https://ntrs.nasa.gov/search.jsp?R=19860010252 2020-03-20T15:12:43+00:00Z

STAR 09 FEB 25 1986

5101-272
Flat-Plate
Solar Array Project

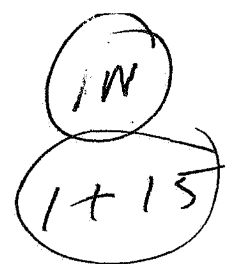
DOE/JPL-1012-109
Distribution Category UC-63b

Proceedings of the Flat-Plate Solar Array Project Workshop on Crystal Growth for High-Efficiency Silicon Solar Cells

(December 3 and 4, 1984, at San Diego, California)

(NASA-CR-176540) PROCEEDINGS OF THE FLAT-PLATE SOLAR ARRAY PROJECT WORKSHOP ON CRYSTAL GOWTH FOR HIGH-EFFICIENCY SILICON SOLAR CEILS (Jet Propulsion Lab.) 296 p HC A13/MF A01 CSCL 10B G3/44

N86-19723
THRU
N86-19738
Unclas
04280



August 15, 1985

Prepared for
U.S. Department of Energy
Through an Agreement with
National Aeronautics and Space Administration
by
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

JPL Publica. .ı 85-59

5101-272
Flat-Plate
Solar Array Project

DOE/JPL-1012-109
Distribution Category UC-63b

Proceedings of the Flat-Plate Solar Array Project Workshop on Crystal Growth for High-Efficiency Silicon Solar Cells

(December 3 and 4, 1984, at San Diego, California)

August 15, 1985

Prepared for
U.S. Department of Energy
Through an Agreement with
National Aeronautics and Space Administration
by
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California

JPL Publication 85-59

Prepared by the Jet Propulsion Laboratory, California Institute of Technology, for the U.S. Department of Energy through an agreement with the National Aeronautics and Space Administration.

The JPL Flat-Plate Solar Array Project is sponsored by the U.S. Department of Energy and is part of the Photovoltaic Energy Systems Program to initiate a major effort toward the development of cost-competitive solar arrays.

This report was prepared as an account of work sponsored in part by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights.

Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This publication reports on work done under NASA Task RE-152, Amendment 66, DOE / NASA IAA No. DE-AI01-76ET20356.

ABSTRACT

A Workshop on Crystal Growth for High-Efficiency Silicon Solar Cells was held December 3 and 4, 1984, in San Diego, California. The Workshop offered a day and a half of technical presentations and discussions and an afternoon session that involved a panel discussion and general discussions of areas of research that are necessary to the development of materials for high-efficiency solar cells. Topics included the theoretical and experimental aspects of growing high-quality silicon crystals, the effects of growth-process-related defects on photovoltaic devices, and the suitability of various growth technologies as cost-effective processes. Fifteen invited papers were presented, with a discussion period following each presentation. The meeting was organized by the Flat-Plate Solar Array Project of the Jet Propulsion Laboratory. These Proceedings are a record of the presentations and discussions, edited for clarity and continuity.

FOREWORD

The Crystal Growth for High-Efficiency Silicon Solar Cells Workshop was held in San Diego, California on December 3 and 4, 1984. Representatives from industrial laboratories, universities, and Government laboratories participated in the meeting and contributed to research planning activities. The Workshop was sponsored by the Flat-Plate Solar Array Project of the Jet Propulsion Laboratory.

The objectives of the Workshop were to define the requirements for silicon sheet suitable for processing into high-efficiency solar cells, to review the state of the art of silicon crystal growth technology (emphasizing the growth-related phenomena that limited device performance), and to identify the future research necessary to produce silicon sheet suitable for fabrication into high-efficiency solar cells. The schedule for this topical meeting divided each speaker's time equally between a formal presentation and a discussion period. In the final session, a panel of experts opened a general discussion of the future research activities necessary to achieve the growth of high-quality silicon crystals. The format for the meeting successfully provided the opportunity for unrestricted technology exchange among those attending.

This Proceedings document includes speaker's presentation material and a transcript of the discussion period following each paper. A transcript of the entire panel and general discussion is also included. All of the discussion sections have been edited with the intent of enhancing the clarity and continuity of each discussion.

It is hoped that this Proceedings document will serve as a useful reference for those interested in the growth of silicon crystals for high-efficiency solar cells.

Katherine A. Dumas
Proceedings Editor

PRECEDING PAGE BLANK NOT FILMED

WORKSHOP ORGANIZING COMMITTEE

Katherine A. Dumas	Chairman
Akaram H. Kachare Andrew D. Morrison Guenter H. Schwuttke	
Mary J. Phillips	Coordinator

PROCEEDINGS STAFF

Katherine A. Dumas	Editor
Jackson D. Collier	
Gretchen L. Hyland	
Maxine J. Koop	
Mary J. Phillips	
Betty J. Sivalon	
Ernest E. Sloman	

PRECEDING PAGE BLANK NOT FILMED

CONTENTS

SESSION I 1

MATERIAL REQUIREMENTS FOR HIGH-EFFICIENCY SILICON SOLAR CELLS
(M. Wolf) 3
Discussion 15

THE STATUS OF SILICON RIBBON TECHNOLOGY FOR HIGH-
EFFICIENCY SILICON SOLAR CELLS (T. Ciszek) 17
Discussion 26

FUTURE APPLICATION OF CZOCHRALSKI CRYSTAL PULLING FOR
SILICON (J. Matlock) 29
Discussion 54

POTENTIAL PRODUCTIVITY BENEFITS OF FLOAT-ZONE VS CZOCHRALSKI
CRYSTAL GROWTH (T. Abe) 55
Discussion 79

SESSION II 81

A NEW OUTLOOK ON CONTROL OF CRYSTALLINE AND CHEMICAL
PERFECTION DURING GROWTH OF SILICON (A. Witt) 83
Discussion 95

MCZ: STRIATIONS IN CZ SILICON CRYSTALS GROWN UNDER VARIOUS
AXIAL MAGNETIC FIELD STRENGTHS (G. Kim) 97
Discussion 107

HIGH-PURITY, LOW-DEFECT FZ SILICON
(H. Kimura and G. Robertson) 109
Discussion 121

DEFECTS IN SILICON EFFECT ON DEVICE PERFORMANCE AND
RELATIONSHIP TO CRYSTAL GROWTH CONDITIONS (L. Jastrzebski) 123
Discussion 141

SESSION III 145

SIMULATION OF THE TEMPERATURE DISTRIBUTION IN CRYSTALS
GROWN BY CZOCHRALSKI METHOD (M. Dudukovic and P. Ramachandran) . . 147
Discussion 172

CONVECTIVE EFFECTS IN FLOAT-ZONE AND CZOCHRALSKI MELTS
(P. Neitzel) 175
Discussion 190

PRECEDING PAGE BLANK NOT FILMED

CONTENTS (Cont'd)

SESSION IV 193

THERMAL-CAPILLARY MODEL FOR CZOCHRALSKI GROWTH OF SEMICONDUCTOR MATERIALS (J. Derby and R. Brown) 195
Discussion 212

IMPURITIES IN SILICON SOLAR CELLS (R. Hopkins) 215
Discussion 231

OXYGEN AND CARBON IN SILICON (J. Corbett) 235
Discussion 257

SOLAR CELL AND I.C. ASPECTS OF INGOT-TO-SLICE MECHANICAL PROCESSING (L. Dyer) 259
Discussion 275

DEFECTS AND DEVICE PERFORMANCE (G. Storti, R. Armstrong, S. Johnson, H. Lin, W. Regnault and K. Yoo) 279
Discussion 290

SESSION V 293

INTRODUCTION 295

PANEL AND GENERAL DISCUSSION 297

APPENDIXES

A. LIST OF SPEAKERS A-1

B. LIST OF PARTICIPANTS B-1

SESSION I

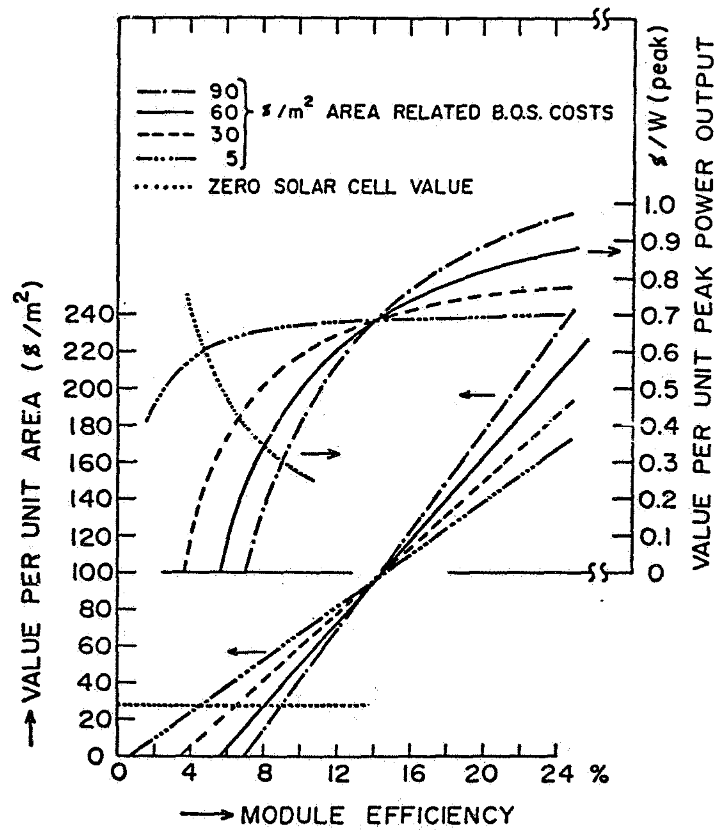
A. D. MORRISON, CHAIRMAN

N86-19724

MATERIAL REQUIREMENTS FOR HIGH-EFFICIENCY SILICON SOLAR CELLS

M. Wolf
The University of Pennsylvania
Philadelphia, PA 19104

(Abstract not received for publication.)



PRECEDING PAGE BLANK NOT FILMED

Primary Causes of Losses

1. <u>LIGHT GENERATED CURRENT:</u>
   - A. OPTICAL SURFACE PROPERTIES (REFLECTION)
   - B. CONTACT COVERAGE
   - C. INCOMPLETE ABSORPTION (THICKNESS)
   - D. RECOMBINATION OUTSIDE DEPLETION REGION (BULK AND SURFACE, INCLUDING CONTACTS)
   - E. ("DEAD LAYERS")

2. <u>OPEN CIRCUIT VOLTAGE:</u>
   - A. RECOMBINATION OUTSIDE DEPLETION REGION (BULK AND SURFACE, INCLUDING CONTACTS)
   - B. BANDGAP NARROWING
   - C. "CURRENT LEAKAGE"

3. <u>FILL FACTOR:</u>
   - A., B., C. } SAME AS OPEN CIRCUIT VOLTAGE
   - D. RECOMBINATION IN DEPLETION REGION
   - E. SERIES RESISTANCE

PRIMARY CAUSES OF LOSSES	SYMBOL	DESIGN PARAM	1970 COM'L CELL	"VIOLET CELL"	"BLACK CELL"	1978 SPACE CELL	1984 EXPER'L CELLS SPIRE	WESTINGH	M.A.GREEN	GOALS 20%	22.6%
		BASE: WIDTH	?	300 μm	300 μm	300 μm (A)	380 μm	375 μm	280 μm	200 μm	200 μm
		$\tau_{n,p}$	3 μs	?	?	?	~40 μm	~23 μm	~25 μm	95 μs	950 μs
		τ_{n,p^+}	—	—	—	?		(0.1 μs)	(0.1 μs)	0.26 μs	2.6 μs
		FRONT: WIDTH	0.4 μm	~0.15 μm	~0.2 μm	~0.2 μm	~0.2 μm	~0.3 μm	~0.3 μm	2 μm	2 μm
		$\tau_{p,n}$	?	?	?	?			1ns – 15μs	0.1 μs	10 μs
		S	?	?	?	?	~10^4 cm s^{-1}	~10^4 cm s^{-1}	10^3 cm s^{-1}	10^3 cm s^{-1}	10^2 cm s^{-1}
		TREATM.	SiO	Ta_2O_5 + GLASS	TEXT'D + Ta_2O_5 + GLASS	TEXT'D + Ta_2O_5	TEXT'D + SiO_2 + TiO_2	TiO_2/SiO_2	ZnS/ MgF_2	DUAL AR	DUAL AR
1. <u>LIGHT GENERATED CURRENT:</u>											
<u>FUNDAMENTAL LIMIT (AM1)</u>	$j_{L,id}$		44 mA cm^{-2}								
A. OPTICAL SURFACE PROPERTIES (REFLECTION)	(1−R)		0.905	0.90	0.97	0.96	0.975	0.966	0.954	0.97	0.97
B. CONTACT COVERAGE	S		0.96	0.95	0.95	0.96	0.965	0.97 (A)	0.948	0.966	0.966
C. INCOMPLETE ABSORPTION (THICKNESS)	} η_{COLL}		} 0.72	0.95 } = 0.90	0.96	0.96 (A)	0.956	0.956	0.973	} 0.92	} 0.95
D. RECOMBINATION OUTSIDE DEPLETION REGION (BULK AND SURFACE, INCLUDING CONTACTS)				0.95	0.94	0.94	0.91	0.915	0.93		
E. ("DEAD LAYERS")	(1−A)			1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
OVERALL COLLECTION EFFICIENCY:	γ		0.63	0.77	0.84	0.84	0.82	0.82	0.82	0.86	0.89
LIGHT GENERATED CURRENT (AM1)	$j_L = \gamma \cdot j_{L,id}$ (mA cm^{-2})		28.1	34.0	37.1	37.0	36.2	36.0	36.0	37.9	39.2
2. <u>OPEN CIRCUIT VOLTAGE:</u>											
<u>FUNDAMENTAL LIMIT:</u>	$(VF)_{fund} = 0.76$		0.836 V ($j_0 = 4.2 \cdot 10^{-16}$ A cm^{-2})								
A. RECOMBINATION OUTSIDE DEPLETION REGION (BULK AND SURFACE, INCLUDING CONTACTS) B. BANDGAP NARROWING	$(VF) = (VF)_{techn} \cdot (VF)_{fund}$		0.522	0.528	0.533	0.555	0.565	0.57	0.59	0.60	0.65
C. "CURRENT LEAKAGE"	(R_{sh})		1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
OPEN CIRCUIT VOLTAGE:	$V_{oc} = (VF) \cdot E_g$ (V)		0.574	0.581	0.586	0.610	0.622	0.627	0.653	0.661	0.715
3. <u>FILL FACTOR:</u>											
<u>FUNDAMENTAL LIMIT:</u>	$(CF)_{fund}$		0.865								
A., B. } SAME AS OPEN CIRCUIT VOLTAGE	$(CF) = (CF)_{techn} \cdot (CF)_{fund}$		0.82	0.823	0.823	0.824	0.83	0.833	0.839	0.84	0.85
C.	(R_{sh})		1.0 (A)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
D. RECOMBINATION IN DEPLETION REGION	$(CF)_{add'l}$		0.91	0.97	0.97	0.97	0.985	0.98	0.982	0.97	0.97
E. SERIES RESISTANCE	(R_s)		0.96	0.985	0.984	0.98 (A)	0.98	0.98	0.984	0.98	0.98
<u>FILL FACTOR</u>	(FF)		0.716	0.78	0.78	0.78	0.801	0.800	0.811	0.80	0.81
RESULTING CONVERSION EFFICIENCY	η		11.6	15.4	17.0	17.6	18.1	18.1	19.1	0.200	0.226

(A) = ASSUMED

The Recent Approach

a. THOUROUGH DEVICE ANALYSIS COUPLED WITH MODELING:

- o TO DETERMINE ALL LOSS CONTRIBUTIONS
- o TO IDENTIFY POSSIBILITIES FOR IMPROVED DEVICE DESIGN.

b. GLOBAL DESIGN VIEW OF DEVICE:

- o OPTIMIZED CONTACT DESIGN
- o DUAL AR OR TEXTURED FRONT SURFACE
- o FRONT SURFACE PASSIVATION (AT LEAST PARTIAL)
- o BSF AND/OR BSR DESIGN (LIMITED EFFECT)
- o SELECTION OF LOW RESISTIVITY FZ Si
- o PROCESSING TO MAINTAIN HIGHER FRACTION OF ORIGINAL L_b
- o OPTIMIZATION OF EMITTER IMPURITY CONCENTRATION FOR PRESENT DESIGN

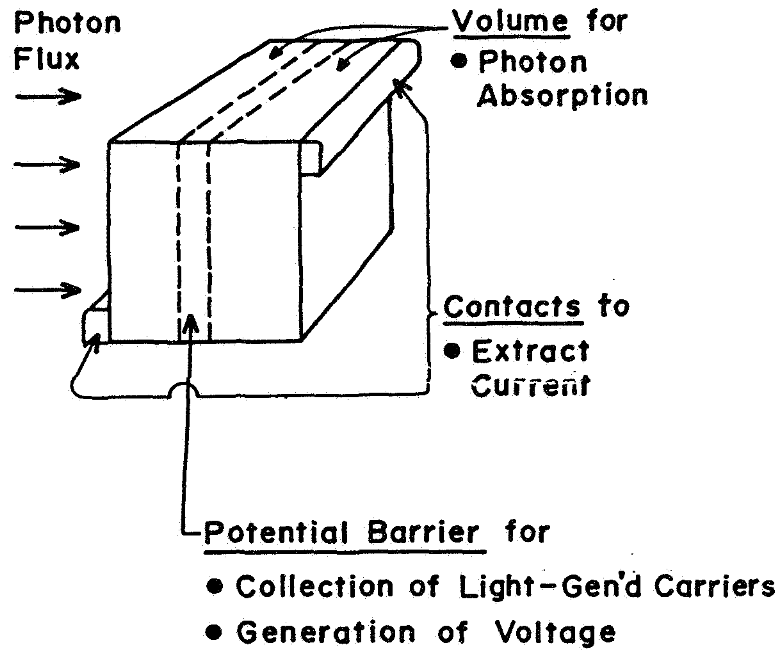
IN SUMMARY:

SQUEEZE A LITTLE MORE PERFORMANCE OUT,
WHEREVER CURRENT TECHNOLOGY PERMITS.

Status of Si Solar-Cell Technology

- TECHNOLOGY IS AVAILABLE TO REDUCE THE CONTRIBUTION OF EACH SECONDARY LOSS MECHANISM (REFLECTION, CONTACT SHADING, SERIES RESISTANCE, ETC.) TO THE MAXIMALLY 2-3% LEVEL.
- INTERNAL COLLECTION EFFICIENCY IS GENERALLY >90%; "SATURATES" WITH FURTHER REDUCED RECOMBINATION.
- OPEN CIRCUIT VOLTAGE CONTINUES TO SUBSTANTIALLY INCREASE WITH DECREASING MINORITY CARRIER RECOMBINATION, UP TO BASIC RECOMBINATION LIMIT (RADIATIVE AND AUGER).
- CURVE FACTOR (FUNDAMENTAL PART OF FILL FACTOR) CAN INCREASE (WITH V_{OC}) BY A FEW PERCENT.

