel inductive heating through capacitive coupling while direct current applied through the secondary electrodes provides a relatively independent means of supplying heat principally to the solid portion of the ribbon. These unique features of the system take advantage of the electrical conductivity changes through the solid-melt phase boundary. The heat sinks maintain a uniform vertical temperature gradient dictated by the desired growth rate of new crystal material. A source of polycrystalline material, placed over the central zone, is independently heated and provides for melt replenishment.

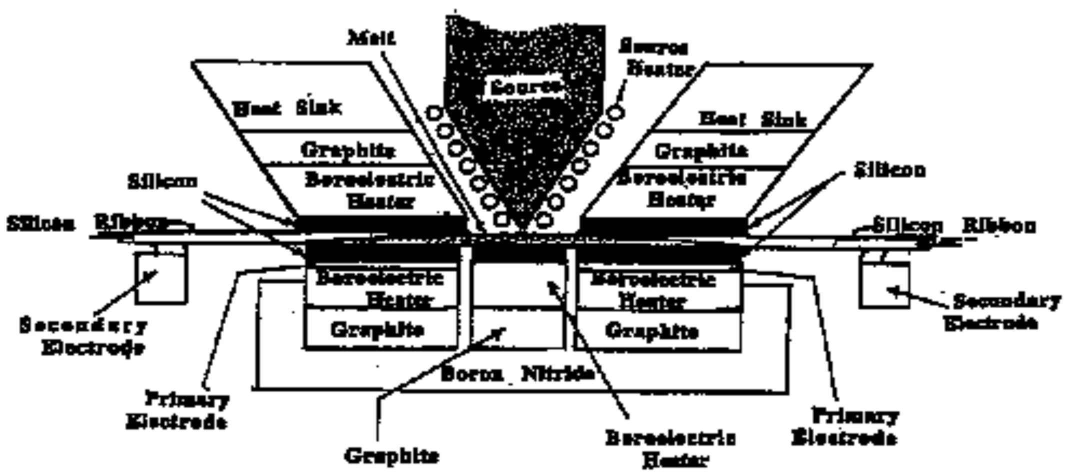

Figure 1 Schematic of the Proposed Processor

The process is initiated by bringing the temperature of the seed and its immediate environment to very near the melting temperature of silicon. When the system reaches equilibrium, the RF power is applied to the primary electrode ensemble, the secondary seed heater and the source heater. Melting occurs initially in the central zone and propagates outwardly to above and just beyond the primary electrode ensembles forming a sloping solid-melt interface above the primary electrodes. When the seed ribbon has just melted through in the region of constant current between the two electrodes, the conditions of stability of the solid-liquid interface are established.

The crystal growth must take place in a clean controlled atmosphere to avoid contamination of the silicon. The nucleation and growth of the silicon sheet requires a very uniform temperature environment. Specific thermal gradients are required to provide uniform growth and avoid dendritic nucleation. Control of the growth, the pull, and the replenishment rates must be carefully monitored and controlled. Under these conditions the production of single crystal silicon sheet will become an efficient commercial process.

Project Objectives:

The goal of this project was to determine the feasibility of the new technology for practical production of semiconductor quality silicon sheet. The following project objectives were established:

1. Assemble a Working Process Chamber: The first stage of this development is to provide a clean working environment to achieve the desired crystal growth. In this environment a very uniform thermal field is mandatory with control of both the field and the gradients. Additionally, the atmosphere surrounding the active process must be controlled providing a means to reduce evaporation of the molten silicon and avoid the inclusion of unwanted impurities. The appropriate chamber also requires multiple means to introduce power, provide cooling water and retrieve control signals governing the process. Finally, ports and the means to pull the sheet must be provided for the extraction of the as grown crystal sheet. The introduction of the polycrystalline replenishment source also requires a special port:

2. Develop the Process Controls; The previous attempts to accomplish the overall goal of this project did not succeed because the necessary process controls were unavailable. The following controls will be developed and when implemented these controls will be synchronized with a computer program to realize the desired growth process.
    a) A circuit to accomplish the controlled temperature environment,
    b) The system to establish the vertical thermal gradient and control the horizontal thermal gradient,
    c) A circuit to establish a uniform pulling speed, especially at startup,
    d) Sensors to position the nucleating tips,
    e) A means to establish the mass rate of flow from the source equal to that of the growing sheet and monitor and control the melt level and
    f) To position of the final point of the solid-liquid interface (exit meniscus).

3. Implement the Computer Monitoring and Control of the Process: The multiplicity of sensors and the control precision required for this process demands a computer interface, which can rapidly monitor and modify if necessary, the primary control parameters of the process. The software will display the growth conditions on the computer screen and provides the operator with a continuous monitoring of all critical parameters. Continuous monitoring and control of the temperature are required to assure a stable environment and maintain selected temperature gradients.

4. Initiate Silicon Sheet Production: Polycrystalline silicon sheet has been produced by horizontal ribbon growth (HRG), a related process. However, only when single crystal silicon sheet growth is achieved will the new process be verified. Then, subsequent production becomes the tool for parametrically determining the quality of the sheet silicon that may be produced with this technology. We will pull crystal silicon sheet at pull speeds (about 35 cm/min) commensurate with the growth rates characteristic of a high quality CZO processor.

5. Verify Silicon Sheet Properties: The physical and electronic properties of the as grown silicon will be determined independently through the services of government and private testing laboratories. The National Renewable Energy Laboratories have agreed to conduct these tests. Some tests will be made in-house. The following list represents the properties to be evaluated and their target values to determine technological success of the process.

Test	Target Quality
a) Structure:	Dislocation free single crystal
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c) Surface:	Unpolished commercial grade--+I- 3 microns
d) Flatness	Commercial Specification +1- 4 microns
e) Solar Cell Efficiency:	>18%

6. Establish the Failure Modes of the Processor: Important failure modes of the process will be identified. Any process that is to become a commercial enterprise should be reviewed with regard to the potential failure modes of the critical components and process function. Failure modes of critical components may alter the forecast of production costs. Prevailing failure of process function could terminate the project. Potential failure modes of the following components and functions will be reviewed: Environmental chamber, sensors, heaters, source feed, the crystal pulling system, thermal field or gradient stability, impurity control and dislocation free single crystal growth.

Project Approach:

The initial approach to this project included the analysis and evaluation of the previous experimental results. This analysis concluded that the major thrust in the new approach should be to resolve and implement the several control problems. Every opportunity to reduce cost was exercised during the development of this project. Several pieces of equipment previously developed for studies of silicon sheet growth were modified and incorporated in this work. This equipment, with a replaceable value exceeding $50,000, included: a diffusion pump vacuum system, two RF power supplies, a small stainless steel cylinder with pump plates, five commercial Boroelectric heaters and one dc, current regulated power supply with ten independent outputs. This equipment set the stage for the following approaches to be used to realize the project objectives within the time and monetary constraints.

1. Assemble a Working Process Chamber: A chamber constructed of stainless steel was designed with detailed modifications to permit the use of an existing chamber with known vacuum characteristics (refer to Figure 2). Compared to aluminum, the stainless steel chamber provides a cleaner working environment with less adsorption of oxygen and water on the inner walls. The ability of stainless steel to support higher wall temperatures aids in this regard. To control the atmosphere surrounding the active process, the system is first evacuated to below 3 x 10 exp-5 torr, then backfilled with argon and again pumped down to l00 torr. This pressure is appropriate to reduce evaporation of the molten silicon (see Appendix A for the vapor pressure of silicon versus temperature). Additionally, the level of oxygen in the argon gas (50 ppb) is reduced to the desired working level. Higher levels of oxygen can be incorporated as the desired product requires.