The Basic Solar Cell

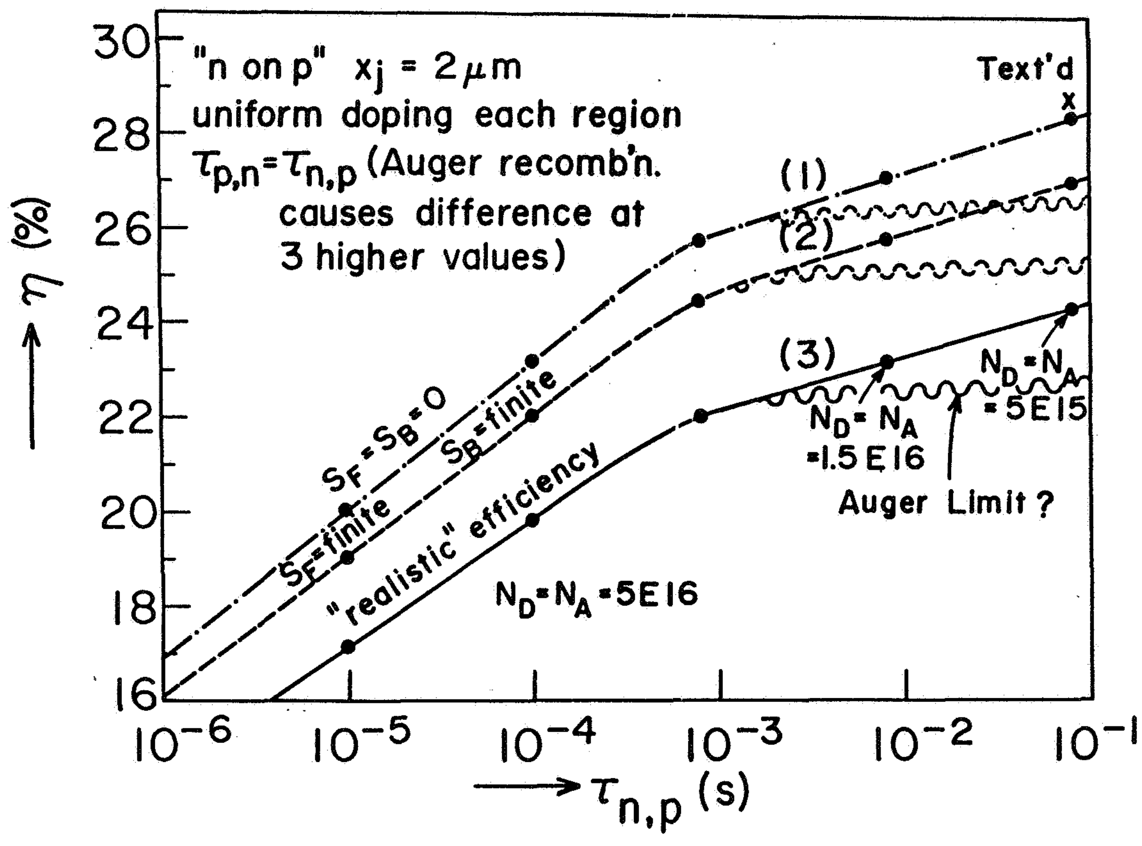


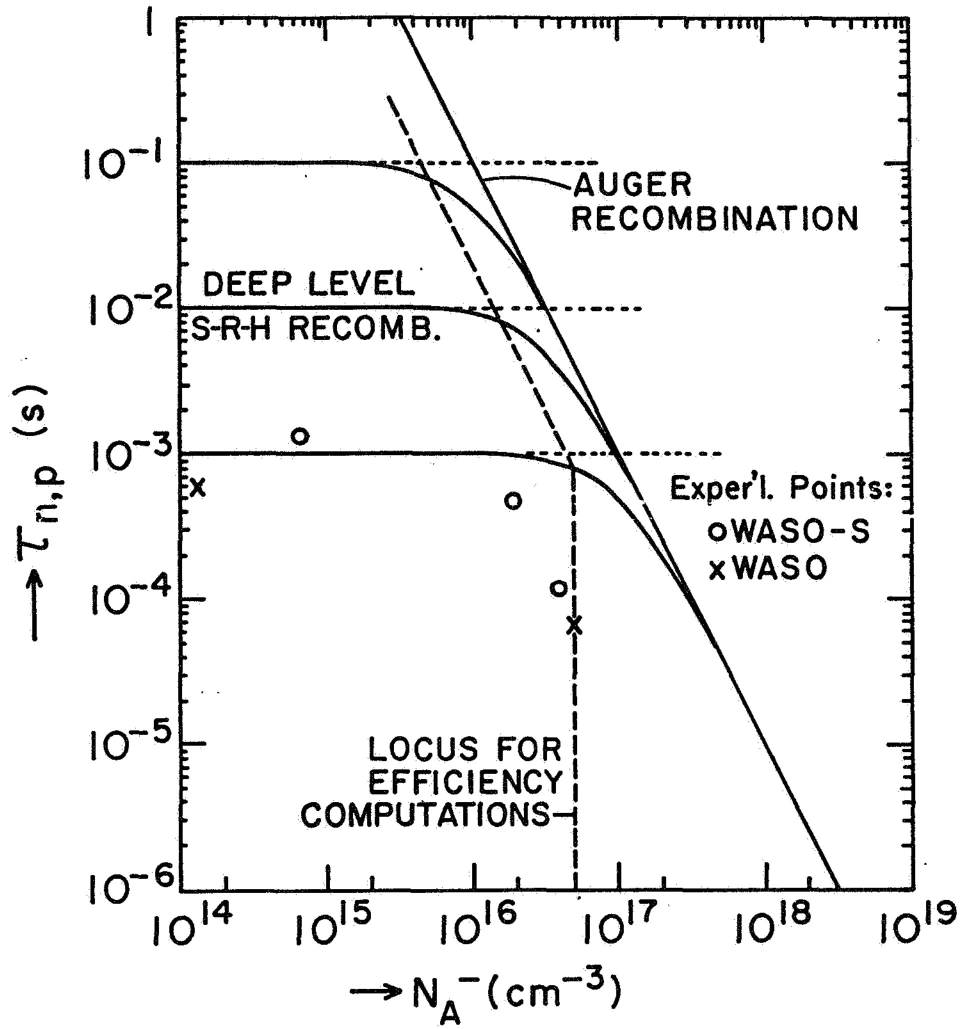
Everything Else

(AR coatings, Hi/Lo Junctions, extra Layers, etc)

to overcome

- Secondary Effects caused by material, process, or design limitations


"n on p" x_j = 2 μm
uniform doping each region
$\tau_{p,n} = \tau_{n,p}$ (Auger recomb'n.
causes difference at
3 higher values)
Text'd
x
(1)
(2)
(3)
$S_F = S_B = 0$
S_B = finite
S_F = finite
"realistic" efficiency
$N_D = N_A = 5E16$
$N_D = N_A$ = 1.5 E16
$N_D = N_A$ = 5E15
Auger Limit ?
→ η (%)
→ $\tau_{n,p}$ (s)
30
28
26
24
22
20
18
16
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}


AUGER
RECOMBINATION
DEEP LEVEL
S-R-H RECOMB.
Exper'l. Points:
o WASO-S
x WASO
LOCUS FOR
EFFICIENCY
COMPUTATIONS
1
10⁻¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
10¹⁴
10¹⁵
10¹⁶
10¹⁷
10¹⁸
10¹⁹
→ τn,p (s)
→ NA⁻ (cm⁻³)

The Three Principal Paths to Reduced Recombination

DECREASE

1. DENSITY OF RECOMBINATION CENTERS
   - IN BULK N_t $[cm^{-3}]$ ⟶ HIGHER τ
   - AT SURFACES $N_{s,t}$ $[cm^{-2}]$ ⟶ LOWER s
2. VOLUME OR AREA CONTAINING RECOMBINATION CENTERS:
   - "THIN" LAYERS
   - "DOT CONTACTS"
3. DENSITY OF EXCESS MINORITY CARRIERS
   - FAST REMOVAL TO OUTSIDE
   - "SHIELDING" WITH POTENTIAL STEPS
   - "ISOLATING" FROM HIGHER RECOMBINATION RATE
   - HIGH DOPANT CONCENTRATION

   (First three: FOR η_{coll}; all four: FOR V_{oc})

High Dopant Concentration

PRINCIPLE:

$$j_d = q\, n_p \cdot \frac{L}{\tau} = q\, n_{p,o}\, e^{\frac{qV}{kT}} \cdot \frac{L}{\tau};$$

$$V = \text{HIGH IF } n_{p,o} = \text{SMALL:} \quad n_{p,o} = \frac{n_i^2}{p_{p,o}}$$

LIMITS:

- HEAVY DOPING EFFECTS.

Is Heavy Doping Needed?

ITS PERFORMANCE-INCREASING APPLICATIONS:

- **REDUCE SHEET RESISTANCE**
- **OBTAIN LARGER HIGH/LOW JUNCTION POTENTIAL STEP, OR HIGHER DRIFT FIELD.**

ITS PERFORMANCE DECREASING ATTRIBUTES:

- **AUGER RECOMBINATION**
- **BAND-GAP NARROWING.**

Effective Bulk Recombination Mechanisms

INTRINSIC (INTERBAND) RECOMBINATION:

RADIATIVE	**ULTIMATELY**
	LIMITS
AUGER?	**EFFICIENCY**

EXTRINSIC (BAND-TO-BOUND STATE) RECOMBINATION:

THERMAL (PHONON ASSISTED) **SRH**
(AUGER?)

EXTRINSIC RECOMBINATION CAN BE DECREASED BY REDUCING THE NUMBER OF BOUND STATES (RECOMBINATION CENTERS, "DEFECTS").

Knowledge of Defects

a. ARE SOME DEFECTS "INTRINSIC"?

(NEUTRAL DEFECT WITH ACTIVATION ENERGY E_a AT PROCESS TEMPERATURE "FROZEN IN." IONIZED FRACTION AT DEVICE OPERATION TEMPERATURE FORMS RECOMBINATION CENTER, PARTICULARLY IN N-TYPE).

b. TRUELY EXTRINSIC (PROCESS-INDUCED) DEFECTS

- o IMPURITIES (O, C, Au, Ti, Mo, Fe, ...)
  - BIG PROGRESS MADE IN DETECTING PRESENCE, DETERMINING CONCENTRATION. OPEN QUESTION OFTEN IS: INTERSTITIAL, SUBSTITUTIONAL, COMPLEXED, OR PRECIPATED?
  - O: PRIMARY SOURCE: CRUCIBLE IN Cz PROCESS. TECHNIQUES KNOWN TO REDUCE O-CONTENT TO 0.1 OF STANDARD LARGE-CRUCIBLE Cz PROCESS. O-CONTENT INCREASES WITH C- OR B-CONTENT.
- o CRYSTAL GROWTH DEFECTS.
  - BIG PROGRESS MADE IN DETECTION, IDENTIFYING CRYSTAL GROWTH DEFECTS.
  - STRONGLY CONNECTED WITH THE CRYSTAL GROWTH TECHNOLOGY APPLIED; TECHNOLOGY APPLIED SEEMS PRIMARILY DETERMINED BY THROUGTHPUT, PRICE, AND WHAT THE MAJORITY OF USERS ARE WILLING TO ACCEPT.

Reduce Volume Recombination Center Density

- ORIGINAL MATERIAL PROCESSING:
  - FEWER IMPURITIES
  - ROLES OF OXYGEN, CARBON?
  - FEWER CRYSTAL DEFECTS (THERMAL ENVIRONMENT IN X-TAL GROWTH?)
  - ROLES OF DEFECT COMPLEXES
- DEVICE PROCESSING:
  - NO NEW IMPURITY INTRODUCTION
  - REMOVE EXISTING DEFECTS (GETTERING)
  - AVOID TRANSFORMATION OF DEFECTS TO RECOMBINATION CENTERS (EFFECTS OF THERMAL PROCESSES?)
  - FOSTER TRANSFORMATION OF RECOMBINATION CENTERS TO HARMLESS DEFECTS (PASSIVATION; CHANGES OF COMPLEXES?; ROLE OF HYDROGEN?)

Steps Toward Reduced Number of Recombination Centers

1.	IDENTIFY "DEFECT(S)" WHICH FORM RECOMBINATION CENTER(S)	- BROAD RANGE OF DEFECTS AND OF ENERGY LEVELS IDENTIFIED - INTERCONNECTION AND RELATIONSHIP TO RECOMBINATION CENTERS MADE IN ONLY A FEW CASES.
2.	IDENTIFY SOURCE(S) OF DEFECT(S)	- USUALLY NOT KNOWN.
3.	FIND WAYS FOR ELIMINATING SOURCE(S) OF DEFECT(S)	- STILL MOSTLY "BLACK ART."
4.	PASSIVATE EXISTING DEFECTS	- LITTLE KNOWN. IS H^+ THE BROAD SPECTRUM ANTIBIOTIC"?

Passivation with Hydrogen

- IT CAN NEUTRALIZE RECOMBINATION CENTERS, APPARENTLY EVEN DEEP IN THE BULK, PARTICULARLY AT GRAIN BOUNDARIES.
- HYDROGEN IMPLANTS PASSIVATE DANGLING BONDS, WHEREVER HYDROGEN IONS REACH THEM.
- HYDROGEN IMPLANTS MAY POSSIBLY ALSO PASSIVATE DEEP LEVELS (IMPURITIES) in Si.
- THE "IMPLANTATION" OF HYDROGEN IONS, EVEN AT LOW ENERGIES CAUSES SPUTTER ETCHING, LATTICE DAMAGE (200 Å DEEP AT 400eV).
- HYDROGEN CAUSES MORE LATTICE DAMAGE THAN ARGON, EVEN AMORPHIZES SURFACE LAYER, BUT FEWER DANGLING BONDS ("PASSIVATES ITS OWN DAMAGE")
- WHETHER PASSIVATION DOMINATES OVER INTRODUCED DAMAGE DEPENDS ON IMPLANTATION ENERGY, PRIOR PROCESS HISTORY.
- HYDROGEN IS ALSO KNOWN TO NEUTRALIZE B AS AN ACCEPTOR.

Low-Cost Crystalline Si Is Primarily:

- "CAST" INGOT MATERIAL (SEMIX, SILSO, HEM, etc.)
- NOT-SINGLE CRYSTALLINE RIBBON (EFG, LASS, etc.)

EFFORTS TO INCREASE GRAIN SIZE, REDUCE DEFECTS, PASSIVATE REMAINING ONES, ALL SHOW PROGRESS.

BUT: IT SEEMS IMPOSSIBLE TO COMPLETELY PASSIVATE ALL THE DEFECTS ASSOCIATED WITH GRAIN BOUNDARIES

ALSO: FASTER, LESS CONTROLLED GROWTH MAY ALWAYS RESULT IN INCREASED NUMBERS OF IMPURITIES, CRYSTAL DEFECTS.

CONSEQUENTLY: THE ULTIMATELY ACHIEVABLE PERFORMANCE MARGIN RELATIVE TO THAT OF SINGLE CRYSTAL DEVICES IS NOT KNOWN.

- WEB-DENDRITE RIBBON IS IN A CLASS BY ITSELF. MAY HAVE POSSIBILITY, WITH INTERNAL GETTERING AT TWIN PLANES, TO SURPASS THE QUALITY OF SINGLE CRYSTAL WAFERS.

IN ALL METHODS, THE CONTROL OF THE THERMAL ENVIRONMENT DURING AND SHORTLY AFTER GROWTH APPEARS IMPORTANT.

The Device Engineer's Wish List to the Materials Engineer

1. SILICON OF LONG MINORITY CARRIER LIFETIME
   (e.g., 0.2 Ω cm p-type with $\tau > 500$ μs)

2. SILICON OF REPEATEDLY UNIFORM LIFETIME
   (not 50-1000 μs)

3. SILICON WHOSE LIFETIME DOES NOT DECREASE DURING NORMAL DEVICE PROCESSING
   (a repeatable, uniform increase is o.k.)

4. SILICON SHEET (WAFER) WHICH IS FLAT, AND STAYS FLAT THROUGHOUT NORMAL DEVICE PROCESSING

5. SILICON WHICH UNIFORMLY HAS REASONABLE MECHANICAL STRENGTH

6. SILICON SHEET OF LOW COST
   (<$50/m^2)

Final Discussion

- FOR HIGHER EFFICIENCIES (AT LEAST > 20%), BETTER SINGLE CRYSTAL Si IS NEEDED.
- IT SHOULD BE POSSIBLE TO BRING Cz Si TO THE SAME LOW-RECOMBINATION LEVEL AS FZ Si.
- HOW CAN DEVICES BE FABRICATED FROM THIS Si WITHOUT GREATLY INCREASING THE RECOMBINATION CENTER DENSITY?
- ARE SPECIAL Si QUALITIES NEEDED TO PERMIT SUCH PROCESSING?
- HOW CAN THE PROGRESS MADE IN MATERIAL SCIENCE BE TRANSLATED INTO BETTER PROCESSING METHODS?
- IF SOLAR CELL FABRICATORS WOULD SPECIFY THE QUALITY OF Si THEY NEED, WOULD Si MANUFACTURERS DELIVER TO THESE SPECIFICATIONS?
- DO SOLAR CELL FABRICATORS KNOW WHAT SPECIFICATIONS TO WRITE?

DISCUSSION

STORTI: How much of a sacrifice in efficiency and lifetime do you see by going down to very low values of resistivity?

WOLF: Calculations of intrinsic defect levels of recombination center densities indicate that the lifetime goes down with one over the impurity concentration. This means that you still would gain by going to a lower resistivity until you reach Auger recombination.

RAO: Regarding hydrogen passivation: are there data that verify if we are passivating the dangling bonds and/or the impurities?

CORBETT: No, it has not been verified. It does passivate sometimes, including the substitutional impurities, and sometimes it doesn't. We have speculations as to why it doesn't but we don't know for sure.

LANE: You've been talking about the defects and their effect on the cell. There is a lot of effort going on in industry today to improve the uniformity of the crystal, the uniformity of the distribution of defects, the uniformity of the impurities, striations, etc. If we get a perfectly uniform crystal and it's still full of impurities or defects, are we no farther ahead or is this effort on uniformity truly important?

WOLF: The device fabricator would like to see ingots all of nearly uniform lifetime from which to make a device.

SCHWUTTKE: If you want high-efficiency solar cells, you must have a uniform minority carrier lifetime over the whole device area. This means the minority carrier lifetime is not allowed to go below a certain limit. It is welcome to go over that limit if you average over the total area.

LESK: Regarding uniformity: I don't think that the material we get today is uniform either, but if making the material uniform drives the cost up too high, then we may still have to accept something that is not uniform but is still pretty good.

JASTRZEBSKI: How far away from the junction do you need a good lifetime?

WOLF: Silicon is an indirect bandgap semiconductor, so some of the photons of the solar spectrum penetrate up to a millimeter. To make devices with high voltage, we make the layers thinner than the diffusion lengths. The lifetime determines how thick we make the layers, therefore, a long lifetime would use a thicker wafer. For a lifetime of 100 µs, a 10-µm-thick wafer would be optimal, while a millisecond lifetime would require 300 to 500-µm-thick wafers.

N86-19725

THE STATUS OF SILICON RIBBON GROWTH TECHNOLOGY FOR HIGH-EFFICIENCY SILICON SOLAR CELLS

T.F. Ciszek

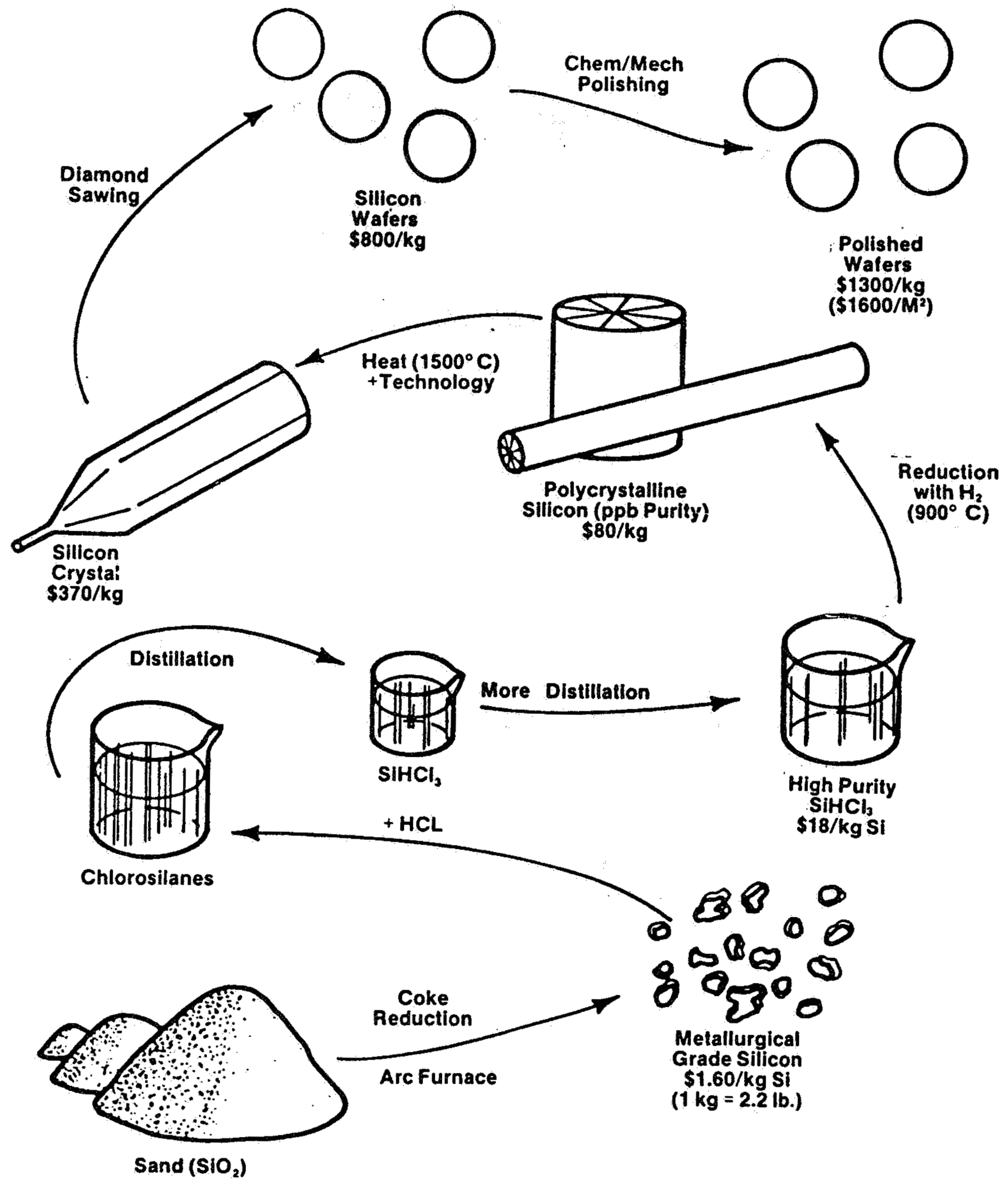
Solar Energy Research Institute
Golden, CO 80401

More than a dozen methods have been applied to the growth of silicon ribbons, beginning as early as 1963. The ribbon geometry has been particularly intriguing for photovoltaic applications, because it might provide large area, damage free, nearly continuous substrates without the material loss or cost of ingot wafering. In general, the efficiency of silicon ribbon solar cells has been lower than that of ingot cells. This presentation reviews the status of some ribbon growth techniques that have achieved laboratory efficiencies greater than 13.5% -- edge-defined, film-fed growth (EFG), edge-supported pulling (ESP), ribbon against a drop (RAD), and dendritic web growth (web).

Conventional silicon ingot technology converts polycrystalline silicon having a market price around $80/kg into polished wafers that sell for about $1300/kg, through cylindrical crystal growth, wafering, and polishing steps. Silicon ribbon growth, starting with the same material, uses one step to achieve damage-free, planar-surface substrates. The accompanying figures detail maximum pulling velocities and surface area generation rates for sheets and ingots, using a simple one-dimensional model. Experimentally, the velocities achieved are 20% to 40% of the calculated ones. Graphical surface area generation rate results from the model are presented both for the case of no rate limitations due to wafering of ingots, and also for the case of combined growth and various wafering technologies. When assessing the relative merits of sheet and ingot growth, in addition to comparing surface area generation rates, one must also remember that ingot technology uses about 100% more raw material and incurs additional wafering and polishing costs.