Power and electronic control feed lines are all electrically isolated from the chamber to minimize RF interference. The only water connections internal to the system are for the heat sinks. Water cooling is provided to the base and around critical areas outside the chamber. Two ports are provided for the withdrawal of the as grown crystal sheet. A special port is provided for replenishment. Additional cooling is provided to reduce the temperature of the crystal sheet before it passes through the pulling mechanism. Inside the chamber in the central region a very uniform thermal field is established over an area 150 mm long and 76 mm wide (see Figure 3). The lower heating assembly is supported on a 12.7 mm thick plate of hot pressed boron nitride. A layer of pyrolytic graphite four millimeters thick, 150mm long and 76mm wide is inlaid the top of the boron nitride. The graphite serves very well as a thermal leveler since the lateral (a and b directions) thermal conductivity is 200 times greater than the vertical (c direction) conductivity (8). Above the graphite, three heaters are placed to provide independent temperature control, using the circuit shown in Figure 4, for the seed and growing crystal sheet. Note that the boron nitride also shows favorable thermal conductivity anisotropy (8). Above the heaters is a silicon sheet that serves to support the solid and molten portion of the silicon seed' and subsequently the growing sheet. Above the seed a similar silicon sheet separates the upper heater, a two mm thick pyrolytic graphite layer for additional thermal leveling and heat sink from the growing crystal sheet.

The heat sinks are constructed of stainless steel (see Figure 3) and each supports a nucleating tip sensor. The structure of each heat sink is designed to permit the removal of as much as 900 watts from the growth area below it. The amount of heat removed from the growth area is controlled by the temperature of the heater below the heat sink. These heaters are controlled by the two potentiometers shown in Figure 4.

2. Develop the Process Controls: Since the implemented control elements must be synchronized to realize the desired growth process, the approach to control the process invokes as much directly-coupled feedback as possible. This approach minimizes the computer and transmission line speed required to maintain control. The approach to the continuous monitoring and control of the temperature is illustrated in figure 4. A controller for each of the five heaters is governed by the computer using signals from the temperature sensors to assure a stable environment.

The vertical thermal gradient is set by the two potentiometers (shown in Figure 4) which control the heating rate of the heaters below the heat sinks, hence the growth rate of