Schematic diagrams of the four ribbon growth methods discussed in detail in the presentation are shown in the figures. All have achieved lab scale cell efficiencies over 13.5% at AM1, and in fact one method has yielded large-area modules (4675 cm^2) with >13% efficiency. A comparison of the characteristics of the four methods is given in the two tables. It can be seen that no single method possesses all of the attributes one desires in a PV sheet material. Perhaps the ideal sheet growth method is yet to be invented.

PRECEDING PAGE BLANK NOT FILMED



PRECEDING PAGE BLANK NOT FILMED

For Ribbon Crystals

$$V_{max} = \frac{1}{L\rho_m}\left[\frac{\sigma\epsilon(W+t)K_m T_m^5}{W t}\right]^{1/2}.$$

FOR CYLINDRICAL CRYSTALS:

$$V_{max} = \frac{1}{L\rho_m}\left[\frac{\sigma\epsilon K_m T_m^5}{r}\right]^{1/2}.$$

WHERE

T_m = MELTING TEMP

K_m = THERMAL COND. AT Tm

ρ_m = CRYSTAL DENSITY AT Tm

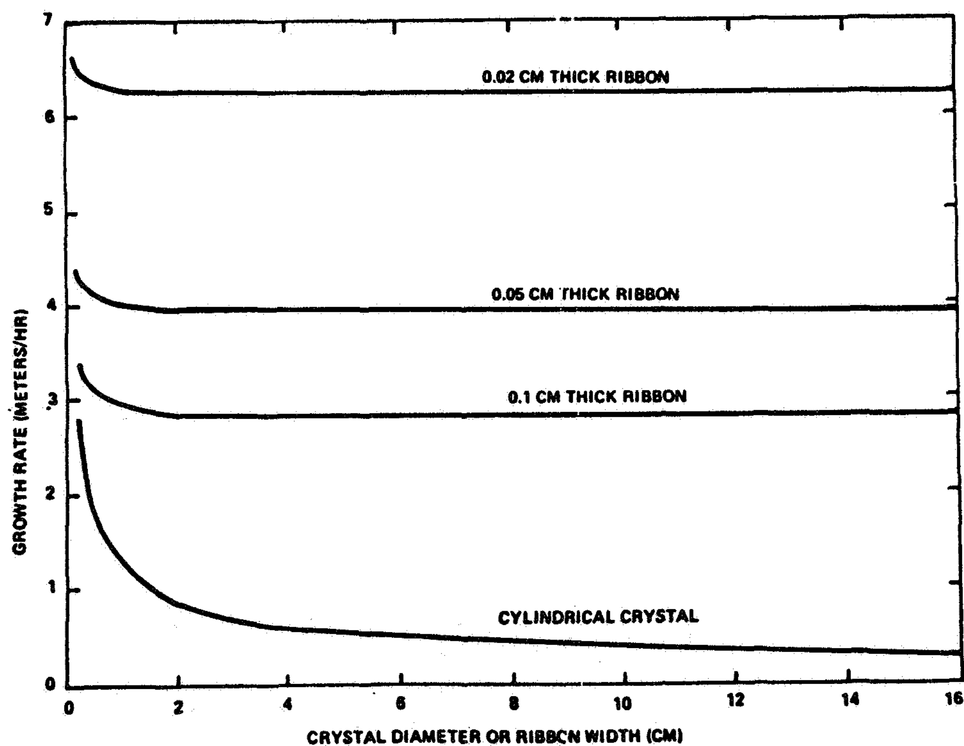
σ = STEFAN-BOLTZMANN CONST.

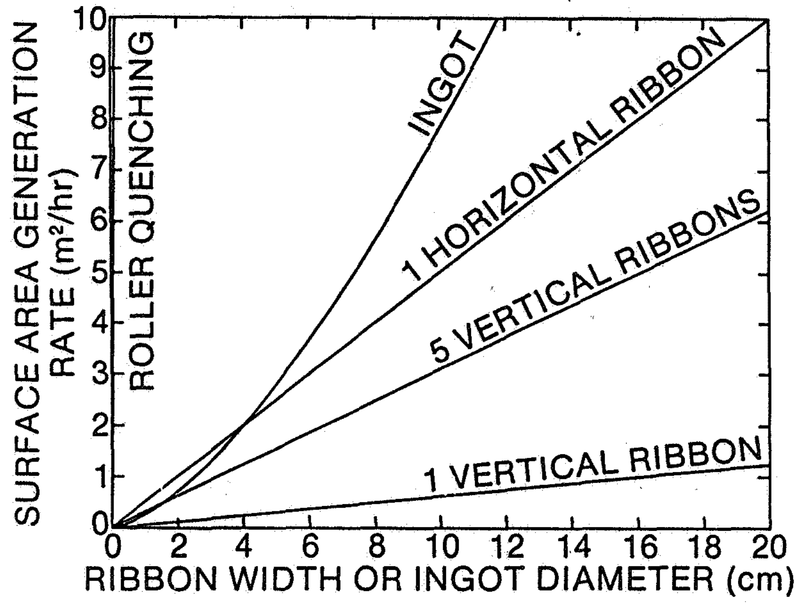
ϵ = EMISSIVITY

W = RIBBON WIDTH

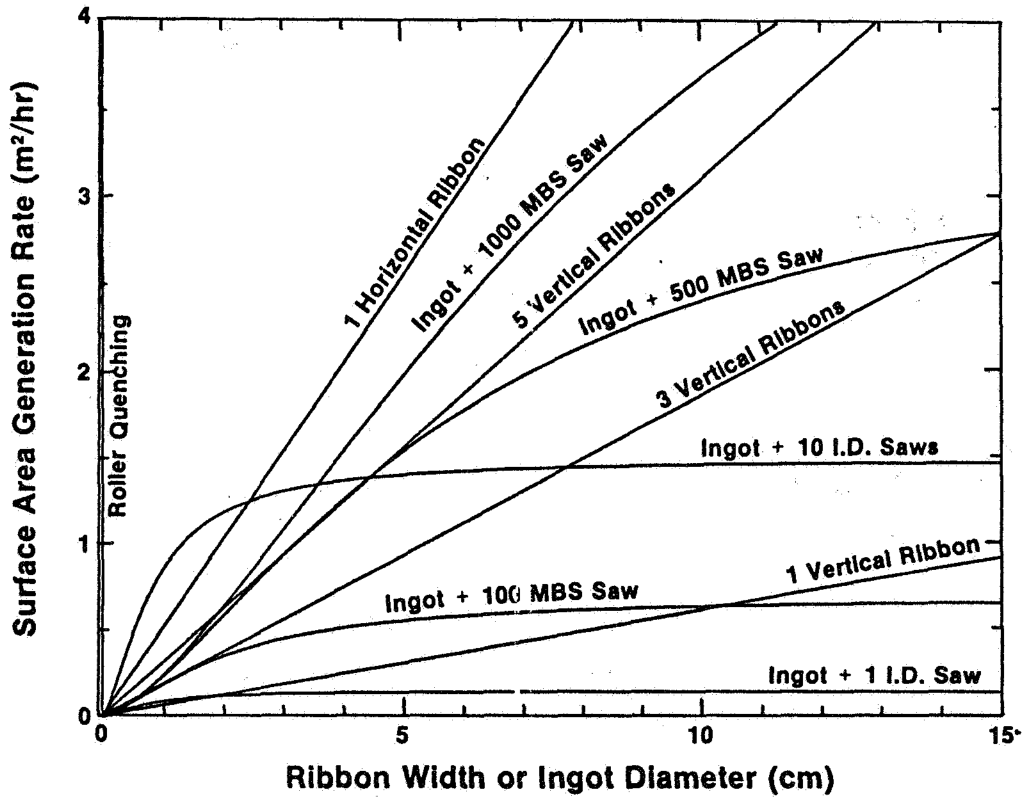
t = RIBBON THICKNESS

r = CRYSTAL RADIUS

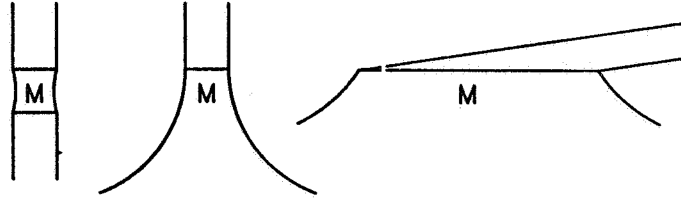




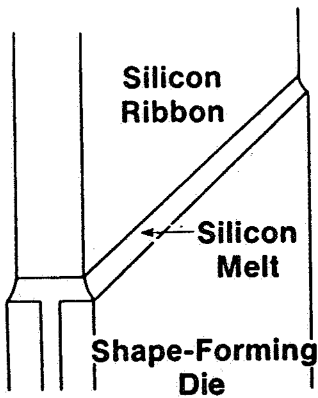
SURFACE AREA GENERATION RATE (m²/hr)
ROLLER QUENCHING
INGOT
1 HORIZONTAL RIBBON
5 VERTICAL RIBBONS
1 VERTICAL RIBBON
0
1
2
3
4
5
6
7
8
9
10
0
2
4
6
8
10
12
14
16
18
20
RIBBON WIDTH OR INGOT DIAMETER (cm)

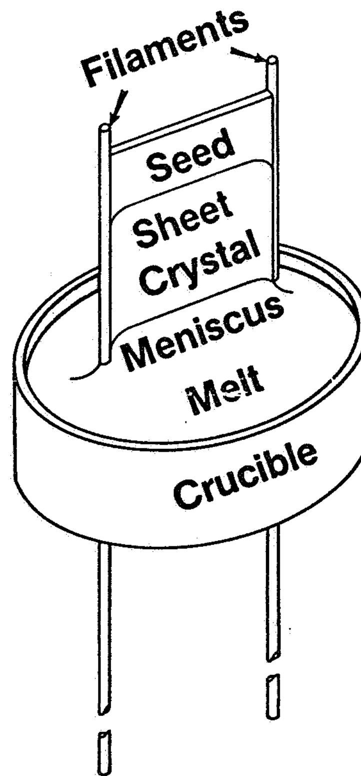


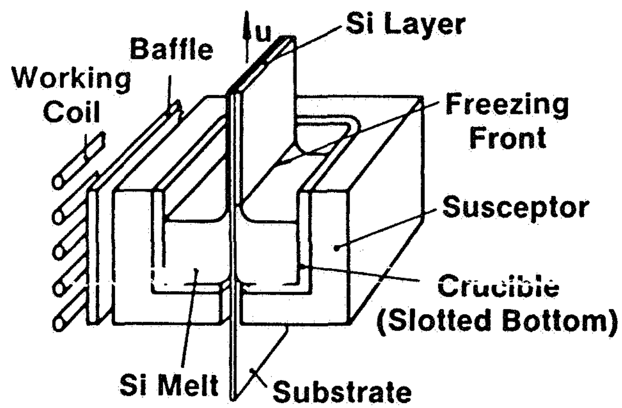
Surface Area Generation Rate (m²/hr)
Roller Quenching
1 Horizontal Ribbon
Ingot + 1000 MBS Saw
5 Vertical Ribbons
Ingot + 500 MBS Saw
3 Vertical Ribbons
Ingot + 10 I.D. Saws
1 Vertical Ribbon
Ingot + 100 MBS Saw
Ingot + 1 I.D. Saw
0
1
2
3
4
0
5
10
15
Ribbon Width or Ingot Diameter (cm)



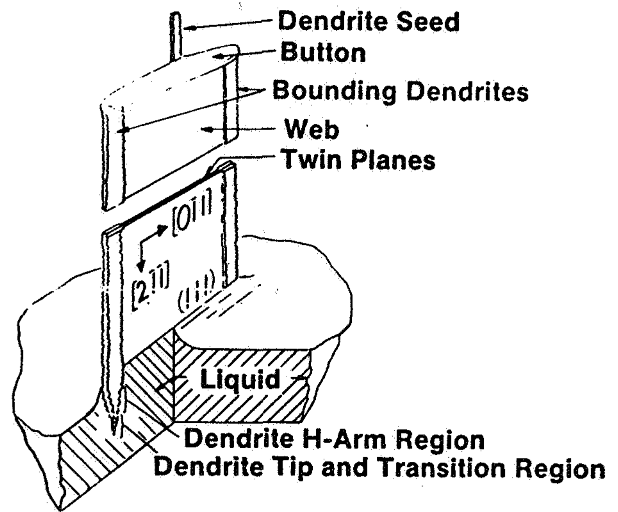
- DENDRITIC WEB (WEB,1963)
- STEPANOV (S,1967)
- EDGE-DEFINED, FILM-FED GROWTH (EFG,1972)
- HORIZONTAL RIBBON GROWTH (HRG,1975/ LASS,1980)
- RIBBON-AGAINST-DROP (RAD,1976)
- RIBBON-TO-RIBBON ZONING (RTR,1976)
- SILICON-ON-CERAMIC (SOC,1976)
- CAPILLARY ACTION SHAPING TECHNIQUE (CAST,1977)
- CONTIGUOUS CAPILLARY COATING (CCC,1977/ S-WEB,1982)
- INVERTED STEPANOV (IS,1977)
- ROLLER QUENCHING (RQ,1979)
- EDGE-SUPPORTED PULLING (ESP,1980)
- INTERFACE-CONTROLLED CRYSTALLIZATION (ICC,1981)



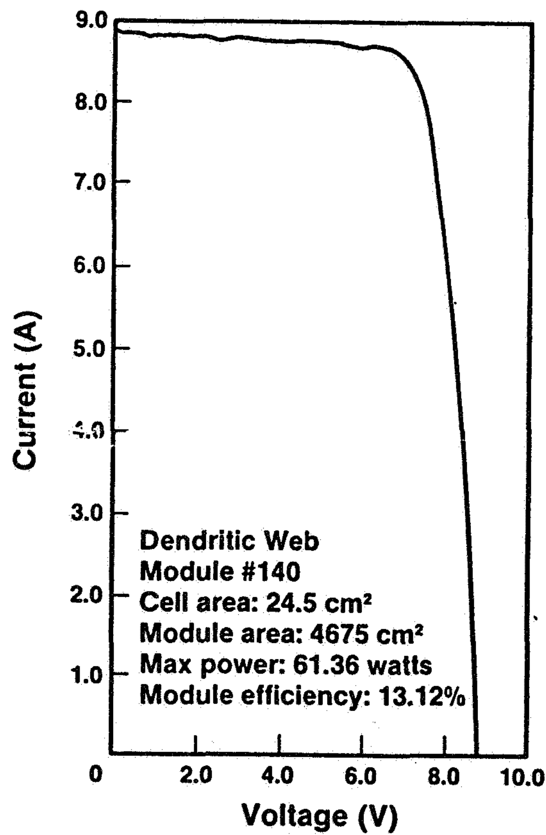




Si Layer
Baffle
Working Coil
Freezing Front
Susceptor
Crucible (Slotted Bottom)
Si Melt
Substrate
u



Dendrite Seed
Button
Bounding Dendrites
Web
Twin Planes
Liquid
Dendrite H-Arm Region
Dendrite Tip and Transition Region



Current (A)
Voltage (V)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.0
4.0
6.0
8.0
10.0
Dendritic Web
Module #140
Cell area: 24.5 cm²
Module area: 4675 cm²
Max power: 61.36 watts
Module efficiency: 13.12%

Stability and Purity

	EFG	ESP	RAD	WEB
MENISCUS HEIGHT (mm)	~0.5	~6	~6	~6
THERMAL CONTROL (°C)	~1	1–10	1–10	0.1–1
SURFACE MORPHOLOGY	RIPPLED, STRIATED	SMOOTH, BOWING	FLAT (2um)	VERY SMOOTH
IMPURITY SOURCES	DIE, CRUCIBLE	FILAMENTS	CARBON RIBBON	HOT ZONE PARTS
IMPURITY SEGREGATION	$k_e \sim 1$	$k_o < k_e < 1$	$k_e < 1$	$k_o < k_e < 1$
USE OF IMPURE SILICON	NO	YES	YES	WITH RESTRICTIONS
AREAS OF CONCERN	IMPURITIES, STRESSES	BOWING, STRESSES	IMPURITIES, STRUCTURE	WIDTH, STRESSES

Growth Characteristics

	EFG	ESP	RAD	WEB
GROWTH RATE (cm/min)	2	2	10	2
MAXIMUM WIDTH (cm)	45	10	10	6
TYP. THICKNESS (microns)	200	200	80	160
MAXIMUM LENGTH (meters)	30	~1	30	11
CRYSTAL STRUCTURE	TWINS,GB'S SIC INCLUS	LARGE GRAINS	NARROW GRAINS	SINGLE (111)TWIN
SOLAR CELL EFFICIENCY (%)	14 (12)	14 (12)	13.5(11)	16 (13)
TECHNOLOGY/ SKILL	HIGH	LOW	LOW	HIGH

Criteria for the ''Ideal'' Sheet Growth Method

- **Good Crystal Perfection**
- **Flat Smooth Surface**
- **High Purity**
- **Easy Control**
- **High Throughput**

DISCUSSION

KALEJS: Regarding your comment on the tolerance for impurities, there are really two issues that have to be distinguished. To control the interface, there is really only one parameter that counts, which is the interface gradient. All these methods have about the same tolerance when it comes to the stability with respect to perturbations due to constitutional supercooling. The tolerance you are referring to was basically the tolerance in the actual amount of impurities segregated where certainly EFG, with K_{eff} equal to unity, is at a disadvantage. When you start using metallurgical grades of silicon, it is only the interface gradient that determines the constitutional supercooling that counts. It has been shown in 1980 in web, for example, that 10^{18} impurities start a significant breakdown of the web dendritic structure. We find that in EFG at about 10^{18}, we have about the same effects. You start losing efficiency, not perhaps because of point-defect impurity problems but because of structural breakdown. Again, this is only a function of the gradient.

CISZEK: For the purpose of this symposium, which is on high-efficiency cells, that point is moot anyway. No one would want to use very impure poly to try to achieve high-efficiency cells. It would become more of a concern if you were trying to make low-cost cells using a lower-cost feedstock at the sacrifice of efficiency.

CORBETT: Can you tell us any more about your comment about the molybdenum and iron?

CISZEK: It's borrowed work from researchers at Mobil. I believe the experiment was done by progressively increasing the amounts of the electrically active dopant to bring the resistivity levels down in the melt during the growth of a single ribbon. When the resistivity was down to about 0.2 Ω-cm then a small amount of molybdenum was added, and then a short time after that a small amount of iron was added, and then the cells were made. It must imply interaction between point defects and non-metallic impurities with these metallic impurities. It's a region of very active research interest now, to try to understand these effects better.

CORBETT: Would you care to speculate on how much improvement continued effort in ribbons might yield?

CISZEK: There is certainly going to be some, and my own personal feeling is that there probably is a ribbon growth method that hasn't even been discovered yet that would have a lot better properties. It should be, in principle, possible to grow a ribbon that is truly single-crystal without twin planes or dislocations. It should have at least as good and probably better properties than the ingots, because of the close proximity of the surface to any point defects within the material during the cooldown cycles, and hence there is

the possibility of eliminating these to the surface, by vacancy climbing or even interstitial moving during the cooldown cycle. This ideal technique has not yet been discovered. With the techniques we have to work with, we make the assumption that we are going to live with coherent twins as a minimum in the material, and we are going to live with oxygen and possibly some carbon in the material, and then we ask how can we passivate or getter the material to get the best results. In that kind of approach you are never really going to get quite as good as ingot material, although you should be able to get to a value perhaps 95% as good as ingot material.

STORTI: Do we have very good numbers on what in fact are the minority carrier diffusion lengths of these different ribbon technologies for the given doping? And do we have an idea as to how much those particular things can be improved or what those particular values are at the moment?

CISZEK: We don't have anything like a round-robin where a particular technique has been applied to measuring the diffusion length in all the materials. I know that there is some variety in the approaches that are used. For example, Belouet and his coworkers working on the ribbon-against-drop method use an electrolytic sort of contact to measure diffusion length in the material. Westinghouse uses the surface photovoltage (SPV) technique and photoconductive decay, and Mobil uses SPV.

STORTI: The reason I bring up the question is that it is possible to process devices in such a way that you can get efficiencies that look quite good, even though the diffusion length is not tremendously high.

CISZEK: We don't have a standardized method that's been used to systematically compare the different growth methods and tell what their diffusion lengths are. Recently there have been some intriguing things noticed about diffusion length or lifetime as a function of cooling rate of some of the ribbon techniques. People are discovering that because the ribbons cool so quickly, there is some sort of a quenching problem that is lowering the lifetime, but this can be recovered by a subsequent heat treatment (around 1000° or higher for some length of time) followed by a slow cooling, which can bring the lifetimes back up.

LESK: What number of slices per inch did you use for your cutting efficiency?

CISZEK: I used 2,000 per meter for ID sawing and 2,500 per meter for multiblade wafer sawing.

KIM: In your calculations, you assumed a relatively simple radiational heat loss. If you included a back radiation from the thermal environment that could decrease your maximum growth rate significantly.

CISZEK: Definitely. The values here are high. I look at them as upper limits, that you are not going to exceed. They are a goal you can

work toward. The calculated values are all too high and, interestingly enough, they are high in a way that real rates are 20% to 40% as high as the calculated rates both for the ingots and for the ribbon. In the case of ingots, the 40% numbers would come from float-zone-type growth and the 20% numbers would come from Czochralski-type growth. The ribbons stay around 20% to 30% of maximum values because if they try to go faster, thermal stresses and buckling and things like that become significant problems.

RAO: Have you grown material from quartz crucibles and from graphite crucibles, and do you see similar kinds of effects between ESP and EFG materials?

CISZEK: We have done all of our ESP work using quartz crucibles. We did use a number of different filament materials including quartz and some graphite filaments. Arthur D. Little Corp. uses graphite crucibles in the technique. I don't think a whole study has been pulled together to compare influences of the different impurities -- even within ESP, let alone comparing ESP to EFG. In principle it could be done, but it has not been done.

N86-19726

FUTURE APPLICATION OF CZOCHRALSKI CRYSTAL PULLING FOR SILICON

J.H. Matlock

S.E.H. America
Vancouver, WA 98662

Czochralski (Cz) crystal pulling has been the predominant method used for preparing for silicon single crystal for the past twenty years. The fundamental technology used has changed little for 25 to 30 years. However, great strides have been made in learning how to make the crystals bigger and of better quality at ever increasing productivity rates. The question that exists today is whether this technology has reached a mature stage. Are limits in crystal size and productivity being reached? The answers at this point are not clear yet.

Currently charge sized of 50Kg of polycrystal silicon are being used for production and crystals up to ten inches in diameter have been grown without major difficulty. The largest material actually being processed in silicon wafer form is 150mm (6 inches) in diameter.

Recent efforts in Cz silicon development have concentrated on continuing the increase in wafer size and in higher productivity for lower costs. Also much effort has been extended in regard to the macroscopic and microscopic control of impurities in Cz crystals. Oxygen content is a special challenge for control as one must balance the dissolution rate of the quartz crucible, the free and forced convection in the silicon melt and the rate of surface evaporation. Much has been done here by programming changes in the crystal growth parameters throughout the process.

For control of dopant incorporation one must look for ways to balance natural segregation effects. The use of programmed reduced pressure (for a volatile element), the double crucible method and recharging have aided in this regard. Growing of crystals in a magnetic field has proved to be particularly useful for microscopic impurity control. Major developments in past years on equipment for Cz crystal pulling have included the automatic growth control of the diameter as well as the starting core of the crystal, the use of magnetic fields around the crystal puller to supress convection, various recharging schemes for dopant control and the use of continuous liquid feed in the crystal puller.

Continuous liquid feed, while far from being a reliable production process, is ideal in concept for major improvement in Cz crystal pulling. It combines a high theoretical productivity with the dopant leveling characteristics of the double crucible method. The buildup of unwanted impurities is much slower than for the use of recharging. It would seem that enough future promise exists for this method that further development is definitely warranted.

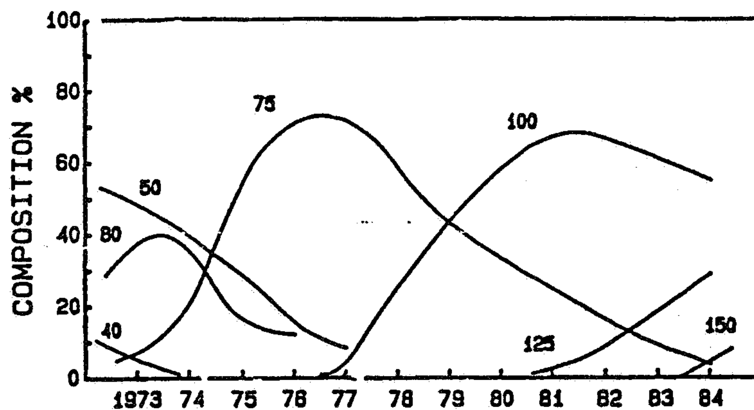
What other major breakthroughs exist for Cz crystal pulling are not certain, but what is clear is that this process will maintain its dominance of silicon crystal production for a number of years.

Cz Process

- LITTLE CHANGE IN FUNDAMENTAL TECHNOLOGY FOR 25 TO 30 YEARS
  - JUST
    MORE
    BIGGER
    BETTER
- ARE REASONABLE LIMITS BEING REACHED?

  IS PROCESS REACHING MATURITY?
  - NOT CLEAR YET

Silicon Wafer Diameter Trend (Area Gain)

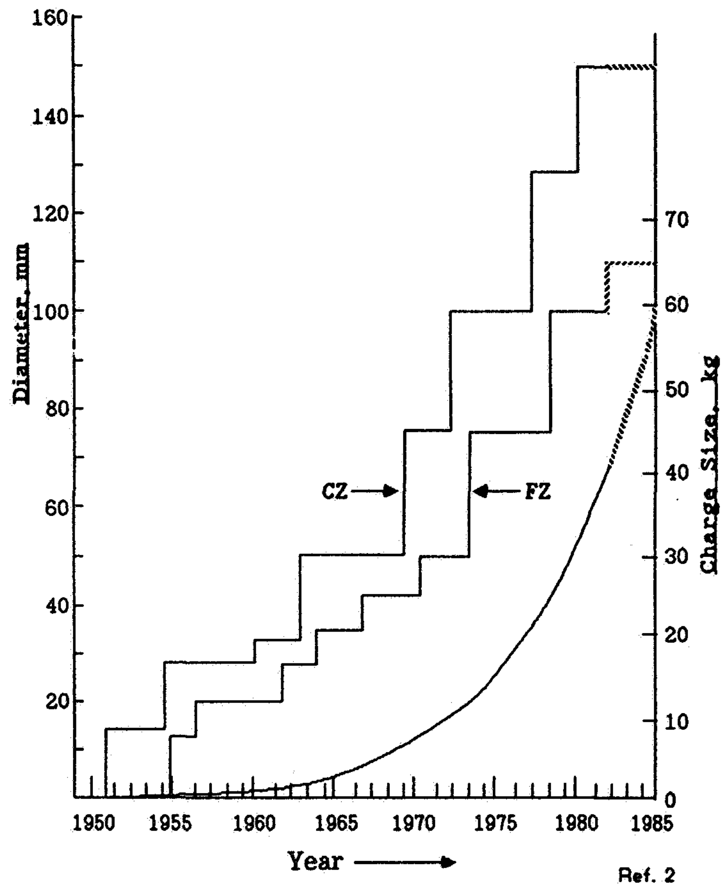


Silicon wafer diameter trend (area gain). 200mm diameter wafers are expected as next generation IC devices.

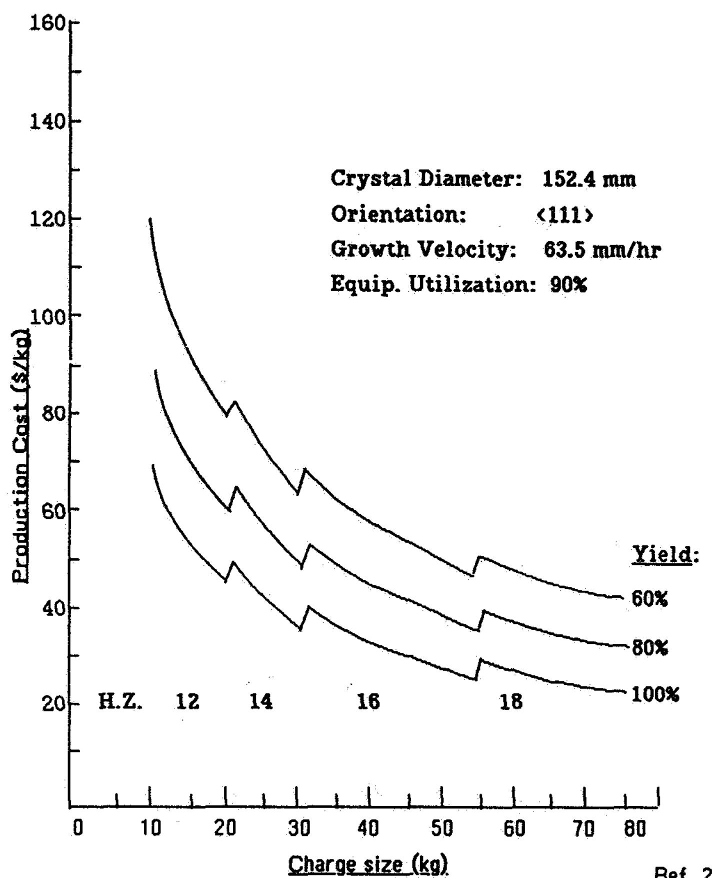
PRECEDING PAGE BLANK NOT FILMED

REF (1)

Cz/FZ Crystal Diameters and Cz Charge Sizes



Crystal Production Costs Dependent on Charge Size and Yield



Ref. 2

Goals of Silicon Cz Development

- LOWER COST / HIGHER PRODUCTIVITY
- LARGER WAFER SIZE
- IMPURITY CONTROL
  - DOPANTS
  - OXYGEN
  - OTHERS
- DEFECT CONTROL

Reduce Cost, Increase Productivity

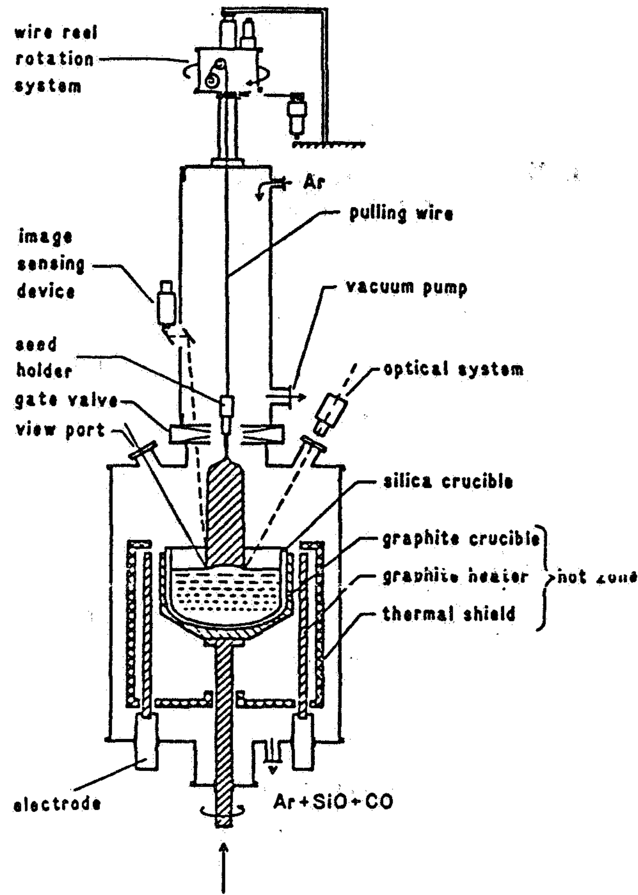
- INCREASE YIELD
- INCREASE PULL SPEED
- INCREASE CHARGE/BATCH SIZE
- DECREASE SUPPLY COST / UNIT

Current Production Process

- 30 - 50 KG CHARGE
- 150MM DIAMETER CRYSTAL
- 12 - 16 INCH HOT ZONE

DEVELOPMENT PROCESS

- UP TO 100KG
- UP TO 250+ MM DIAMETER
- 16 - 18 INCH HOT ZONE



Schematic drqwing of a Czochralski pulling equipment with heating, automatic optical and image sensing diameter controls, a valve between furnace and front opening chamber and wire reeling system.

REF (1)

Impurity Control

- OXYGEN - MAJOR IMPURITY
  - CONTINUOUS ADDITION FROM CRUCIBLE DISSOLUTION
  - SEGREGATION COEFF ≈ 1.0

    MUST CONSIDER:

    DISSOLUTION RATE

    FREE CONVECTION

    FORCED CONVECTION

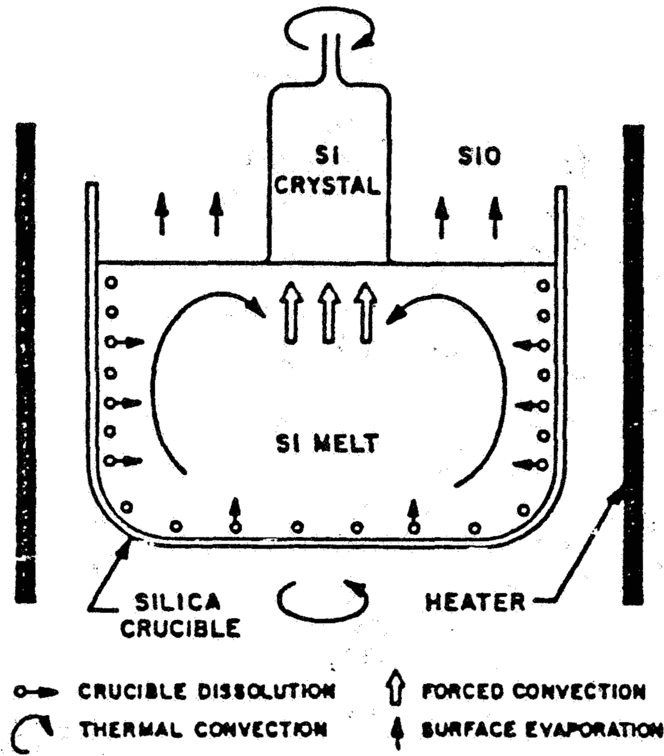
    SURFACE EVAPORATION
- DOPANTS

  MUST COMBAT SEGREGATION EFFECTS

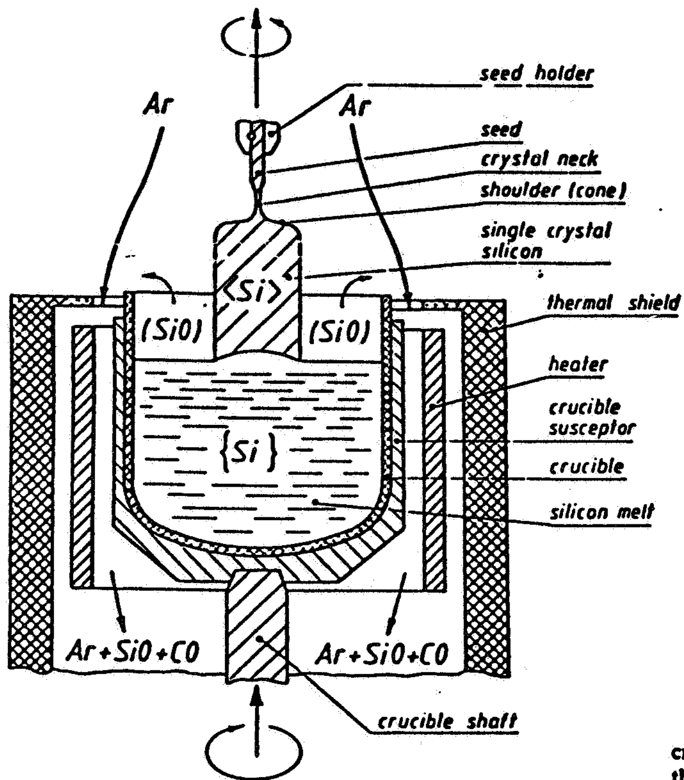
  AND KEEP AT DESIRED LEVEL
- OTHER IMPURITIES (INCL. C)

  MUST COMBAT SEGREGATION EFFECTS

  AND KEEP AS LOW AS POSSIBLE

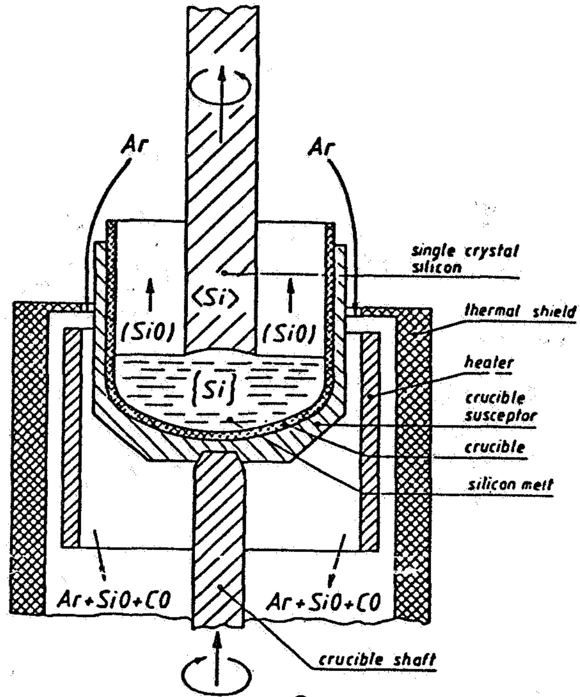


Schematic of a CZ growth system showing relationship between oxygen controlling functions.

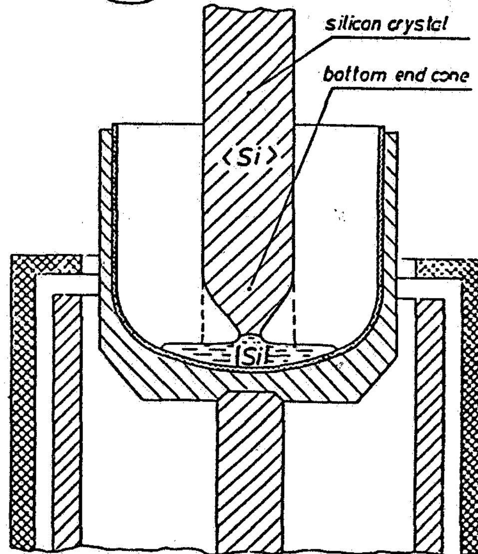


Czochralski single crystal pulling; initial stage of the process

REF (4)

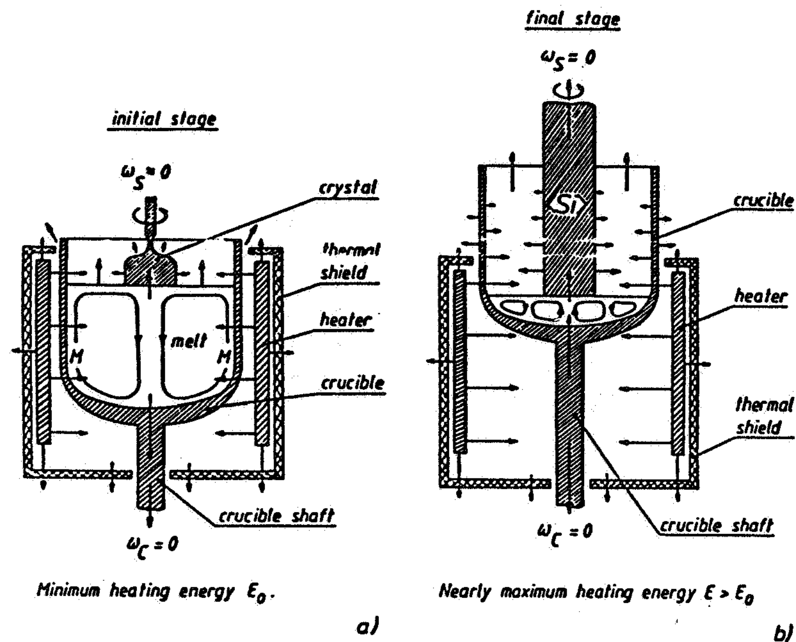


Czochralski single crystal pulling; advanced stage of the process



REF (4)

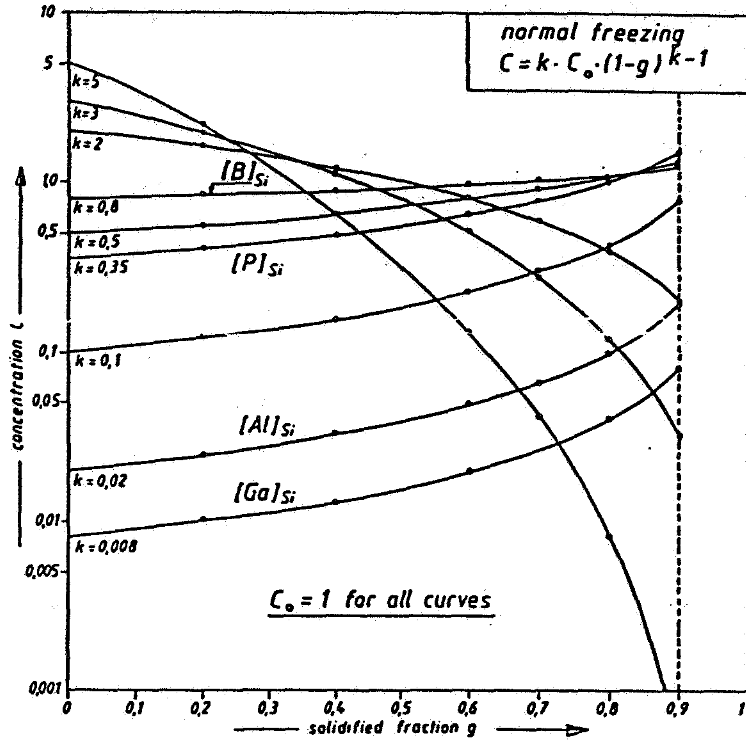
Czochralski single crystal pulling; final stage of the process. If the crystal would have the shape of the dashed lines, it could not be finished dislocation-free