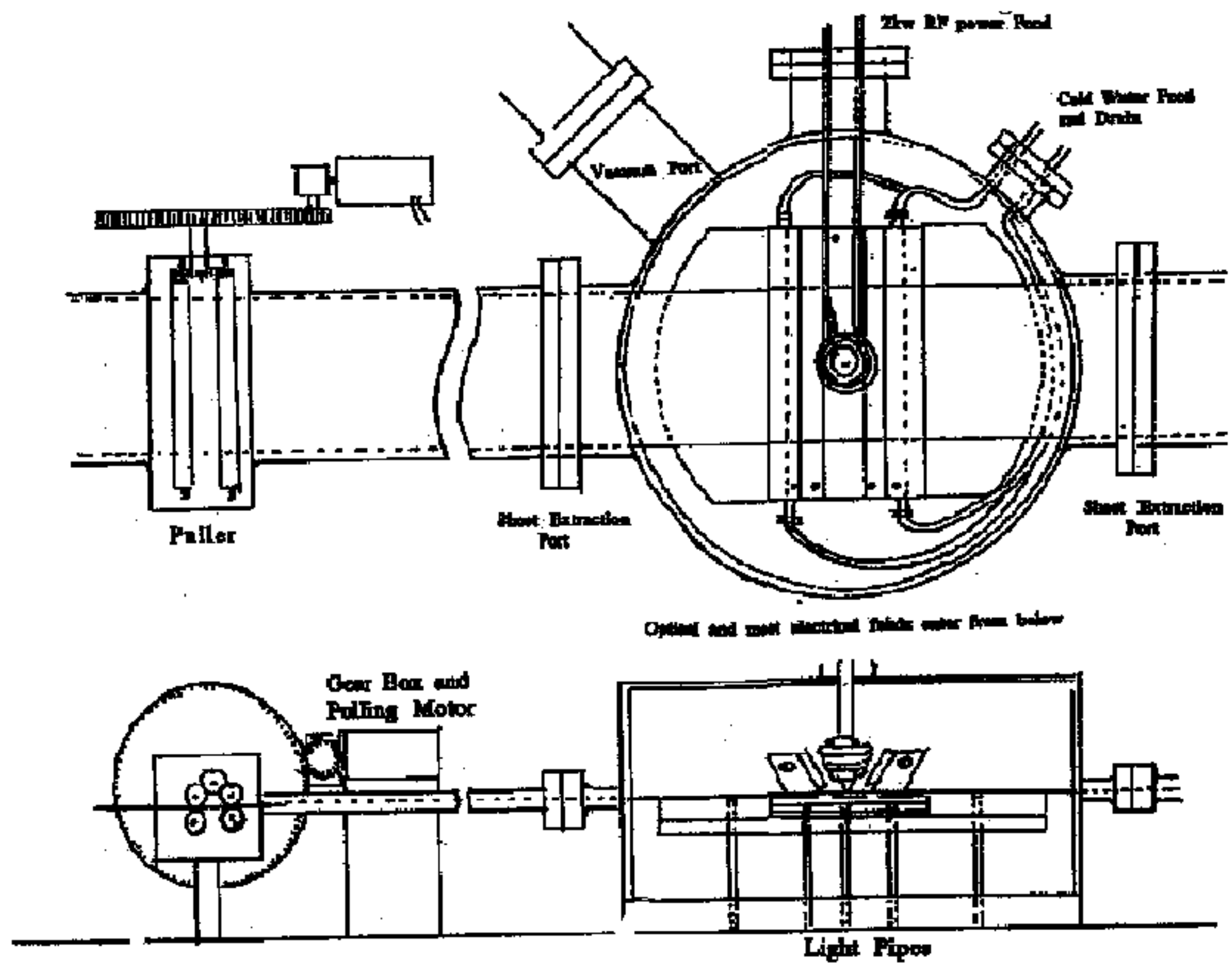


Figure 2. Drawing of the Processing Chamber

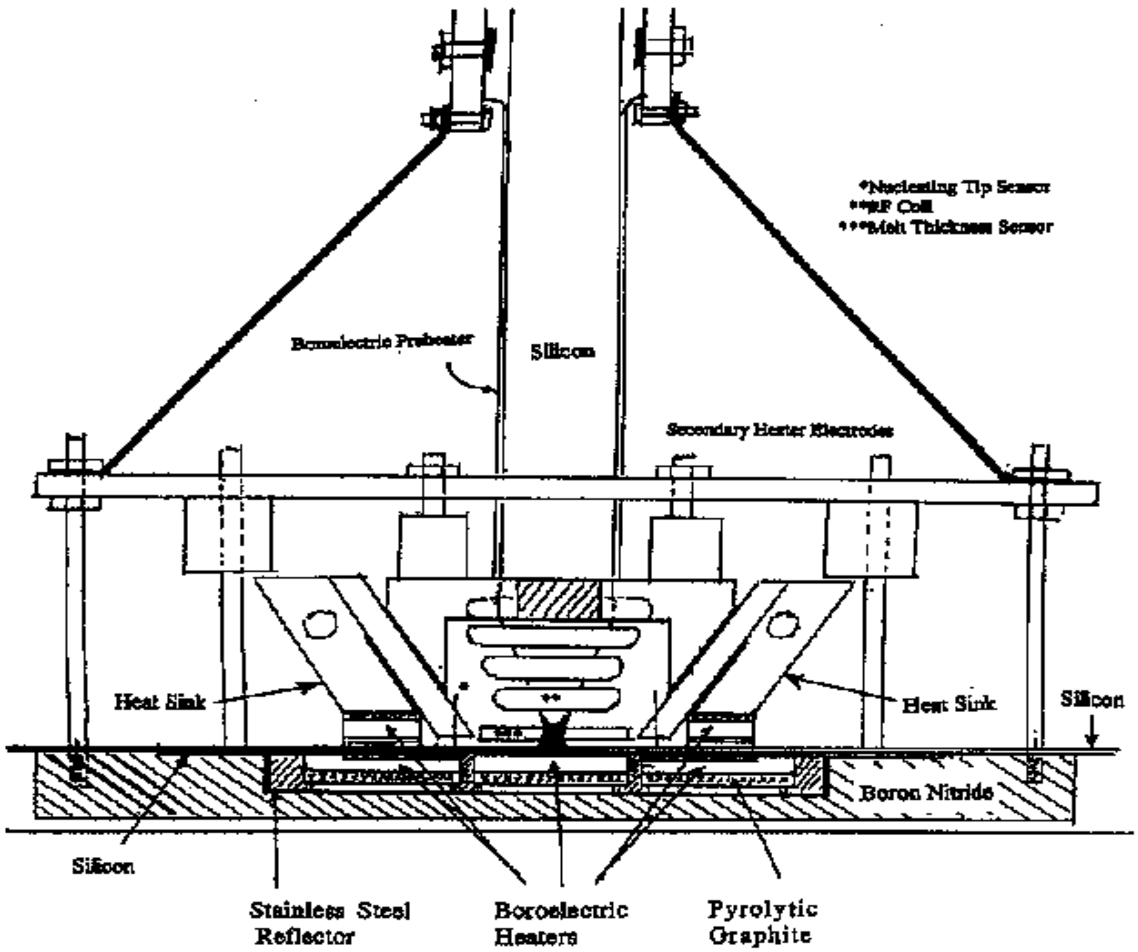


Figure 3. Lower Heater Assembly and Heat Sink Details

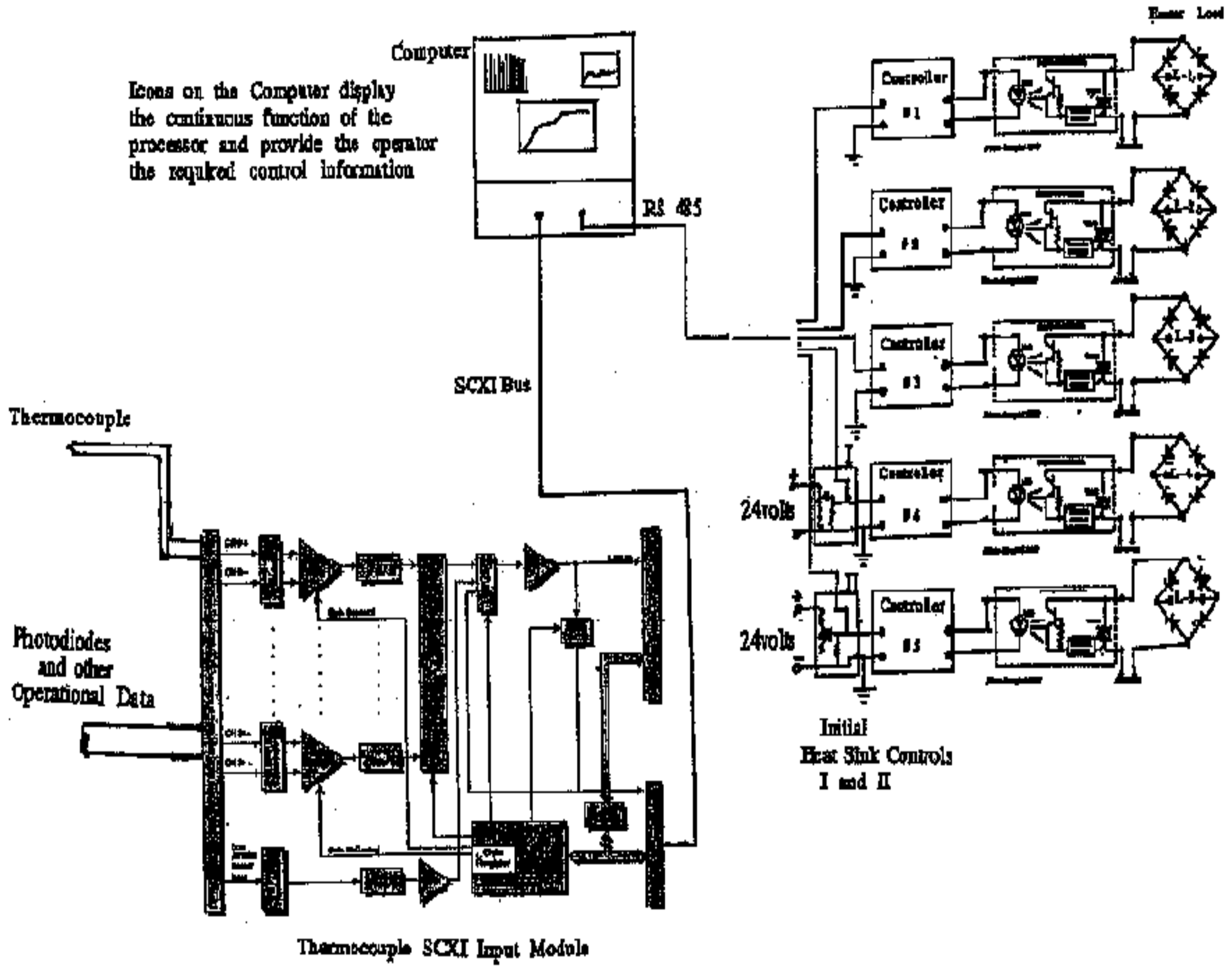


Figure 4. Control Circuit for Heaters

the crystalline sheet. The horizontal temperature gradients are controlled by the dc current provided by the secondary electrode ensemble. The power supply shown in Figure 5 controls the secondary current used to establish the horizontal thermal gradient.

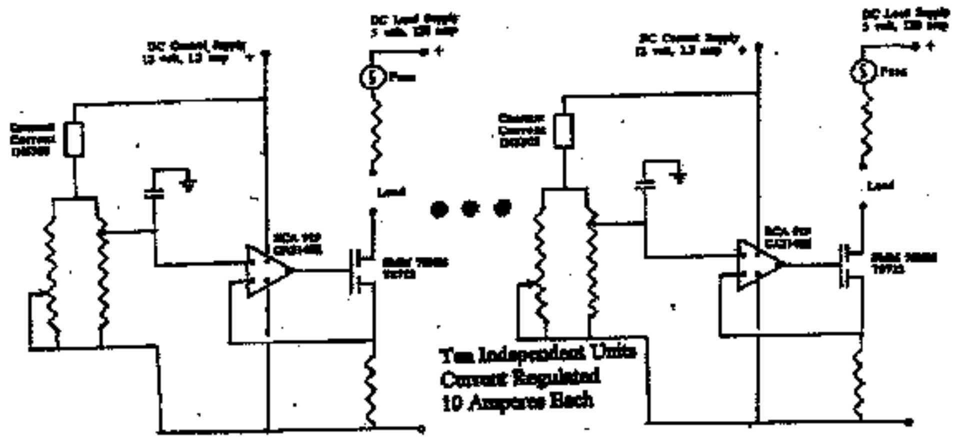


Figure 5 Power Supply for the Secondary Heater System

The pulling speed must be uniform, especially at startup. The pulling rate is determined by the rate of increase in the thickness of the growing sheet near the tip (see Figure 6). The tip thickness is measured by the sensors supported by the heat sink The control circuit is also shown in the Figure. To assure continuous processing, the position of the nucleation tip must be kept away from the heat sink area and toward the central portion of the melt zone.

The mass rate of flow from the source is kept equal to that of the growing sheet by monitoring the melt level (see figure 7), and directly modulating the 2kW RF power supply to keep the melt level within specified limits. The melt level control is especially critical at start up and shut down because of the differential thermal expansion and the volume change across the phase boundary.

The position of the final point of the solid-liquid interface (exit meniscus) is determined by observing the resistance between two points across the phase boundary. The position of the meniscus must not be allowed to attach to the primary electrode.

3. Implement the Computer Monitoring and Control of the Process: The control precision required for this process demands a computer interface, which can rapidly monitor and modify if necessary, the primary control parameters of the process. Computer monitoring and control was implemented using the Lab View system and a Gateway computer. To establish the desired thermal field, ten optical sensors and one pt/Pt 10%Rh thermocouple

were used. The optical sensors were water cooled germanium photodiodes isolated from the hot zone by quartz light pipes. The system temperature was controlled by the thermocouple until the RF power was turned on. At that time the control was switched to the germanium photodiodes. The control transfer could be set between ~ 1300K and 1680K.
All of the process control parameters are monitored, shown on the computer screen as.illustrated in Figure 8 and also stored.