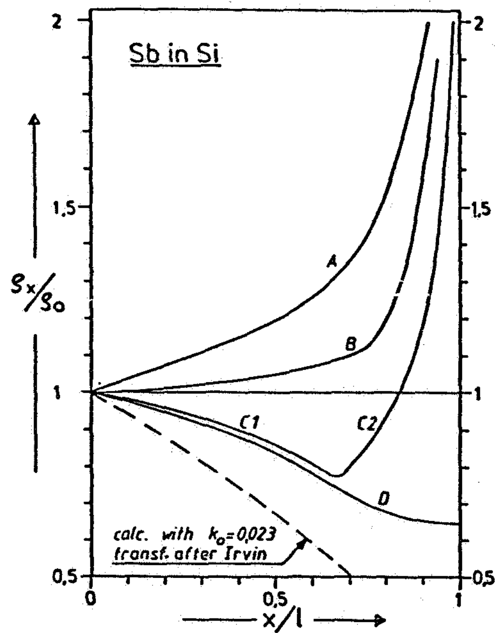
Heat flow conditions during CZ crystal growth. The *arrows* indicate the approximate direction of the heat flow. a shows the initial stage (= short crystal) and b the final stage (= end of cylindrical crystal) of the growth

Dopant Control

- PRESSURE CONTROL
  (FOR VOLATILE ELEMENT)
- DOUBLE CRUCIBLE
- RECHARGE
- MAGNETIC FIELD
  - MICROSCOPIC CONTROL

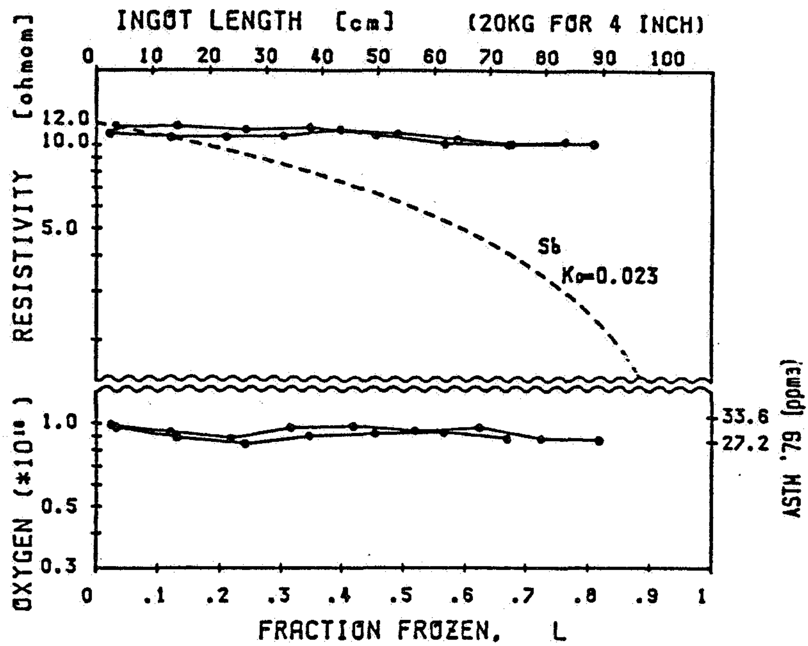


Axial impurity distributions for normal freezing and different k values according to Pfann[33, 34)]



Axial resistivity variations in antimony-doped CZ Si single-crystals. The initial doping concentration (= 0.018 Ωcm), melt volume and crystal diameter were the same for all curves. Due to the high vapour pressure of Sb, a great variety of axial resistivity profiles can be realized by applying different pressure and gas flow conditions. *Curves A* and *B:* Same pressure of 11 mbar but different gas flow characteristics. *Curve C:* 67 mbar in region C1, 11 mbar in region C2. *Curve D:* 75 mbar

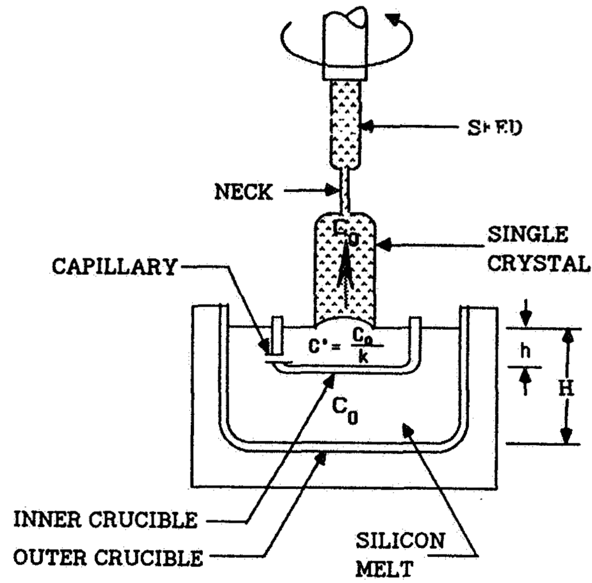
Improved Sb Concentration Distribution by Pressure Control



Constant resistivity distributions along the growth direction. The resistivity and oxygen distributions of lightly Sb-doped CZ crystals were grown by the controls of furnace pressure and crucible rotation rate for Sb an oxygen, respectively.

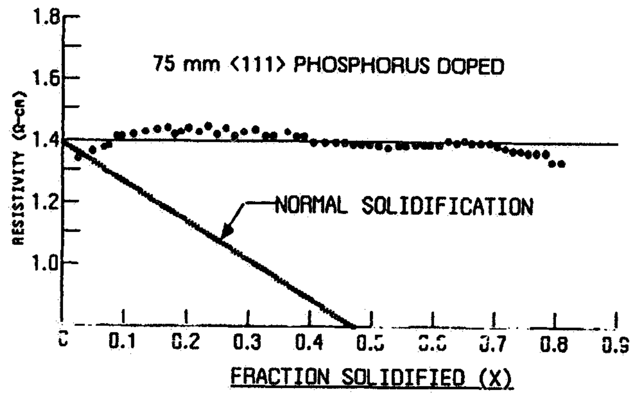
REF (1)

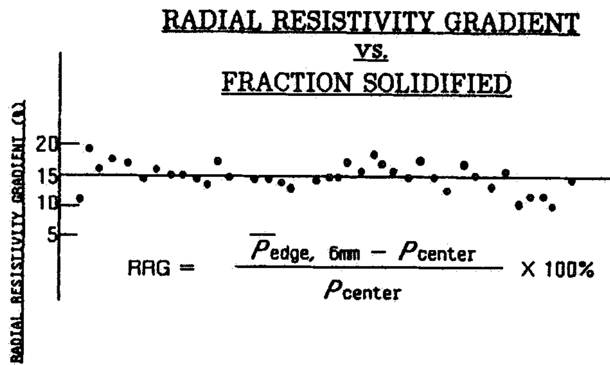
Schematic Representation of a Double-Crucible Growth Arrangement



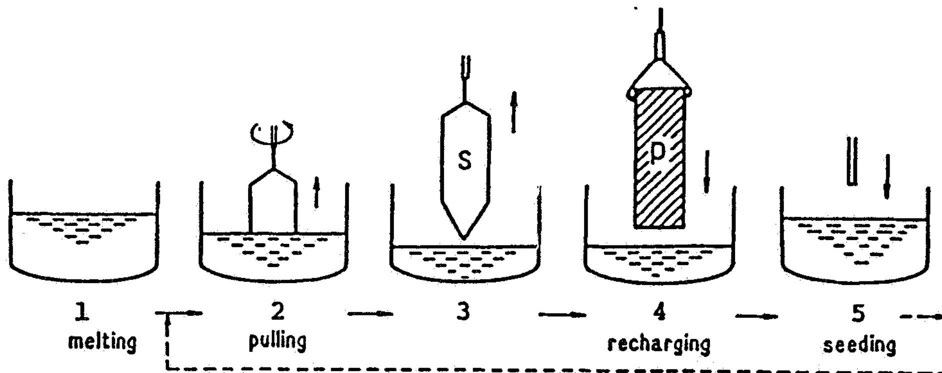
REF (3)

Axial Resistivity Profile of Double-Crucible-Grown Crystal



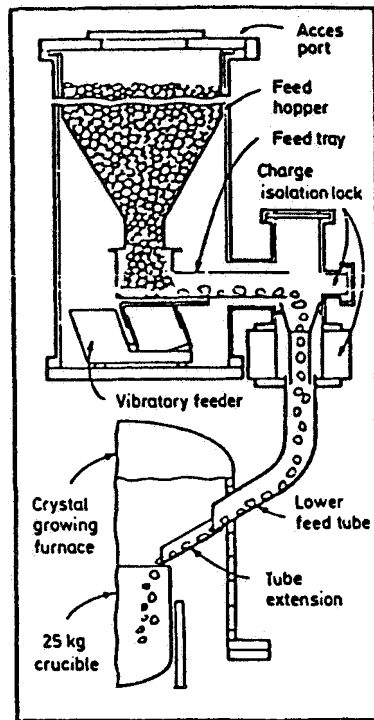


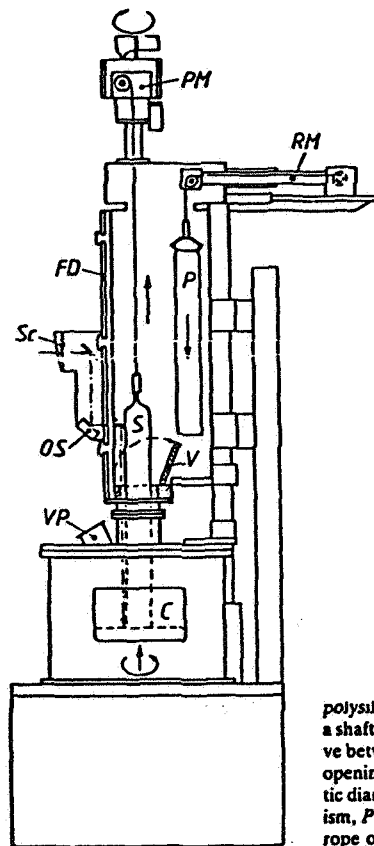
REF (3)



Recharging method. The tight resistivity ranged crystal is pulled with leaving Si melt in a crucible and then feed material together with dopant impurity are melted to grow the second crystal.

Recharging the Hot Crucible With Polysilicon Chips





CZ crystal puller with recharging equipment for a polysilicon rod and crystal pulling by rope or chain instead of a shaft. *S* = single crystal, *C* = crucible, *V* = separating valve between furnace and front opening chamber, *FD* = front opening door, *Sc* = screen, *OS* = optical system for automatic diameter control, *VP* = view port, *PM* = pulling mechanism, *P* = poly-silicon rod, *RM* = recharging mechanism with rope or chain. According to Lane and Kachare[237]

Defect Control

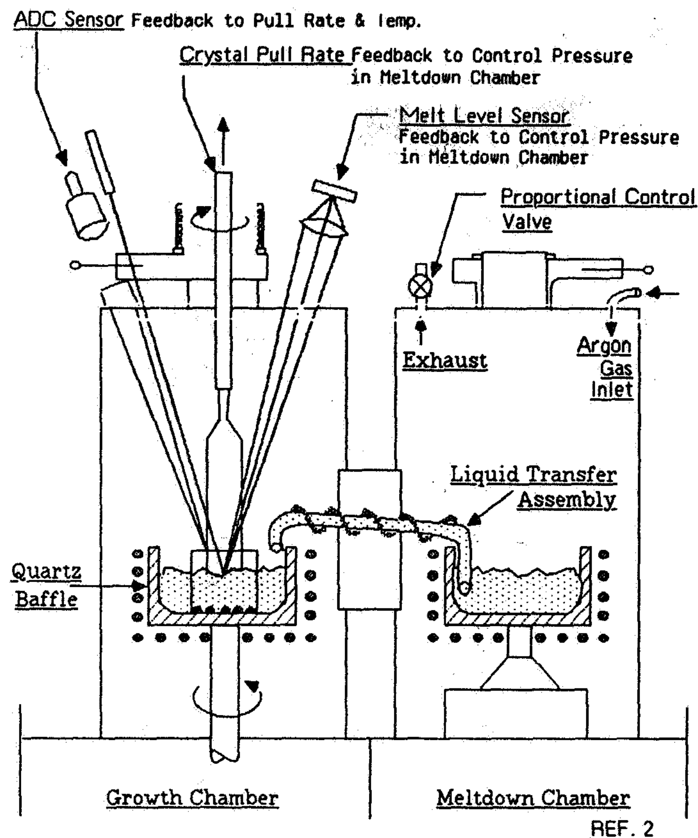
CONSISTENT
THERMAL ENVIRONMENT
NEEDED THROUGHOUT
CRYSTAL GROWTH CYCLE.

Major Equipment Developments

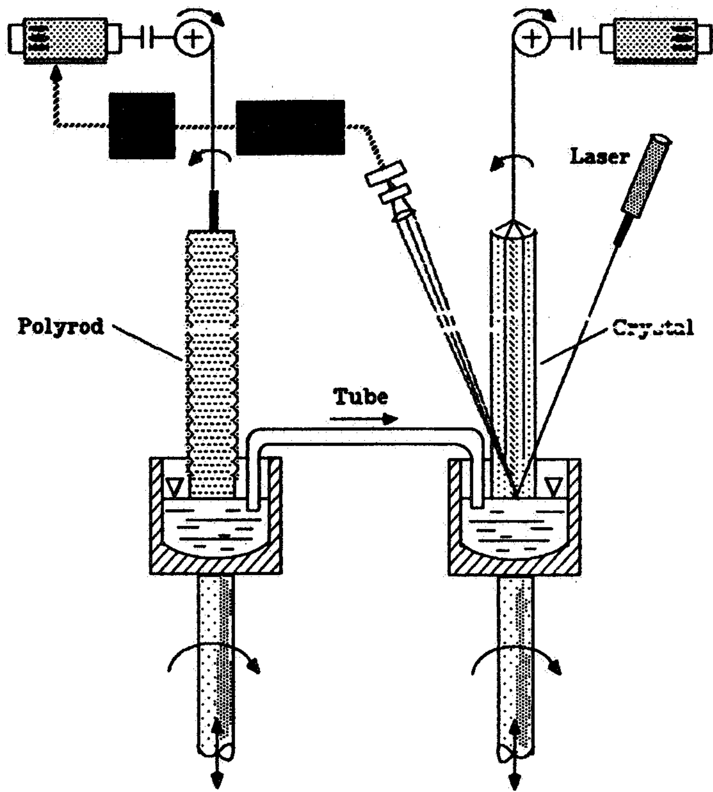
- AUTOMATIC GROWTH CONTROL
  - DIAMETER
  - CONE
- MAGNETIC CZ
- RECHARGING
- CONTINUOUS LIQUID FEED
  - IDEAL IN CONCEPT

ORIGINAL PAGE IS OF POOR QUALITY

Concept of CLF Furnace

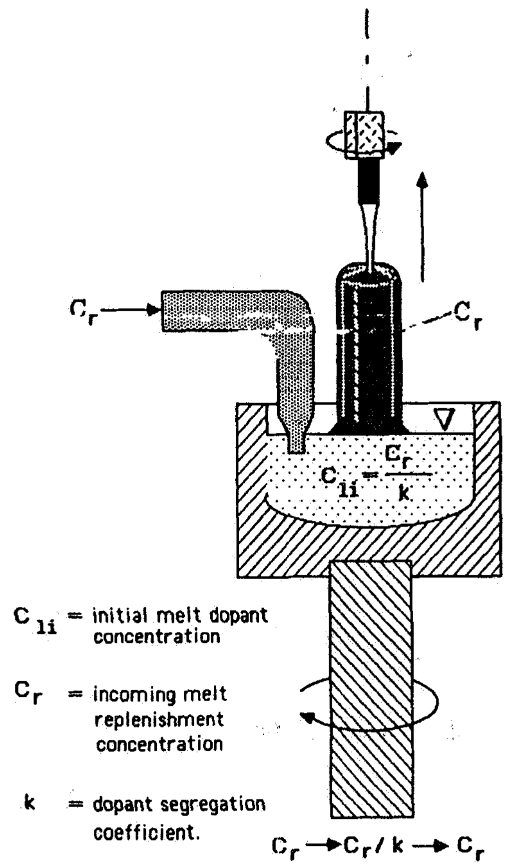


Arrangement for Continuous Melting and Solidification



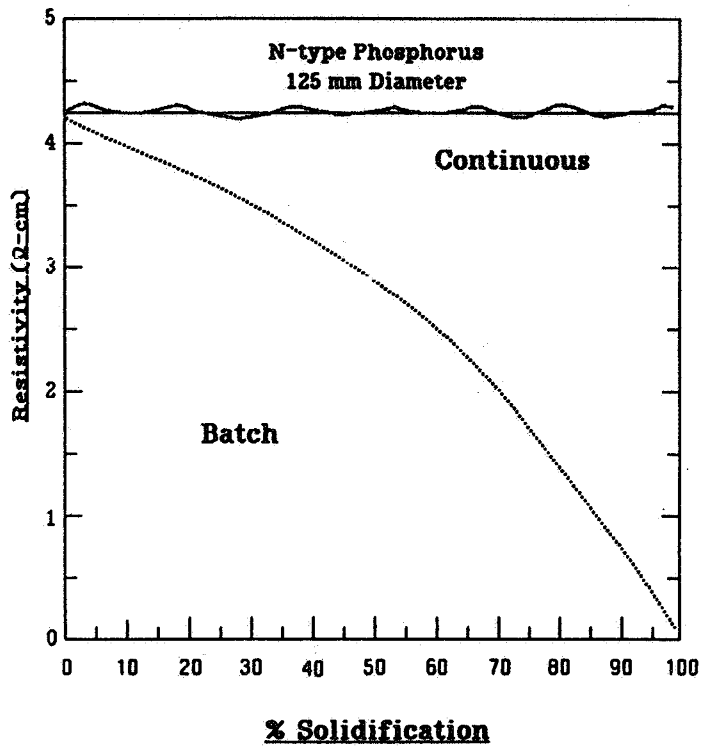
Ref. 2

Doping Concentration Relationship, CLF Furnace



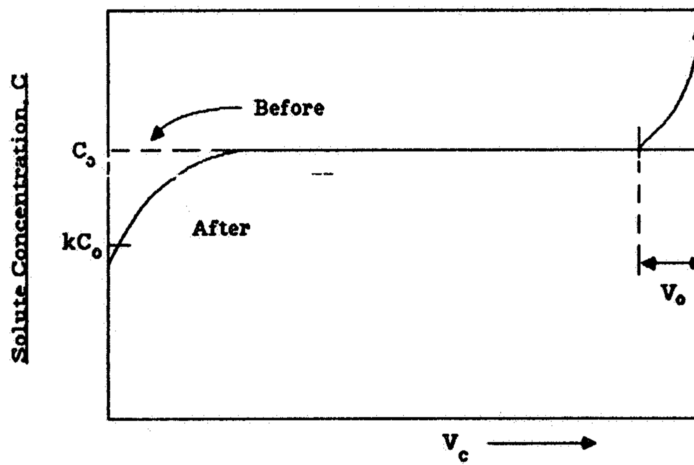
Ref. 2

Axial Resistivity Profile, CLF Furnace



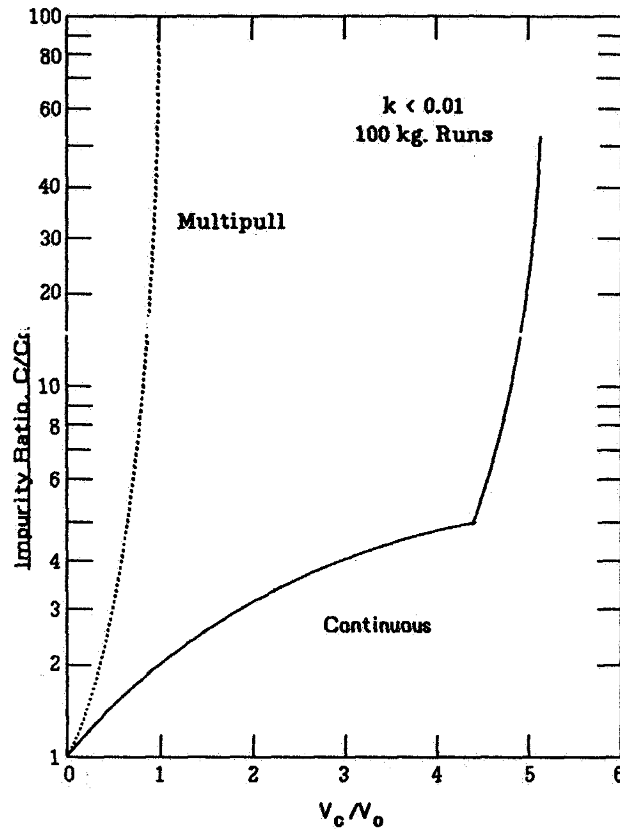
Ref. 2

Solute Concentration Buildup, CLF Furnace



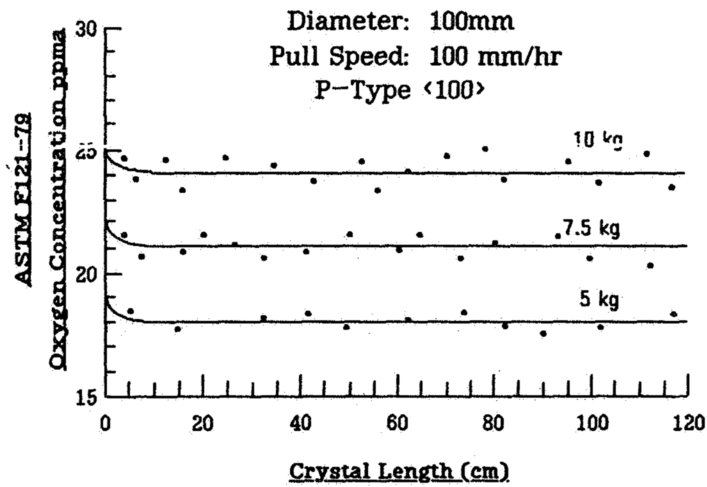
Ref. 2

Impurity Buildup, Continuous vs Batch

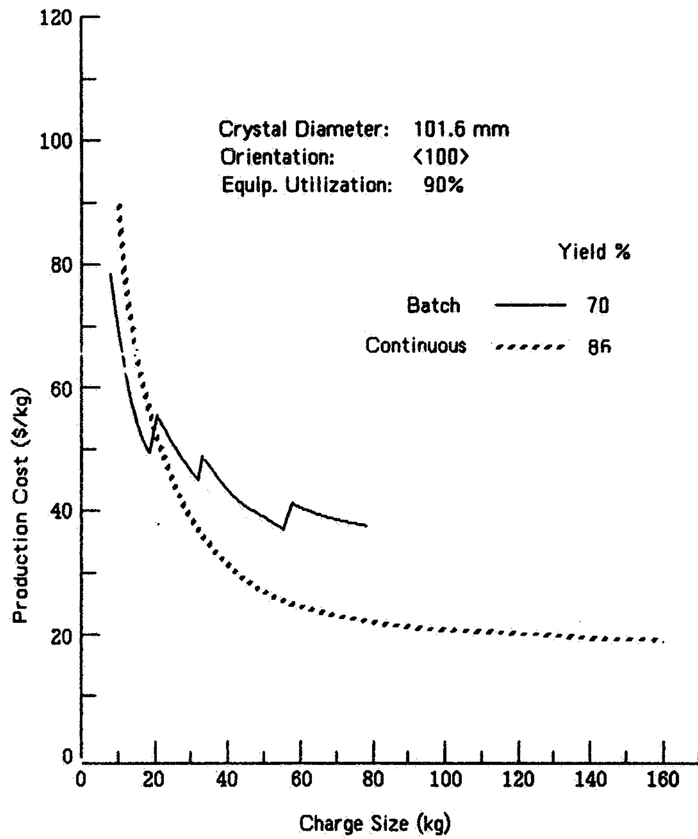


Ref. 2

Oxygen Distribution in Crystal, CLF Furnace



Crystal Production Costs, Batch vs Continuous



Ref. 2

What is the Future of the Cz Process?

- MAIN EFFORTS NOW
  STILL

  MORE
  BIGGER
  BETTER

  OF SAME PRODUCT
  AND PROCESS

- WHAT IS NEXT???

References

(1) T. Abe, to be published.

(2) G. Fiegl, Solid State Technology, August 1983, p.121.

(3) K. Benson, W. Lin, E. Martin, Semiconductor Silicon - 1981, ECS, 1981, p.33.

(4) W. Zulehner and D. Huber, Crystals - 8, 1982.

(5) W. Lin, D. Hill, Silicon Processing, ASTM STP 804, ASTM, 1983, p.24.

(6) A. Murgai, Silicon Processing, ASTM STP 804, ASTM, 1983 p.39.

(7) P. Burggraaf, Semiconductor International, October 1984, p.54.

DISCUSSION

LESK: Do you feel that 70% production yield is a good practical figure?

MATLOCK: On a standard Czochralski process, yes.

STORTI: What are the primary sources of the heavy-metal impurities?

MATLOCK: One of the sources is the polycrystal itself, particularly as it is enriched through the process. The reactors where the polycrystals are grown have a lot of silver in the environment, and nickel parts. The Czochralski chamber and the seed holder have metal parts where some evolution of that metallic impurity is bound to occur.

MORRISON: We are led to understand that a very open dialogue exists between producers and users in Japan and that part of the success of the industry in Japan is due to that open dialogue. Do you see any kind of a dialogue opening up in this country that is going to help the users and the producers reach some state of excellence and understanding?

MATLOCK: Yes, I certainly do, and I think that a number of companies have become very intimately involved in that kind of interactive dialogue to maximize material effects on device performance.

N86-19727

POTENTIAL PRODUCTIVITY BENEFITS OF FLOAT-ZONE vs CZOCHRALSKI CRYSTAL GROWTH

Takao Abe

Shin-Etsu Handotai (SEH)
Japan

An efficient mass production of single crystal silicon is necessary for ULSI fabrication, as well as high-efficient silicon solar arrays for the coming decade. However, it is anticipated that much difficulty to grow such volumes of crystals using conventional Cz method exists. The productivity of single crystals might increase with crystal diameter increase. Even if we succeed, however, to grow large diameter Cz crystals, there are the following two barriers for mass production: One is the long cycle time of operation due to slow-growth rate and large heat-capacity of the furnaces. Second is the large resistivity gradient along the growth direction of crystals due to impurity segregation.

On the other hand, the possibilities of using the FZ method for mass production are described in this paper. Until now, this method has not been heavily used due to the technical and operational issues for growing crystals and the quality issues of the lack of intrinsic gettering (IG) and weakness from dislocation generation.

The comparisons between FZ and Cz crystal growth on the basis of 150 mm in diameter show that the productivity of FZ method is two to four times higher than that of the Cz method. This markedly large productivity is brought from high-growth rates and the steady-state growth system of FZ method in regard to maintaining the dislocation-free condition and impurity segregation, respectively. In addition, the strengthening effects of dislocation generation are introduced from our recent studies.

We will emphasize that to get high-effective productivity, large-shaped polysilicon suitable for FZ growth are absolutely necessary.

CONTENT:

1. Single Crystal Yield (Y)
2. Productivity (P) and Effective Productivity (P x Y)
3. Quality
4. Keys for FZ Mass Production

PRECEDING PAGE BLANK NOT FILMED

Cz Single Crystal, 250 mm in Diameter
45 kg in Weight

ORIGINAL PAGE IS
OF POOR QUALITY

FZ Single Crystal, 100 mm in Diameter
1.6 m in Length

Growth Conditions in 5-in. FZ and Cz Methods

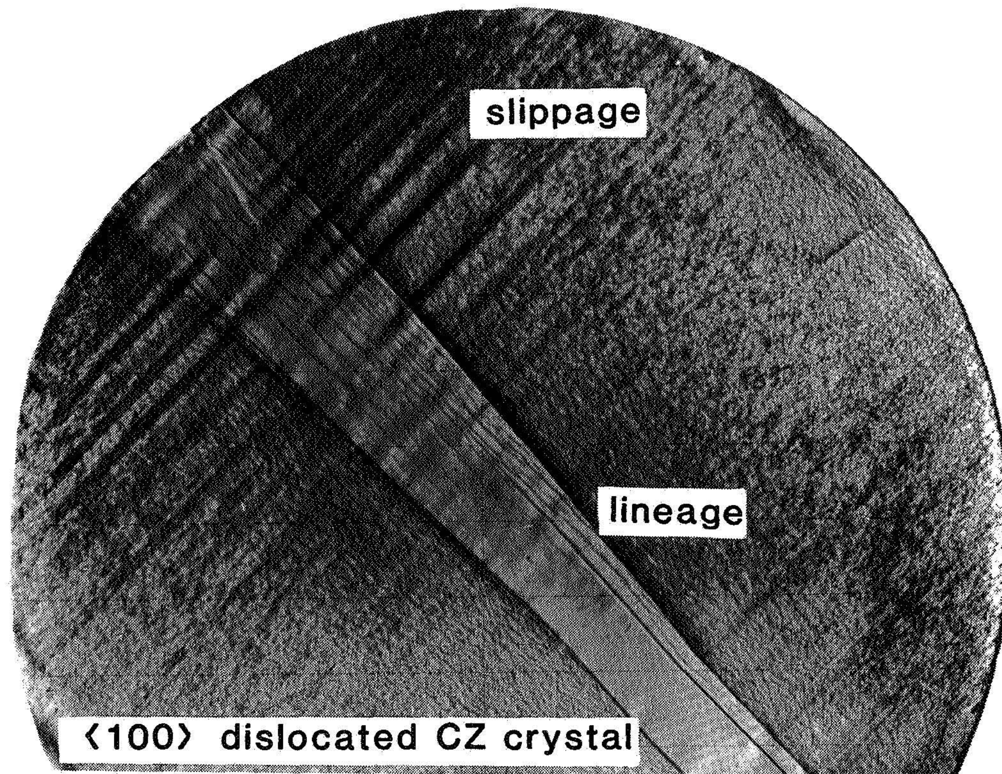
	FZ* (1st + 2nd)	CZ
DIAMETER (mm)	128	130**
DIRECTION	<100>	<100>
POLY DIA LENGTH (mm)	128 1800	——
POLY WEIGHT (kg)	50	30***
GROWTH RATE (mm/min)	1st 4 2nd 3	1

* 2pass FZ shows higher single crystal yield than that of single pass FZ.

** FZ diameter control is easeir than that of CZ.

*** 30 kg charge in 5" shows the most effective productivity (productivity x yield).

ORIGINAL PAGE IS
OF POOR QUALITY



X-ray topograph of <100>-grown CZ crystal with slippage and lineage dislocation. Lineage formation: First, dislocations are introduced as slippage placed on the oblique (111) plane from the periphery of a crystal. Then, they are rearranged to array their lines along the growth direction on the (110) planes for form lineage as to decrease their formation energies by climbing motion.

Optimum Charged Weights and Crucible Diameter on Crystal Diameters for P x Y

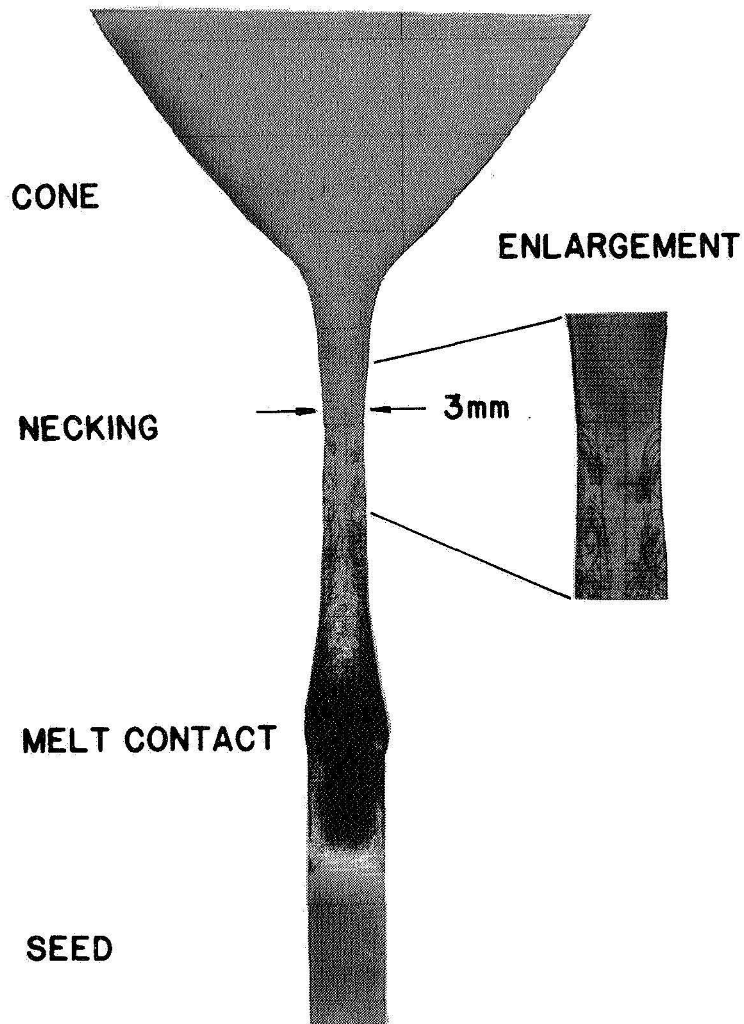
CRYSTAL DIAMETER (INCH)	5	6	7	8	9	> 10
CHARGED WEIGHT (KG)	30	45	60	80	100	>120
CRUCIBLE DIAMETER (INCH)	14	16	18	20	22	> 22

Keys for FZ Mass Production

1. EQUIPMENT
2. LARGE DIAMETER OPERATION
3. QUALITY
4. POLYSILICON

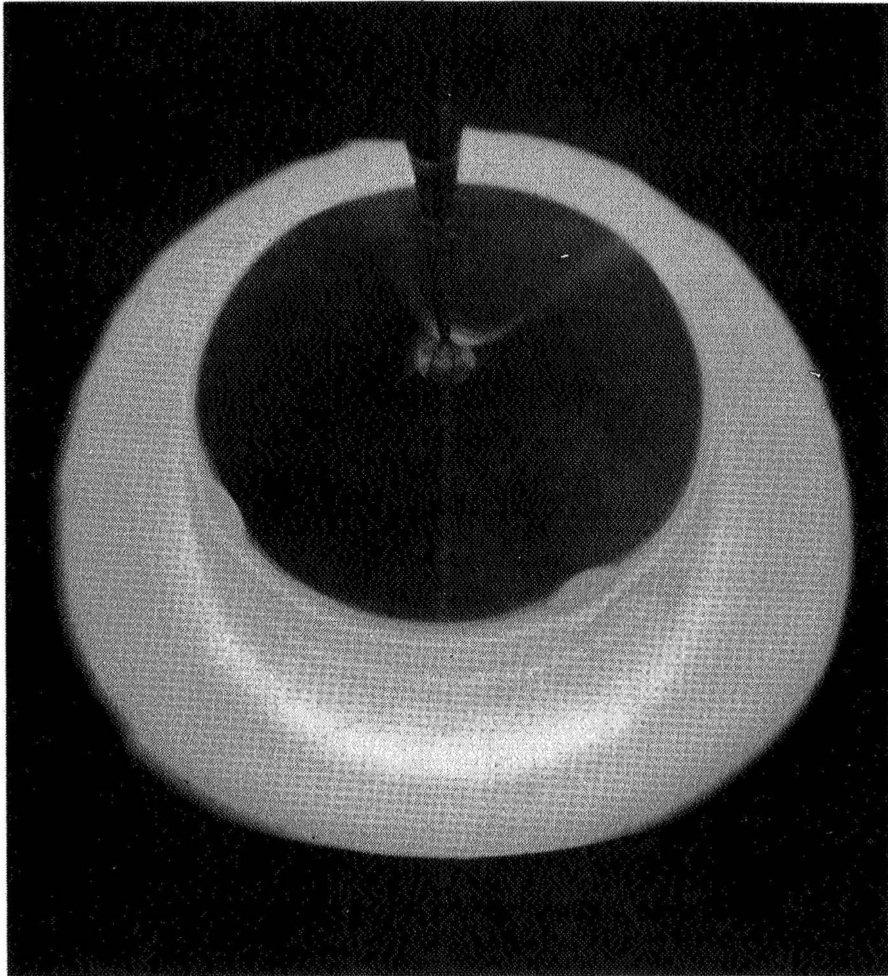
Crystal Quality

	FZ	CZ
1. STRENGTH	n_I - DOPE	LOWER O_I
2. IG		DISLOCATION DIELECTRICS DONOR DEFECT
3. RESISTIVITY	MICRO	MACRO

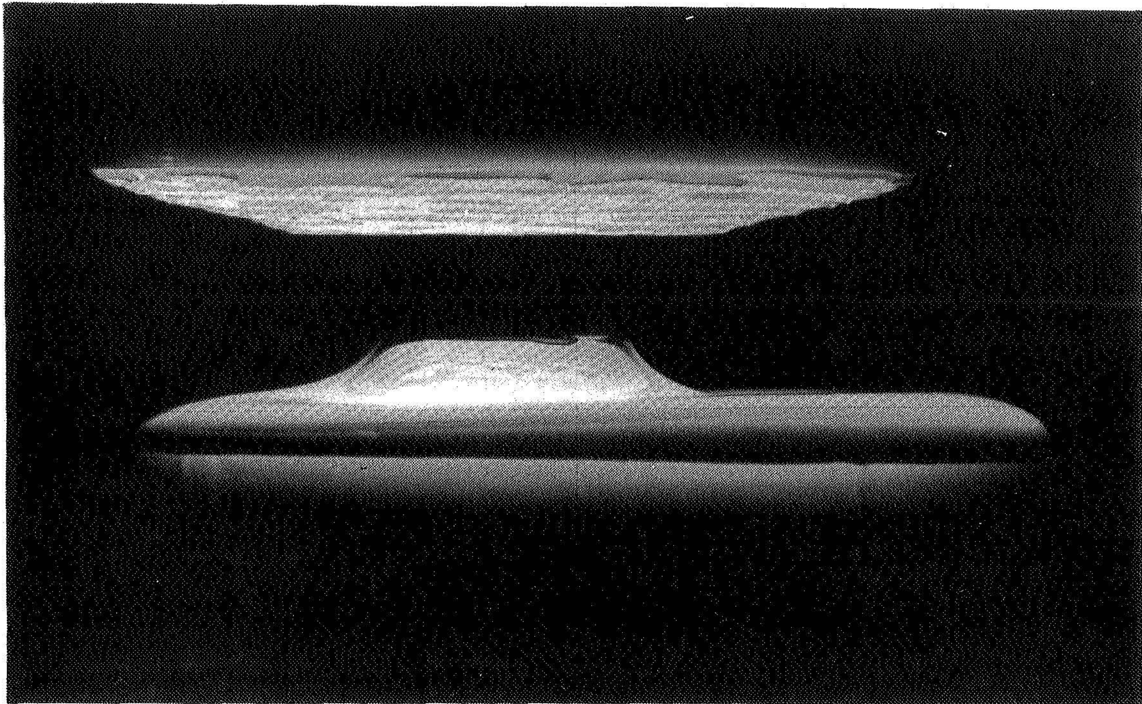


X-ray topograph of seed, necking, and conical part of a crystal. Dislocations generated at the end of seed crystal contacted with a molten zone and then faded away on the side surface of necking. If dislocation-free state is obtained, as the upper yield point for dislocation introduction is very high, large diameter crystals with high growth rate can be grown even under strong thermal stresses.

A Growing Cz Crystal

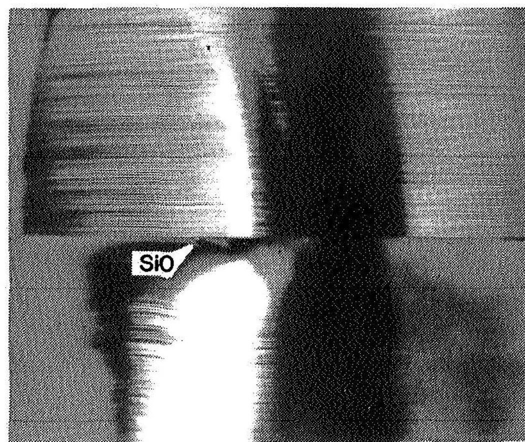


ORIGINAL PAGE IS
OF POOR QUALITY

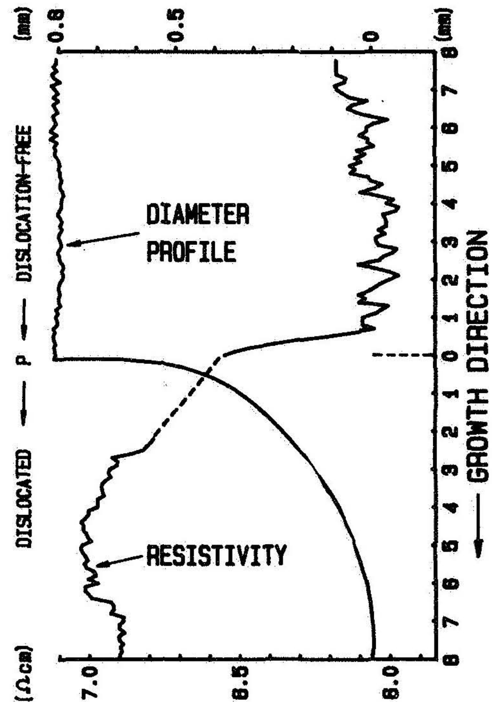


Growing 5-inch-diameter FZ crystal with <100> direction. Diameter is controlled by adjusting both feed and single-crystal movement. The emissivity of the molten zone is lower than that of the solid phase.