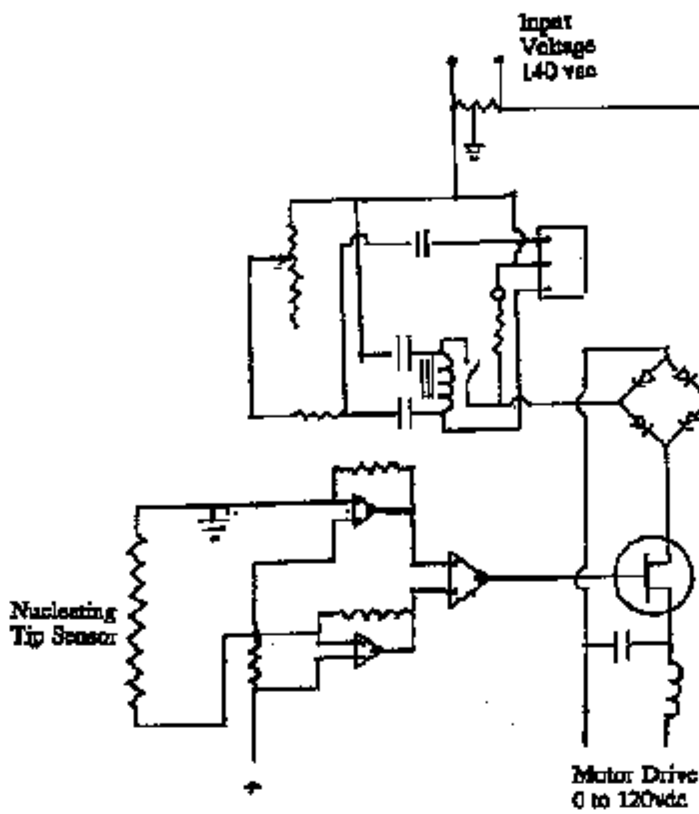


Figure 6 Nucleation Tip Sensor and Pulling Speed Control

4. Initiate Silicon Sheet-Production: Only when single crystal silicon sheet growth is achieved will the new process be verified. Having demonstrated the initial success of the process, we propose to pull crystal silicon sheet at pull speeds (about 35 cm/min) commensurate with the growth rates characteristic of a high quality CZO processor. Previous investigators of the HRG process have reported pulling, speeds for polycrystalline ribbons in

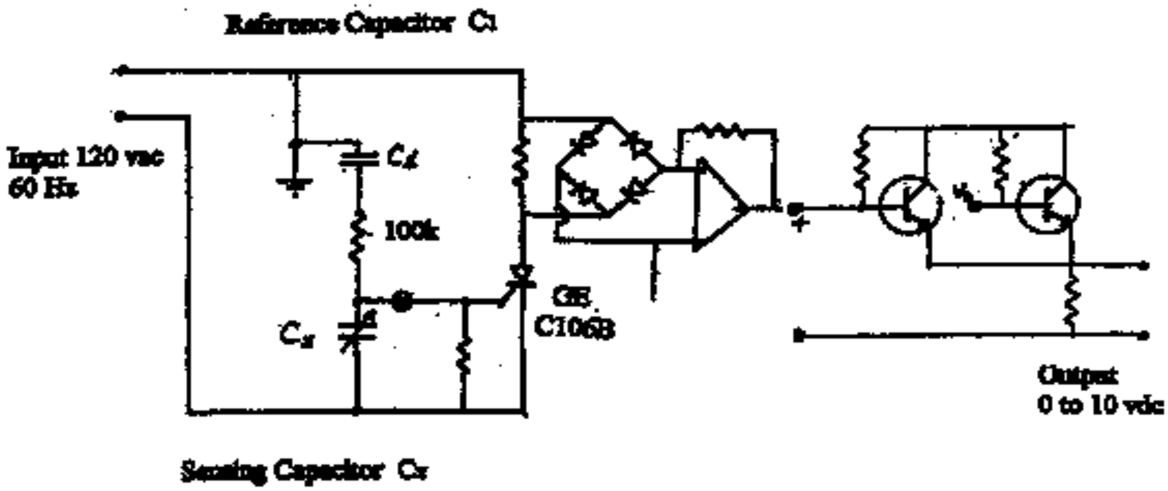


Figure 7 Melt Level Sensor Schematic

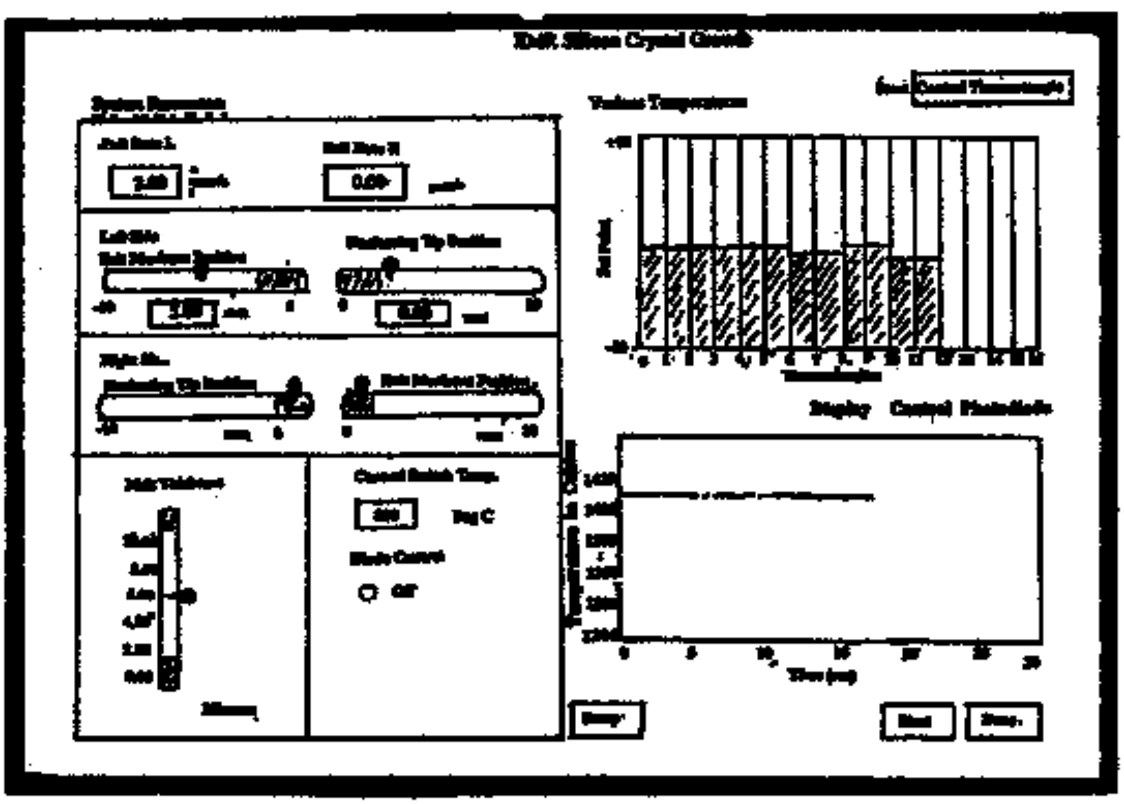


Figure 8. Sketch of Computer Screen Showing a Typical Display

excess of 35 cm/min for conditions in which the nucleating tip is one third to one half of the ribbon thickness. Moreover, in our method, the nucleating tip can be less than one tenth of the ribbon thickness and hence, if the system remains stable, the maximum permitted pulling rate is predicted to be more than 10 times higher. At a pulling speed of35cm/min., our processor pulling two ribbons 10 cm wide at one time, can produce 3.6 square meters per hour.

At this time, subsequent production becomes the tool for parametrically determining the quality of the sheet silicon that may be produced with this technology.

5. Verify Silicon Sheet Properties: The physical and electronic properties of the as grown silicon will be determined independently through the services of government and private testing laboratories. The National Renewable Energy Laboratories have agreed to perform these tests. Some tests will be made in-house. The following list represents the properties to be evaluated and their target values to determine technological success of the process.

Test	Target Quality
a) Structure:	Dislocation free single crystal,
b) Impurity levels	Unaltered from the source
c) Surface:	Unpolished commercial grade--+I- 3 microns
d) Flatness	Commercial Specification +1- 4 microns
f) Solar Cell Efficiency:	> 18%

6. Establish the Failure Modes of the Processor: Important failure modes of the process will be identified. Any process that is to become a commercial enterprise should be reviewed with regard to the potential failure modes of the critical processor components and process function. Failure modes of critical components may alter the forecast of production costs. Prevailing failure of process function could terminate the project. Potential failure modes of the following components and process functions will be reviewed:

a) Environmental chamber: Seal performance (fixed, rotary and translational)
b) Sensors: Repeatability, accuracy, noise and life under thermal stress
c) Heaters: Performance under thermal strain, surge voltage and currents
d) Source feed. Verify control under power surge,
e) The crystal pulling system: Stability, oscillation and interference
f) Thermal field or gradients stability: Pulling speed interference, dendrite control
g) Impurity control: Segregation coefficient versus pulling speed
h Dislocation free single crystal growth: Dendrite and dislocation production.