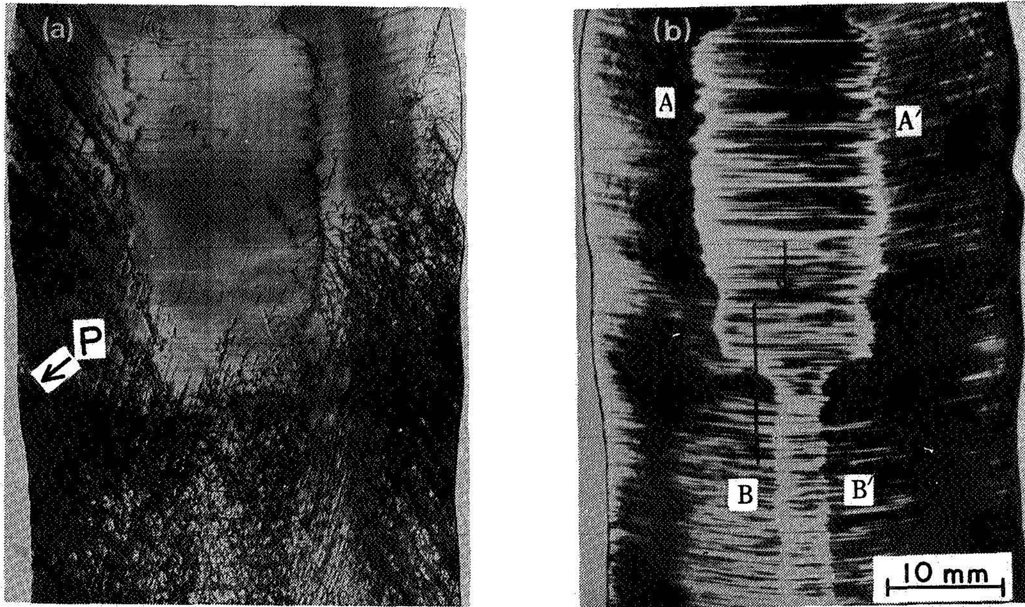
SURFACE MORPHOLOGY CHANGE FROM DISLOCATION-FREE TO DISLOCATED GROWTH



PHOTOGRAPH

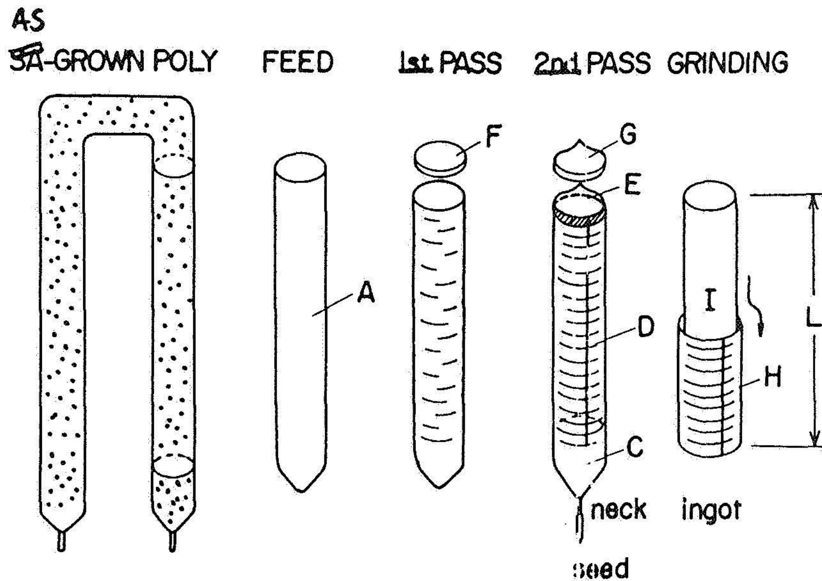


Surface morphology change from dislocation-free dislocated growth in <111> growth crystals with a concave shape interface toward the melt. (a) and (b) X-ray topographs (220 Ref. Moka) showing a crystal diameter (75 mm) with peripheral facet. Both decrease because of dislocation introduction, and lineages exist in the dislocated growth area. The growth interface shape contrast is obtained by oxygen precipitation on striations induced by annealing (1000°C, 16 hr in Ar) after growth. (c) SiO particle-induced dislocations, and (d) surface morphologies: corrugated smooth, growth habit fading; and diameter decreasing, resistivity increasing.



(a) X-ray topograph (220 Ref. Mo$K\alpha_1$) showing that dislocations were introduced from the periphery (indicated by P) during growth, and (b) its etched surface (Sirtl etching) showing that the facet diameter was diminished.

FZ Processing and Silicon Losses



One-Processing Cycles on FZ and Cz Crystal Growth

HOURS

	process	FZ* (1st + 2nd)	CZ
1	charge	1.0	0.9
2	gas	1.0	0.9
3	preheat (FZ) melt (CZ)	1.3	2.0
4	stabilize		0.6
5	seed / neck	0.5	1.2
6	cone (top)	2.0	1.5
7	body	14.5 (61%)	13.1 (45 %)
8	cone (bot)		2.0
9	cool	2.0	2.9
10	take out / clean	0.5	2.7
11	maintenance	1.2	1.5
	total	24.0	29.3
		5" 1.8m 50kg	5" 30kg 0.99m

* 2 pass FZ shows higher single crystal yield than that of single pass FZ.

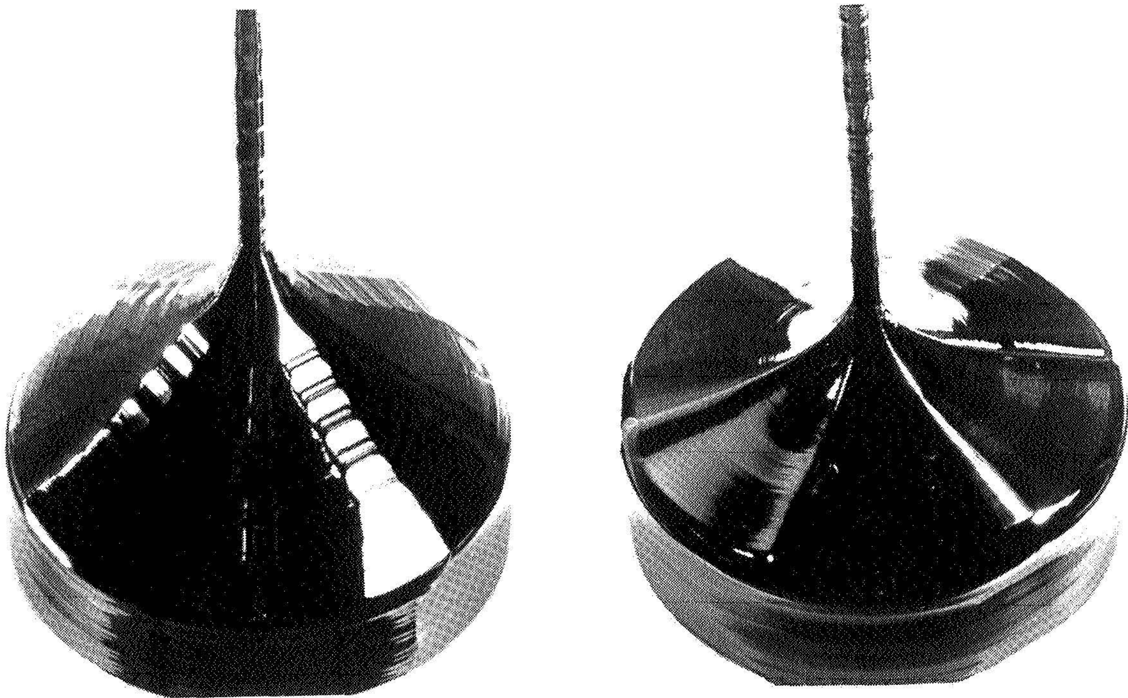
Growth Parameter Differences Between FZ and Cz Growth

	PARAMETER	FZ	CZ	RESULT
1.	THERMAL GRADIENT	LARGE	SMALL	GROWTH RATE
2.	MELT CONVECTION	SMALL CONSTANT	LARGE CHANGE	DISORDERING
3.	MENISCUS SHAPE	CONSTANT	UNSTEADY	GROWTH RATE
	AUTOMATION	EASY	DIFFICULT	

FZ Single-Crystal Yields and Productivities on Crystal Lengths for 5 in.

	SIMBOL	CRYSTAL LENGTH (m)		
		1.0	1.8	3.0
FEED (kg) (6")	A	28(40)	50(72)	83(120)
AS GROWN DIAMETER (mm)	B	128 →		
CONE (kg)	C	3.0 →		
BODY (kg)	D	20.5	42.5	75.5
CONE (kg)	E	1.5 →		
CHUCK (kg)	F G	1.5 → 1.5 →		
GRINDING (kg)	H	1.0	2.2	4.0
INGOT (kg)	I	19.5	40.3	71.5
YIELD (%)	Y	70	81	86 →
BODY LENGTH (m)		0.74	1.54	2.74
PRODUCTIVITY PAR DAY		27.5	40.3	49.7 →

ORIGINAL PAGE IS
OF POOR QUALITY



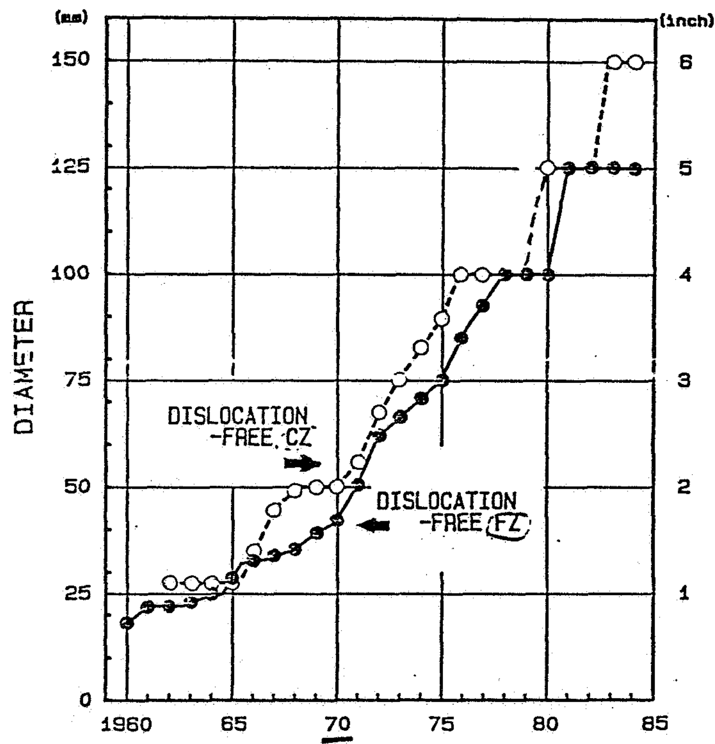
Photographs of necking and conical shaping of (a) <100> orientation and (b) <111> orientation. Dislocation-free grown crystals only give their brilliant crystal habit lines. Maximum weight for 3-mm-diameter necking crystal is estimated as 200 kg.

Summary

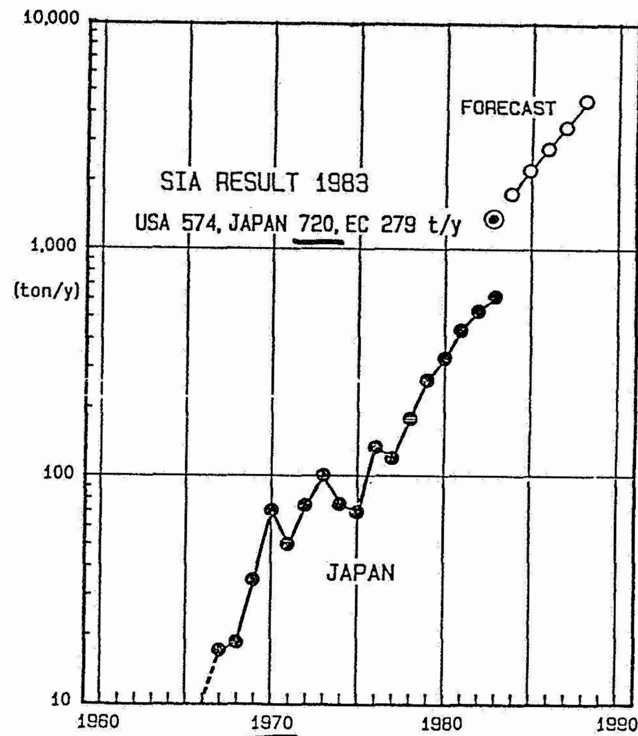
1. SINGLE CRYSTAL MASS PRODUCTION
   N-TYPE FOR C-MOS/MOS EPI

2. RELATIVELY LOW OXYGEN MATERIALS
   24 ± 4 PPMA ('79 ASTM)
   NITROGEN-DOPE FZ/CZ

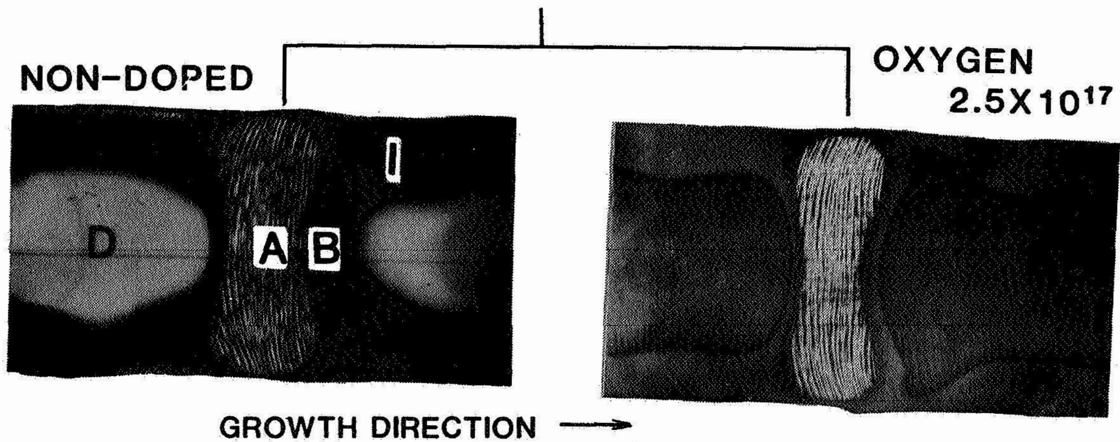
Maximum Diameter Trend in Production



Results and Forecast of Si Crystal Production



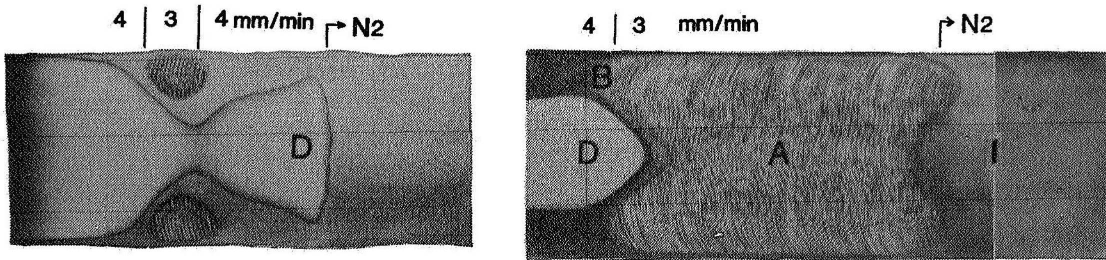
Swirls and D-Defects Formation: In-Situ Annealing (2 min)



X-ray topographs of copper-decorated FZ crystals that were in situ annealed during growth. Right-hand crystal is oxygen doped with silica plate insertion into the melt.

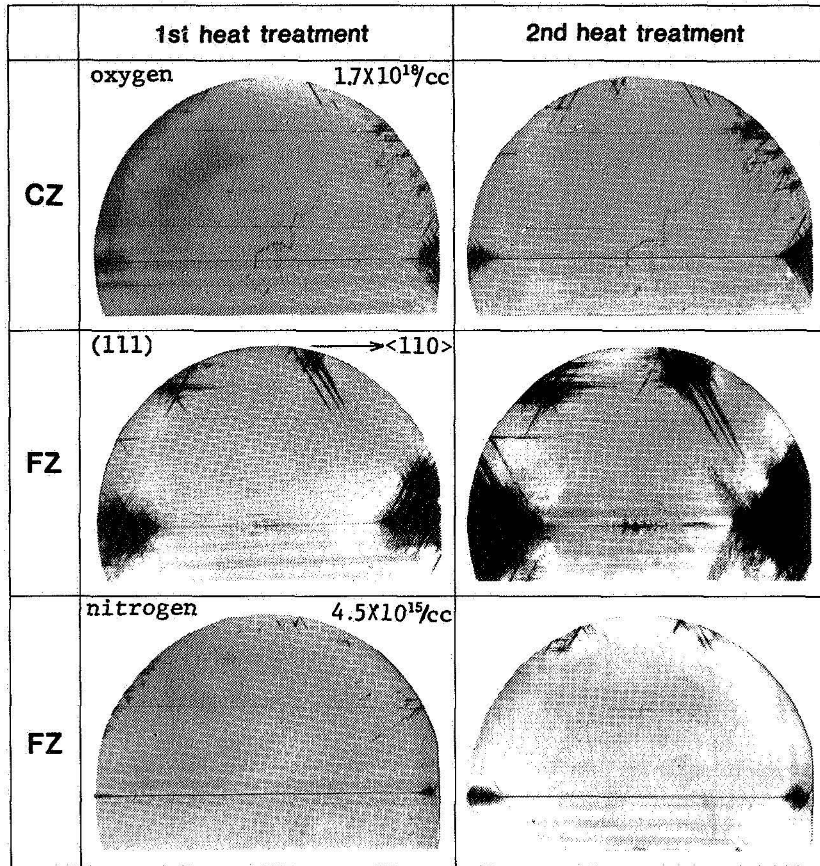
ORIGINAL PAGE IS
OF POOR QUALITY

Nitrogen Suppression of Swirls and D-Defects



Suppression effects on nitrogen in silicon on swirls and D-defects. (a) D-defects and (b) swirls elimination due to nitrogen gas doping. (From Abe et al [38].)

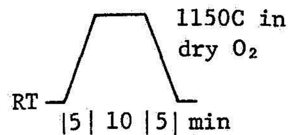
Effects of Nitrogen on Dislocation Nucleation and Movement in Silicon



Scratched conditions

- Crystal diameter: 3 inches
- Diamond weight: 10g
- Scratching speed: 10 mm/sec

In diffusion funrace



Effects of nitrogen on dislocation nucleation and movement in silicon. X-ray topographs obtained from three kinds of (111) wafers prepared from conventional CZ and FZ and nitrogen-doped FZ. Left- and right-hand-side topographs were taken after first and second heat treatments under the same conditions, respectively.

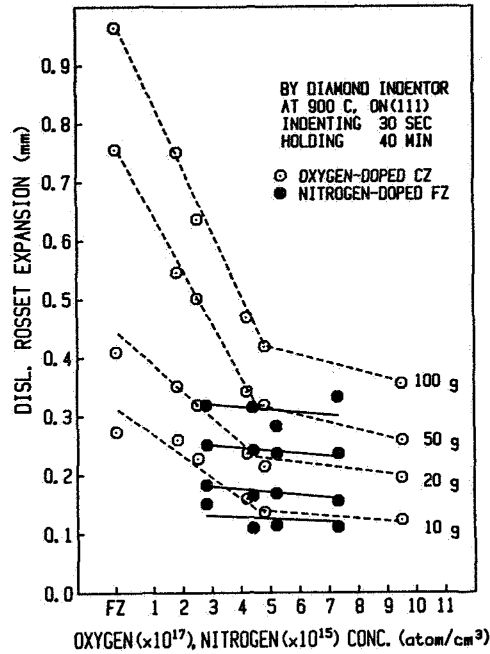
Real Problems for Mass Production

1. RESISTIVITY DISTRIBUTION

2. CRYSTAL DISORDERING DURING GROWTH

FZ	CZ
° Expansion of Swirls	° SiO Particles
° Freezing and Spilling of Melt	° Lattice Mismatch by Dendritic Growth
° Understandable	° Uncontrollable

Dislocation Generation and Movement on Oxygen and Nitrogen-Doped Materials



Toughness against dislocation generations explained by dislocation Rossett expansion as functions of oxygen and nitrogen concentration in CZ and FZ crystals, respectively. Toughness is lost in the lower concentration range of oxygen 5 x 10^{17} atoms/cm^3 in CZ crystals. Nitrogen-doped FZ crystals have same toughness with CZ crystals. Nitrogen concentrations in FZ crystals are as low as two orders of magnitude compared with that in CZ crystals.