Project Outcomes:

Not all of the objectives listed above have been reached. While the performance tests were simulated and did not involve a molten silicon, the following represents the status in each area.

Process Chamber: A stainless steel vacuum chamber has been assembled and continues to function in all process temperature and pressures ranges. The system contains ten optical couplers and one thermocouple feed for temperature sensing. There are ports for forty-two electrical feeds for the heaters and sensors, one quartz window, six water feeds, two exit ports for extracting the as-grown crystal and one port for introducing the replenishment source. Protective thermal shielding is placed inside the chamber perimeter and a water- cooling jacket is mounted internally at the base and also at selected areas externally. To evaluate the residual oxygen in the system, a sheet of tantalum was placed in the chamber at high temperature under various vacuum conditions for 30 minutes. Tests showed that at 1500K tantalum oxide could be formed in air down to 3x10 exp-5 torr, and under one atmosphere of argon but did not form in argon at l00 millitorr .

To keep the process zone flat and level, the internal structure is mounted on a boron nitride slab. Every attempt possible was made to obviate differential expansion problems. The only known failure induced by differential expansion was in a commercial Boronitride heater purchased from Advanced Ceramics. The two heat sinks, which were each designed to remove 900 watts uniformly through a temperature difference of 1380K, performed successfully. Typical performance of the heat sink system can be found in Appendix C.

Measurement of the profile of the thermal field was particularly satisfying. Success here in maintaining a very uniform thermal field is attributed to the temperature dependence of silicon and the thermal leveling provided by pyrolytic graphite and boron nitride. The thermal gradients under growth conditions are yet to be determined.

Process Controls: Several sensors were developed to locate the position of the nucleating tip of the growing silicon sheet. The concept used measured the apparent thickness of the silicon sheet near the tip to infer the location of the tip. This system was possible because of the difference in electrical conductivity across the phase boundary at the melting point. The element making contact with the solid silicon may not bond with nor dissolve in the silicon. Graphite was used for the contacts. Two sensors are required when pulling in two directions.

The signal from the nucleating tip sensor is processed and used to activate the pulling mechanism and maintain the position of the nucleating tip dependent only on the rate of tip growth (i.e. the rate of removal of the heat of fusion). A braking system was introduced to correct for the pulling motor step function behavior at startup. A plot of pulling speed versus the inferred growth rate of the silicon sheet is shown in Figure 9.

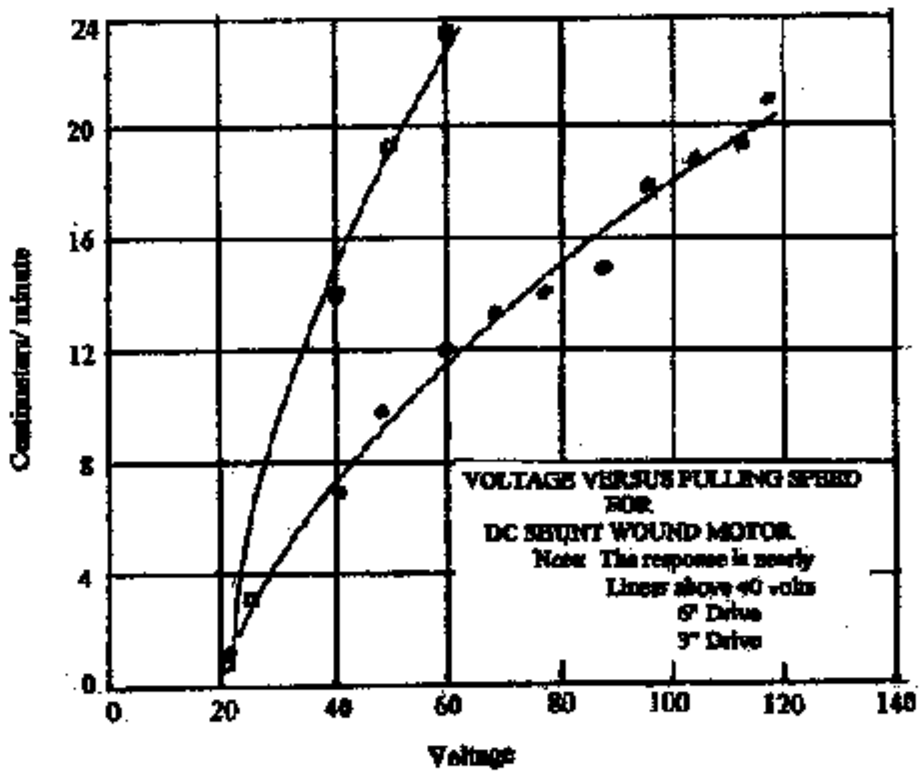
It was originally intended to also use the signal activating the pulling mechanism to control the drive moving the source material toward the melt zone. The unpredictable response of the motor drive at startup and the risk of ramming the system below the melt made this approach impractical. Periodic manual adjustment was used instead. These problems may be resolved with a stepping motor (See Appendix D) or by a system to feed from below.

A sensor based on a capacitor response was designed and constructed to monitor and control the level of the melt. Several systems were considered but, to avoid the possible interference, a simple capacitor comparison system was exploited. The output of the device was successfully used to remotely control the power level of the replenishment power source.

A system similar to the positioning of the nucleating tip, which was planned to monitor the position of the exit meniscus, was untested. Control in this region is less stringent.

Recommendations:

Continue development with existing equipment to support next phase. Assemble a mockup of the new processor with desired changes and include the material handling additions to address the overall processor mechanical operation. Seek sufficient funding to implement



commercial quality equipment designed to simplify operation, construction and repair for commercial production of silicon sheet.

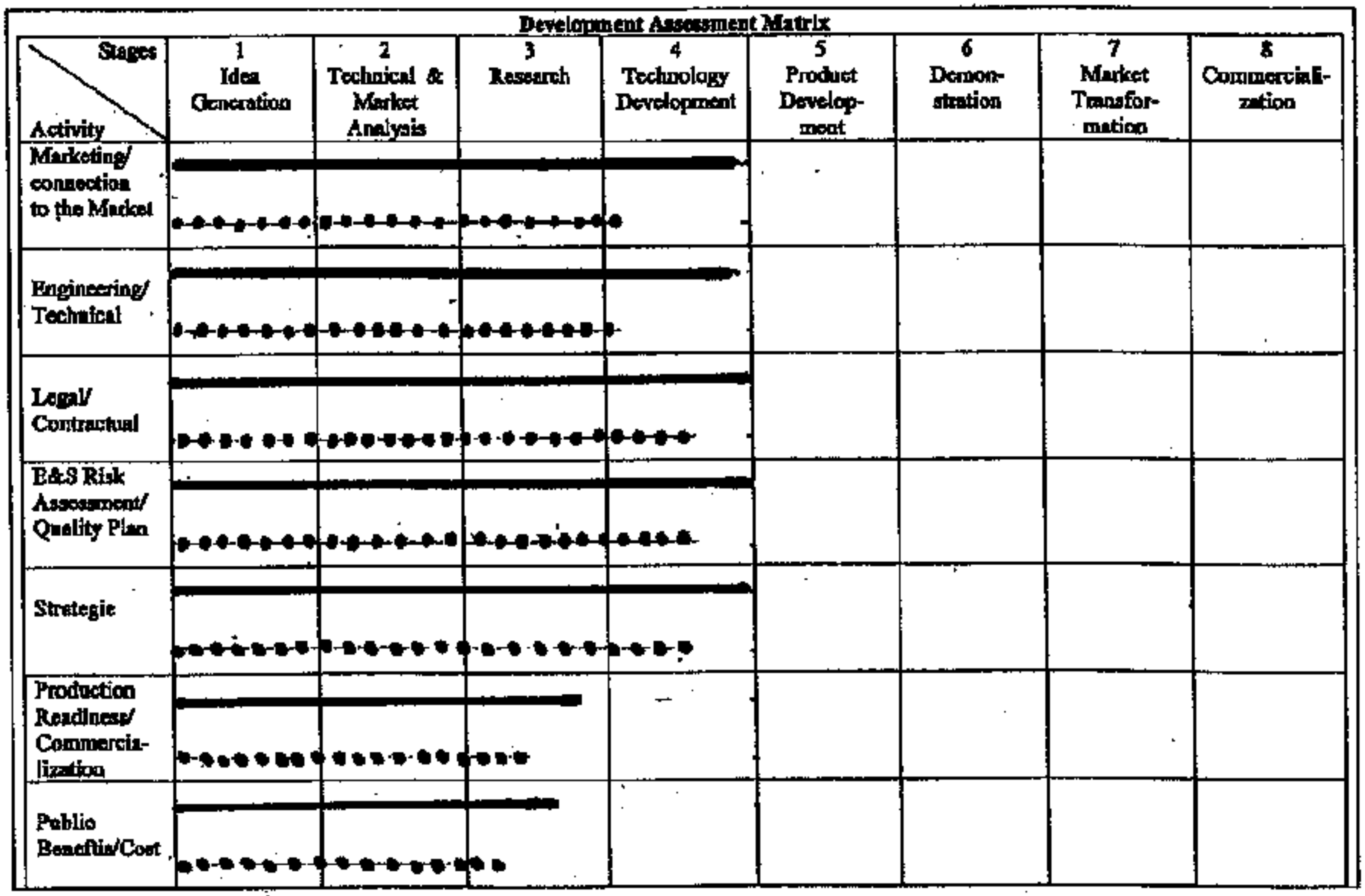
Public Benefits to California and the Nation:

Success in achieving project objectives will:

Permit lower energy and material costs for solar collectors by over 50%
Increase the solar energy market and lower costs for the electronics industry
Educe an important source for mobile electric power (hydrogen).
Reduce the dependence on fossil fuels,
Waste of crystalline silicon in production reduced,
Production rate of electronic quality silicon sheet increased,
Just-in-time production developing in-line processing.

Development Stage Assessment:

The analysis of the project development is based on continuous input since the original introduction of the Horizontal Ribbon Growth technology in the 1960's. It was clear could payoff their startup expenses within a two year period. Today the payoff period is even shorter. Hence, to meet the commercial market demands, a well established product must exist. It must meet all current production requirements and move smoothly into the production stream. Using these criteria, the development of the technology included in this report follows:


Development Assessment Matrix
Stages
Activity
1 Idea Generation
2 Technical & Market Analysis
3 Research
4 Technology Development
5 Product Develop-ment
6 Demon-stration
7 Market Transfor-mation
8 Commerciali-zation
Marketing/ connection to the Market
Engineering/ Technical
Legal/ Contractual
E&S Risk Assessment/ Quality Plan
Strategic
Production Readiness/ Commercia-lization
Public Benefits/Cost

Two independent marketing surveys sponsored by the Department of Energy have been completed. Those surveys emphasized the eventual exploitation of the technology within the electronics industry rather than the solar photovoltaic industry. The clearest result of those surveys is that the commercialization of this technology if successful will occur in the solar energy industry first. The detailed and continuously changing production requirements of the electronics industry will take more time to satisfy. In the chart below the solid lines are appropriate for the solar energy analysis while the dotted lines refer to the electronics industry.

The engineering and technical development of this technology has reached a level approaching the product development stage. The final stage of the current project will open or close the gate to the product development. Independent investors, aware of this work, have expressed serious interest in the final outcome of this development.

The legal status of this technology is based primarily on the intellectual property held by the principal investigator. Six patents have been issued. There is a likely prospect of additional patent applications as this technology approaches commercialization. The current sole proprietor business is expected to become a corporation when the product development stage is reached. The company has no organizations under contract. There are no legal barriers to the next stage.

Evaluation of the risk assessment and quality plans is an ongoing program. Financial risk to any investor includes the possibility that the process will fail fundamentally. Multiple analyses of possible fundamental failure suggest a very low risk exists at this stage of development. The market for the product is constantly changing and other technology developments could bypass this technology. Therefore, it is important for the current development stage be completed at an early date and realistic financing be obtained to minimize the risk to future investors. Poor market timing is another possible risk. In the long term both the solar and electronic industries appear quite stable and growing.

Based on the general understanding of the two main markets for this product, the emphasis should remain with the solar energy industry until full commercialization has been reached. Early incursion into the solar energy market is suggested. It would be a good strategy to cooperate with current producers of solar cells to take advantage of their expertise. The initial product would be the silicon sheet. However, the market may suggest that the process be licensed, the processor be manufactured or that new technology development be the company business. As the developing product achieves the production requirements of the electronics industry expansion into that industry will become feasible.

Production readiness remains in the research stage. There are several production problems for which solutions have been proposed but the newest engineering developments may suggest other solutions. These problems are mostly in the material handling area and are important to production readiness

The assessment of public benefits from the technology began with the idea generation. Success with this project will reduce costs in several areas. The first cost reduction is in the product itself. Secondly, the production cost of photovoltaic modules can be reduced. These cost reductions can promote new business ventures. Fina1ly, the cost of electrical energy may be reduced through the use of solar collectors providing a direct return to the public. The reduced need for power production from fossil fuels can have a stabilizing influence on the economy. Last but not least improvements in the environment are realizable benefits.

References:

I. A.Agrawal, A Pilot Plant Processor for the Production of Silicon Sheet, ERIP Recommendation #721. Prepared for the U. S. Department of Energy , Office of Inventions and Innovation by New Horizon Technologies, Inc.(1998)
2. T.F. Ciszek, I. Crystal Growth .QQ, 655 (1984)
3. C.E. Bleil, J. Crystal Growth, --5-,99 (1969)
4. I.A. Zoutendyk, J. Appl. Phys., .4.2., (No.7, 3927) (1978)
5. B. Kudo, J. Crystal Growth, 2Q, 247 (1980)
   H.E. Bates and D.M. Jewett, 15th IEEE Photovoltaic Spec. Conf. Record, Kissimmee FI., (1981) (IEEE New York 1981 p. 255).
6. T. Koyanagi, Proc. 12th Photovoltaic Spec. Conf., Baton Rouge (IEEE, New York 1976) p. 627
7. C.E. Bleil, I. Crystal Growth, lQ:1:, No.1, 29 (1990).

Appendices:

A. List of Physical Properties of Silicon and Other Special Materials

B. Relationship between Thermocouple and Photodiode Response to Temperature

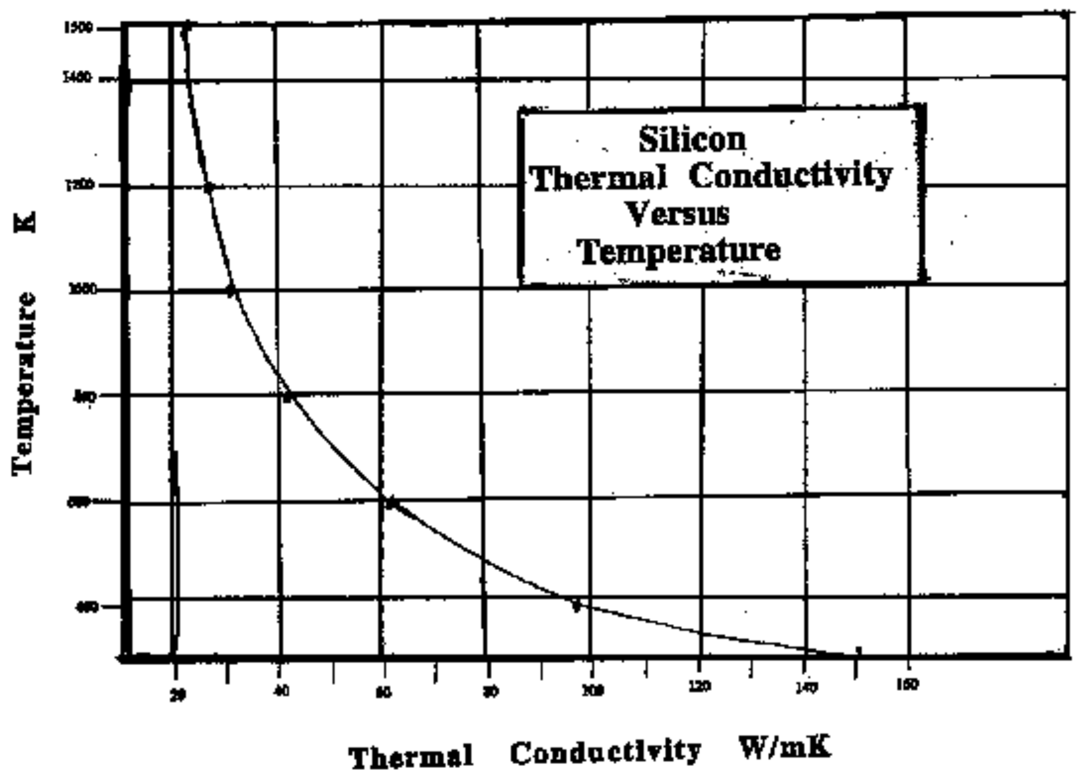
C. Heat Sink Performance Tests

D. Boroelectric Heater and Replacement Heater Design

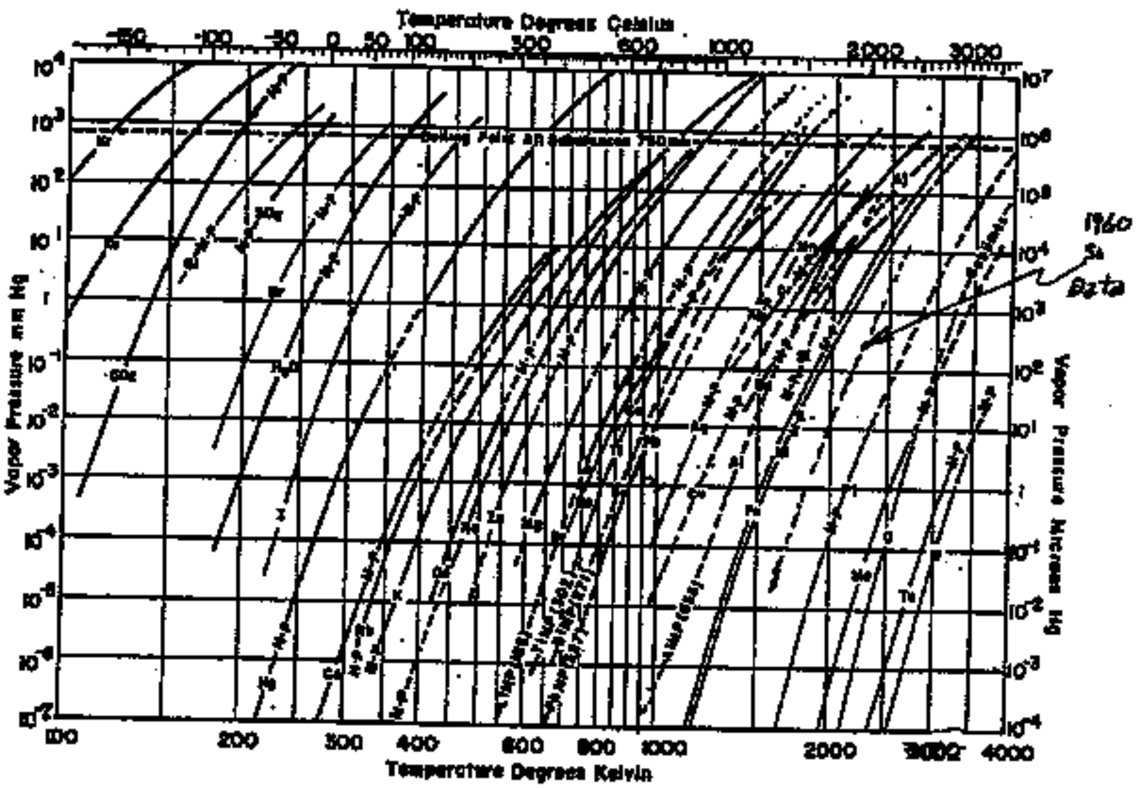
Appendix A

Properties of Silicon

Melting Point	$T_m = 1685K$	**Heat of Fusion**	$Ls = 1810$ J/g
Density	$\rho_S = 2.33$ g/cm^3		
	$\rho_L = 2.53$ g/cm^3	**Specific Heat** C_S at T_m	$= 1.04$ J/gK
Emissivity	$\varepsilon_S = 0.46$	**Solid-Melt Surface Tension**	720 dyn/cm
	$\varepsilon_L = 0.23$		
Thermal Conductivity	$K_S = 0.216$ W/cmK	**Solid-Melt Contact Angle**	11 degrees
	$K_L = 0.6$ W/cmK		
Resistivity	$\sigma_S = 2400$ μΩ cm		
	$\sigma_L = 80$ μΩ cm		
Crystal Structure	Diamond Cubic		



	Diffusivity (m²/s) at Various Temperatures (K) (10^{-6})							Melting Temp	Density	Thermal Expansion
Material	300	400	500	800	1000	1200	1500	Tm (K)	(Kg/m³)	α
Silicon	89.2	57.2	38.4	19.8	14.1	11.4	9.6	1685	2330	2.6–4.1
SiO_2	0.82	0.7	0.7	0.8	1.1	1.5		1883	2220	0.54
Si_3N_4	9.86	7.4	5.8	3.6	3.1	2.7	2.2	2173	3400	2.8–4.0
TiO_2	2.8	2.0	1.3	1.0	0.9	0.8		2143	4157	
Al_2O_3	11.9	7.6	3.8	2.3	1.6	1.3	1.0	2320	3970	
Chromium	29.1	26.8	20.7	17.1	14.6	12.8	10.2	2118	7160	8–10
Molybdenum	53.7	50.0	44.7	40.4	37.0	33.3	30.1	2894	10240	5–7
Tungsten	68.5	60.1	49.3	44.6	41.3	36.3	33.1	3660	19300	5.2
Boron	9.79	4.6	2.2	1.7	1.5			2573	2500	5.0
7059	5.3							(872)	2760	3.6–4.0

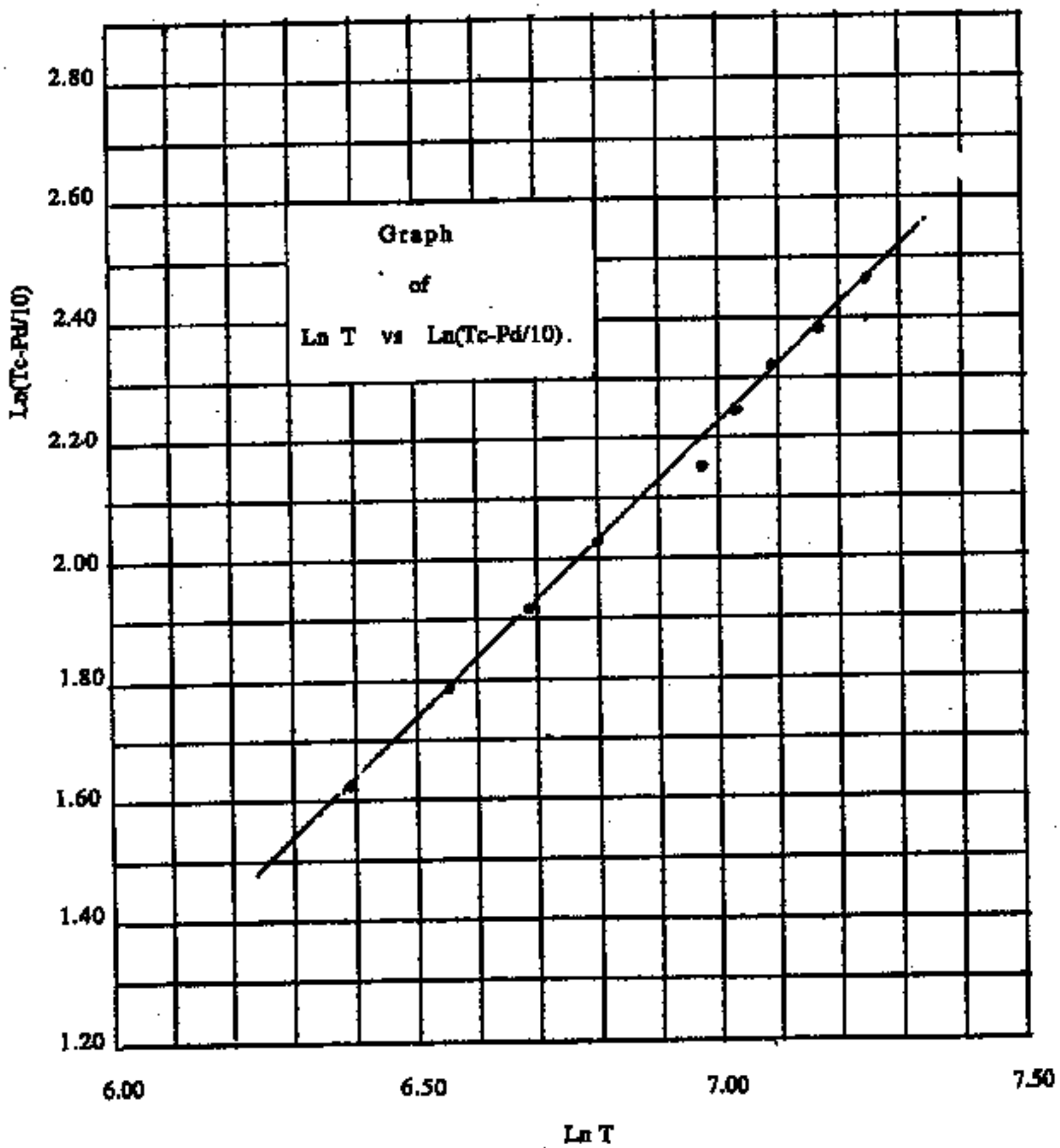


Vapor-pressure data. [*Compiled by R. E. Law, Rev. Sci. Instr.* 19, 920 (1948).]

Appendix B

Comparison Data
for
S Type Thermocouple vs Germanium Photodiode
over the temperature range
870K < T < 1685K

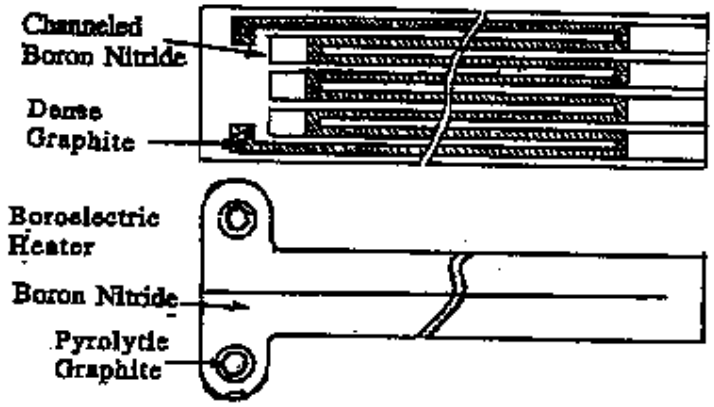
Temp C	LnT	Thermocouple Type S ma	Ge Photodiode	(Tc-Pd/10)	Ln(Tc-Pd/10)
600	6.3969	5.239	1.85	5.054	1.620
700	6.5511	6.275	3.20	5.955	1.784
800	6.6846	7.345	4.80	6.865	1.926
900	6.8024	8.449	7.80	7.669	2.037
1000	6.9078	9.587	10.0	8.587	2.150
1100	7.0031	10.757	13.0	9.457	2.247
1200	7.0901	11.951	16.9	10.261	2.328
1300	7.1701	13.159	23.5	10.809	2.380
1400	7,2442	14.373	27.0	11.673	2.455

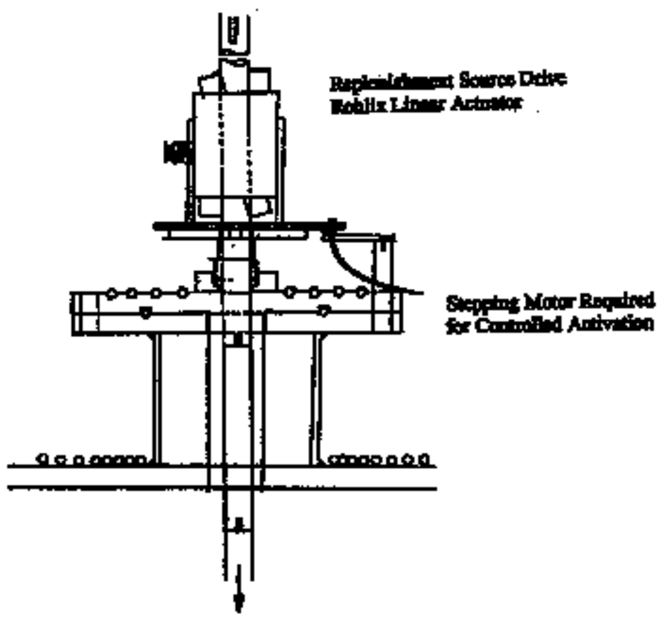

Graph
of
Ln T vs Ln(Tc-Pd/10).
Ln(Tc-Pd/10)
2.80
2.60
2.40
2.20
2.00
1.80
1.60
1.40
1.20
6.00
6.50
7.00
7.50
Ln T

Appendix C

EMR Heater Design
Subject to Failure
a) Assembly Breakage
b) Manufacturing defects

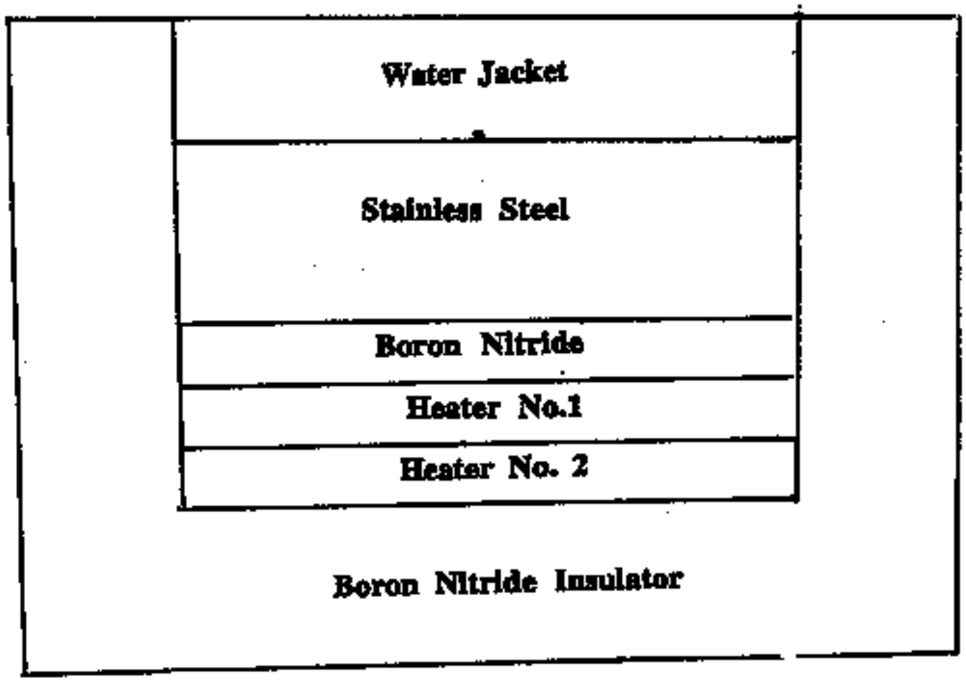
Boroelectric Heater Design
Subject to Failure by
a) Differential Expansion
b) Contact Erosion





Appendix D

Heat Sink Performance Test



Testing Arrangement

Heater No.1		Heater No. 2 Simulated Heat of Fusion Extraction			Remarks
i	Power			*i*	
amp	watts.	∇T	watts	amp	Time was allowed between measurements to accomodate for the specific heat. The mass of the lower heater was about 10 gms
10	1600	0	0	0	
9	1296	6	304	4.9	
8	1024	11	575	6.6	
7	784	.19	818	7.3	
6	576	24	1075	8.2	
5	400	29	1205	9.0	