Optimum Charged Weights for Each Diameter

SINGLE CRYSTAL YIELD X PRODUCTIVITY = EFFECTIVE PRODUCTIVITY IN 30 Kg CHARGED CZ GROWTH

as grown diameter	simbol	diameter (inch φ)			
		4	5	6	7
DIAMETER (cm)	A	10.5	13.0	15.5	18.0
cone (kg)	B	0.5	0.9	1.5	2.5
body (kg)	C	25.5	24.3	22.5	19.5
cone (kg)	D	1.0	1.8	3.0	5.0
resid. melt (kg)	E	3.0	3.0	3.0	3.0
grinding (kg)	G	2.4	1.8	1.3	1.0
ingot (kg)	F	23.1	22.5	21.2	18.5
yield (%)	Y	77.0	75.0	70.7	61.7
body length (cm)	L	126	78.6	51.6	33.0
productivity ratio(per day)	P	1.0 (15.0)	1.21 (18.4)	1.25 (19.0)	1.15 (17.5)
effective productivity (Y x P)		77 (Y x P)	90.8 (Y x P)	88.4 (Y x P)	77 (Y x P)

* calculation

$$\text{yield}(Y) = \frac{\text{ingot}(F)}{\text{charge}(M)}$$

$$M = B + C + D + E$$

$$G = \left\{ \frac{A^2 - (A-0.5)^2}{4} \times \pi \times d \right\} \times L$$

$$F = \left\{ \frac{(A-0.5)^2}{4} \times \pi \times d \right\} \times L$$

$$L = \frac{C}{\left(\frac{A^2}{4} \times \pi \times d \right)}$$

$d = 2.33$ (g/cm)

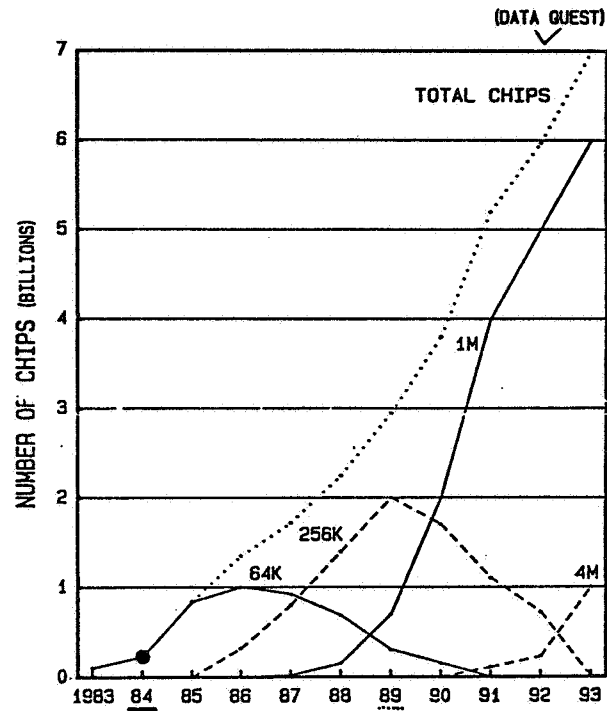
M = charged weight 30kg

$$P = \left(\frac{M \times Y}{\text{operating time}} \right)$$

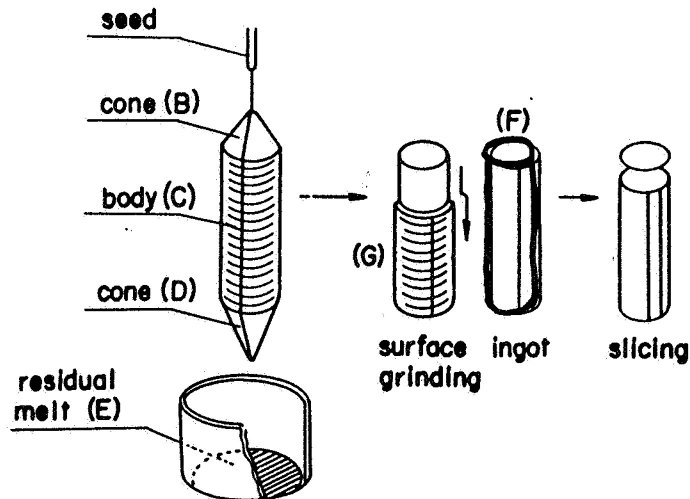
Dia x 0.7 = cone(B) length

Dia x 4 = cone (D) length

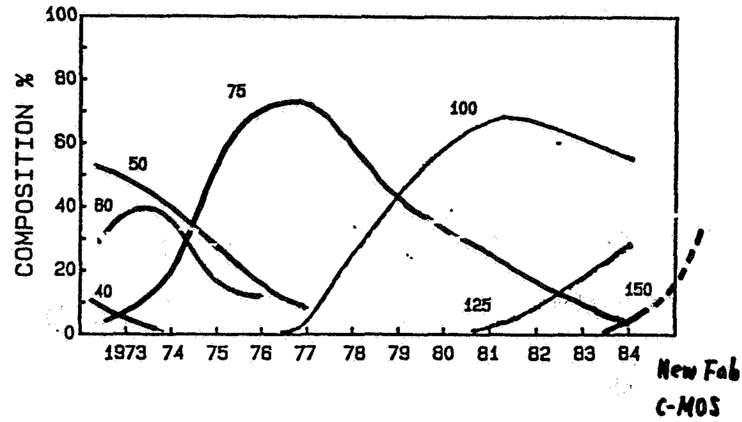
Worldwide D.RAM Demand Forecasts



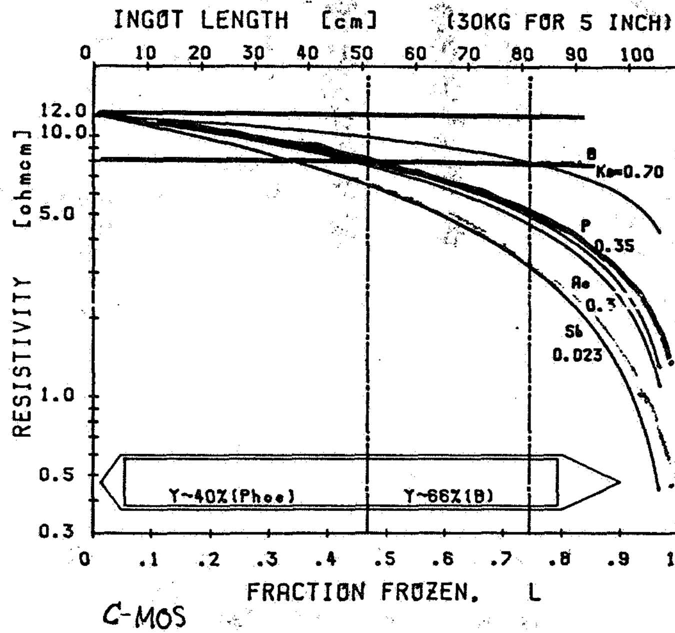
Cz Processing and Silicon Losses

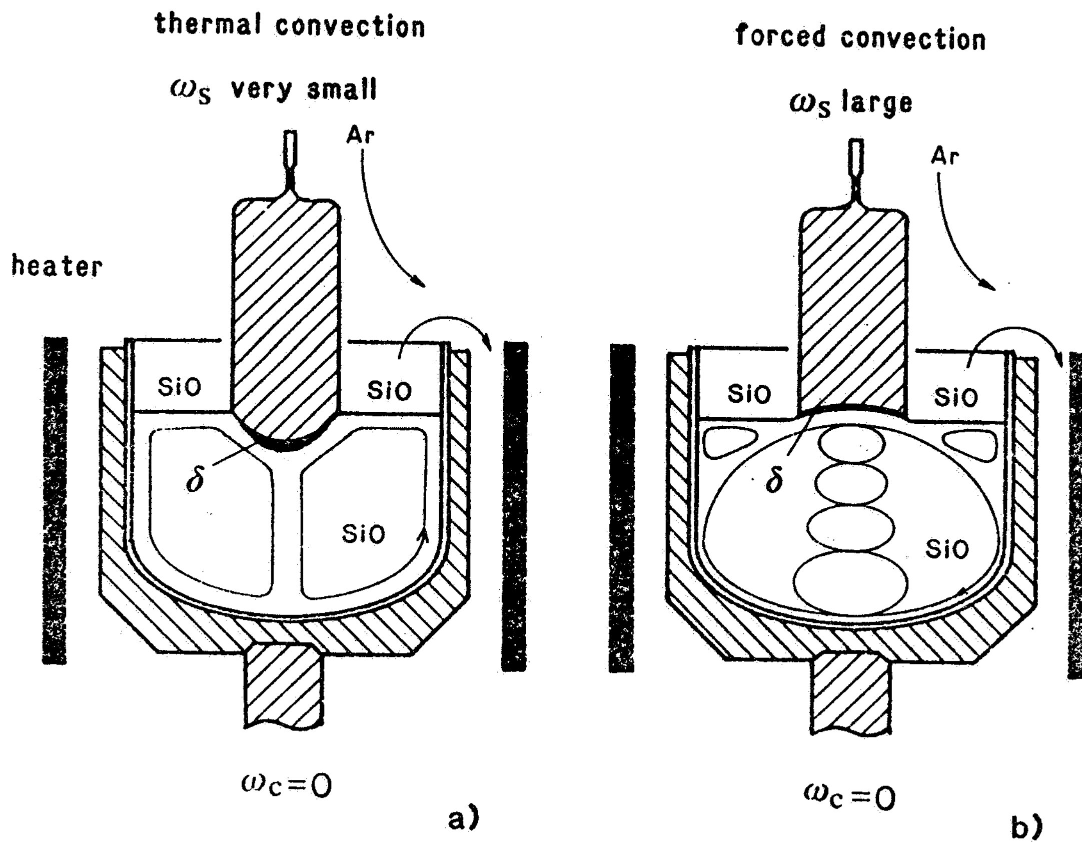


Silicon Wafer Diameter Trend (Area Gain)



Impurity Segregation and Crystal Yield





Diffusion boundary layer thickness distribution variations due to (a) confection and (b) stirring in the melt. Crystal rotations are responsible for controlling of growth interface shape and diffusion boundary layer thickness. For (a) thermal convection, ω_S is very small; for (b) forced convection, ω_S is large.

DISCUSSION

CORBETT: Is the nitrogen stable or does it undergo heat-treatment effects?

ABE: In the FZ crystal case, the nitrogen is very stable. For Cz, however, we have recently found a 900°C temperature change to inactive nitrogen for the infrared absorption. It is still stable as far as toughness for dislocation generation is concerned.

CORBETT: What other impurities do you get in the nitrogen-doped float-zone material?

ABE: We tested only for germanium, carbon, and hydrogen. The other impurities have a secondary effect. Carbon is not good for device performance.

CORBETT: What kind of carrier lifetime do you get in this material?

ABE: Using the photoconductive decay method, the lifetime is about the same level as non-doped FZ materials, namely 1000 to 2000 µs depending on the resistivity.

CORBETT: Then nitrogen makes no difference.

ABE: That is correct.

CISZEK: One of the production limitations may be the diameter to which crack-free polycrystalline silicon can be made. Could you tell us your experience about how large a diameter SEH is able to make the polyrods without cracking?

ABE: I showed polycrystals almost 13 cm in diameter, 2 m long, that were crack-free.

KIMURA: You showed nitrogen concentrations that were about 7×10^{15} maximum. Your solubility limit is 4.5×10^{15}. Do you have precipitation?

ABE: I don't believe the literature data. Our case is not in steady state so sometimes it can exceed the solubility limit.

KIMURA: Regarding the suppression of D-swirl defects with nitrogen, is that because of the increase in the critical residual stress by adding nitrogen?

ABE: I'm not sure how nitrogen effects the D-swirl defects, but perhaps the nitrogen deactivates the vacancies and/or interstitials to form equilibrium states or concentrations.

KIM: Regarding float-zone ingots, is there an upper limit for diameters that you can scale up to?

ABE: I feel no dislocation generation limitation for large-diameter ingots at the present time. We experience no dislocations but sometimes the ingot does crack during the growth at very low temperatures.

KIM: Too much oxygen in Czochralski silicon is bad. Could you speculate what would be a reasonable oxygen level where you have optimum mechanical strength and to some extent gettering due to oxygen?

ABE: Roughly speaking, the standard oxygen concentration according to ASTM is around 30 ppma. I recommend 20 to 25 or 30 ppma. Such a relatively low concentration material has gradual intrinsic gettering effects through the processing.

SESSION II

R. LANE, CHAIRMAN

N86-19728

NEW OUTLOOK ON CONTROL OF CRYSTALLINE AND CHEMICAL PERFECTION DURING GROWTH OF SILICON

A.F. Witt

Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Significant progress has been made in our understanding of the Czochralski crystal growth process with the realization that the incorporation of oxygen into silicon is directly related to the internal gettering capability of wafers during device fabrication. Stringent oxygen concentration requirements in silicon brought about intensive studies of crucible (SiO_2) dissolution, oxygen accumulation in the melt, its transport to the growth interface, and its incorporation into the growing solid. In context, it was also recognized that the electronic properties exhibited by silicon during various stages of device fabrication were significantly affected by the thermal history of the silicon during the post-growth cool-down period. These studies led to a comprehensive analysis of the heat and mass transport behavior in conventional Czochralski growth systems, and resulted in the evolution of new concepts for their control.

Turbulent melt convection, induced by unavoidable destabilizing thermal gradients, was found to interfere with homogeneous dopant (and oxygen) incorporation and to influence markedly the dynamics of non-equilibrium point defects in the solidified silicon matrix during the cool-down period.

PRECEDING PAGE BLANK NOT FILMED

Moreover, both segregation and point defect dynamics appear adversely affected by asymmetry in heat transfer to and from the melt.

Growth control, with the crystal diameter as the primary control objective (ADC), while responsive to optimized silicon throughput requirements, is now considered inadequate (if not inappropriate) in view of stringent bulk property requirements.

In view of the unavoidability of destabilizing thermal gradients in conventional crystal growth configurations, melt stabilization through the application of magnetic fields is generally considered as a viable approach. Large melts do experience pronounced damping of temperature oscillations and a corresponding decrease in non-rotational segregation effects under applied vertical and horizontal magnetic fields . The accompanying reduction of the rate of heat transfer in the melt, however, generates complications through changes in the prevailing temperature gradients and in the time constant of the hot-zone which still have be overcome. An additional side effect of magnetic field stabilization is the spatial reorganization of convective melt flow patterns which may alter the radial temperature distribution and thus lead to changes in segregation behavior.

Control of heat input to the melt through heat pipe systems, as used during growth of germanium, cannot be applied to industrial growth of silicon. Required heat pipe systems with operating temperatures of about 1400°C are as yet not available; moreover, the effectiveness of peripheral heat pipes in generating radially symmetric thermal fields in the melt is found to decrease with increasing cavity diameter. Recent studies have

shown that heat exchange systems located coaxially about a growing crystal can be used to stabilize and control not only heat transfer in the grown crystal, but also in the melt adjacent to the solidification interface. This approach is expected to provide for controllable, quantifiable, and reproducible thermal boundary conditions at critical parts of growth systems and shows promise as a parameter for growth with bulk crystal perfection as the control objective.

FIGURE CAPTIONS

Fig. 1 Heat transfer system associated with Czochralski growth of semiconductor systems. The defect structure of material obtained by this technique reflects the non-uniformity and uncontrolled nature of heat input and heat loss; related thermal gradients in the melt are destabilizing and give rise to turbulent convection; thermal field distribution is asymmetric, leading to non-axisymmetric convective flow patterns and to related deficiencies in segregation.

Fig. 2 Microsegregation behavior exhibited by silicon doped with antimony. Compositional variations on a microscale revealed by differential etching reflect growth perturbations at frequencies ranging from 10-0.1 Hz caused by temporal and spatial variations in convective melt flows.

Fig. 3 Schematic presentation of convective interference with equilibrium segregation during liquid-solid phase transformation of binary system in Czochralski configuration.

Fig. 4 Origin of rotational (semi-macro) and non-rotational (micro) segregation during Czochralski growth.

Fig. 5 Achievement of radially symmetric heat input to a semiconductor melt through the use of a heat pipe located coaxially between the graphite heater and the melt confining crucible. This approach is as yet limited to operation at less than 1100°C because of the unavailability of high temperature heat pipe materials. It should also be noted that the effectiveness of this approach is limited to heat pipe cavities with I.D.'s of less than about 4"; at larger cavity diameters, unavoidably asymmetric heat losses lead to asymmetric thermal field distributions and to related segregation effects.

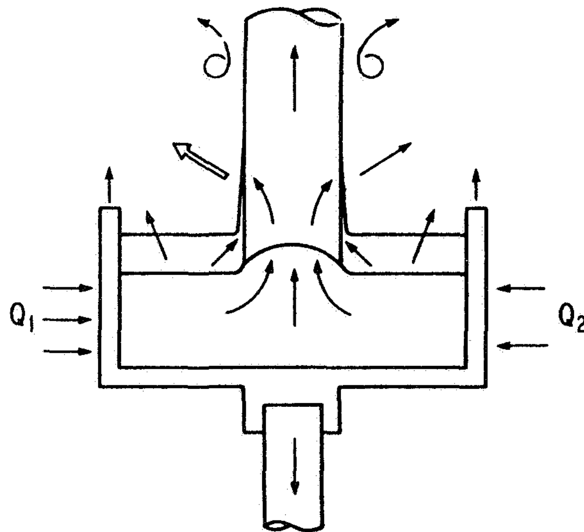
Fig. 6 Heat pipe based heat exchange system to control thermal gradients in growing semiconductors. The heat pipe located coaxially about the growing crystal provides for constnat, controllable ambient temperature which significantly affects thermal stress generation and the dynamics of supersaturated point defects. Using Peltier heating or cooling respectively, it is possible to maintain ambient temperatures ranging from about 500-1100°C.

Fig. 7 Radial thermal stress distribution in GaAs during LEC growth with and without controlled heat exchange. It should be noted that the resolved shear stress at all axial locations exceeds critical resolved shear stress by up to one order of magnitude.

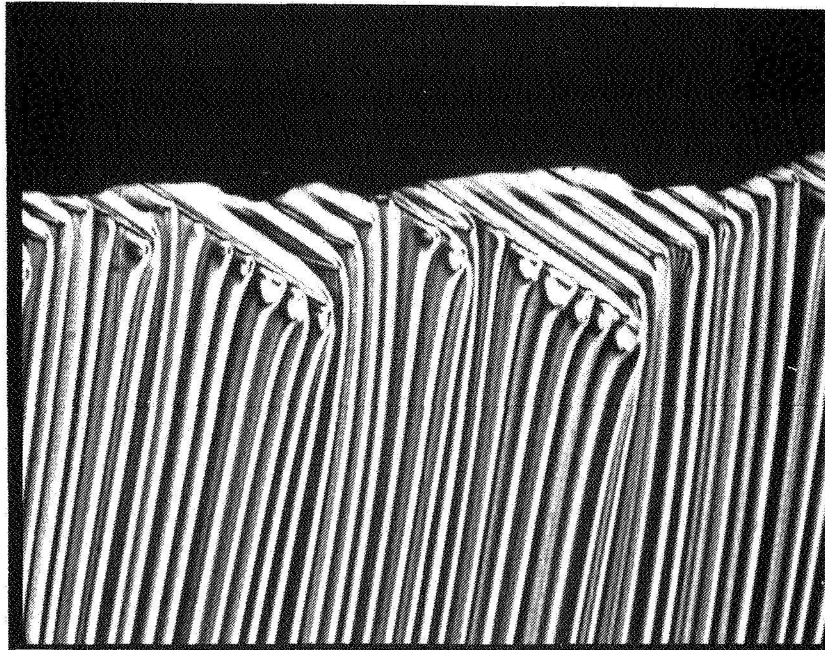
Fig. 8 Heat exchange system providing for controllable axial thermal gradient in crystal grown by the Czochralski technique.

Figure 1. Conventional Cz and LEC Growth Without Heat Transfer Control

- Asymmetric heat input and loss
- Interface Morphology to a limited extent controllable by speed rotation
- Encapsulation film thickness uncontrolled
- Vertical thermal gradient about interface not easily controllable
- Radial thermal gradient in crystal uncontrolled
- History of temperature field, $T(\hat{x}, t)$, in growing crystal unknown and uncontrollable



ORIGINAL PAGE IS
OF POOR QUALITY



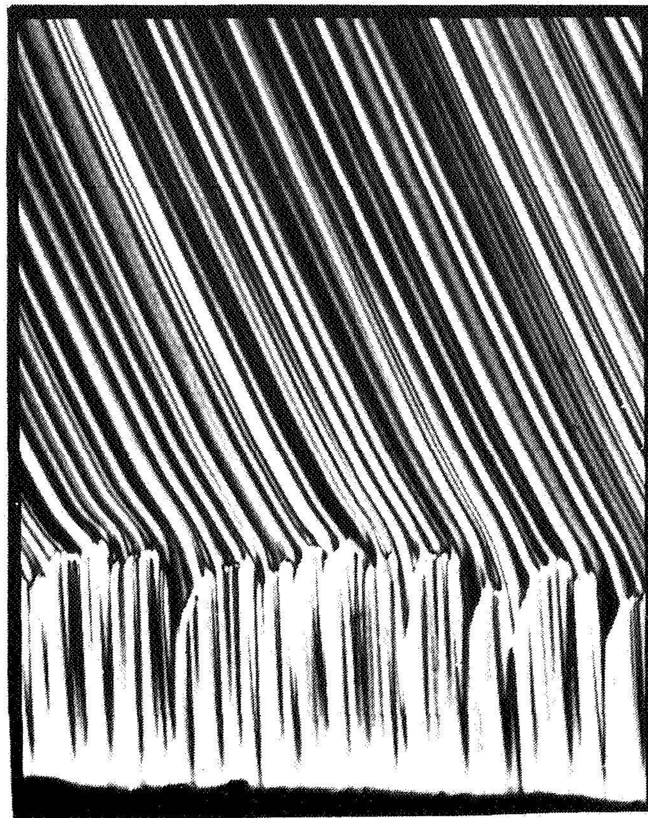
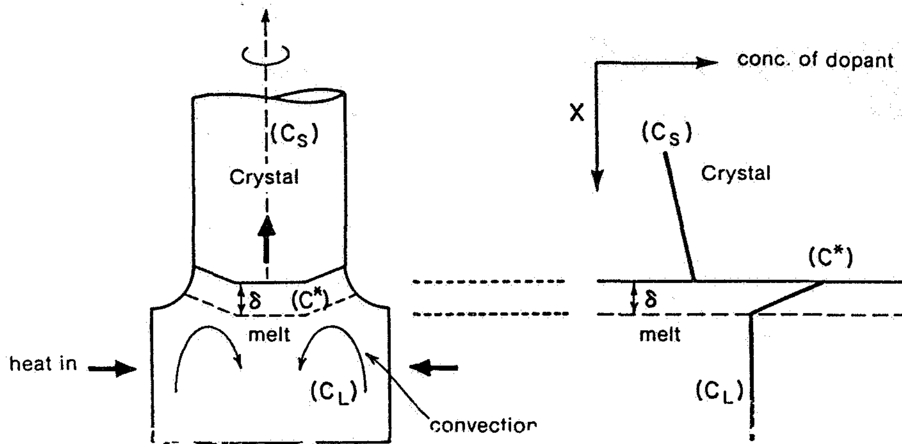


Figure 2

Figure 3. Melt Growth Configuration and Associated Composition Profile



C = concentration of minority constituent: (C_S) in solid
(C_L) in melt
(C^*) at melt-crystal interface

δ = diffusion boundary layer thickness (controlled by convection and/or crystal rotation)

Convection: leads to longitudinal *macrosegregation:*

$$C_S\ (X) = k_{eff}\, C_L(O)(1-g)^{k_{eff}-1}$$

$k_{eff} = \frac{C_S}{C_L}$

g = fraction melt solidified

$C_L\ (O)$ = starting melt composition

Temporary perturbations: lead to *microsegregation:*

$$C_S = \frac{k C_L}{k+(1-k)e^{-\frac{\delta R}{D}}}$$

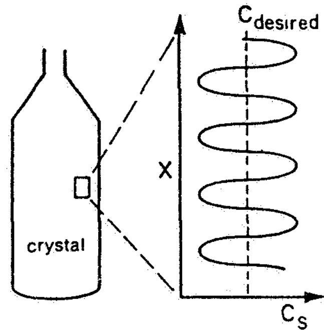
$k = \frac{C_S}{C^*}$

D = diffusion constant

R = rate of growth

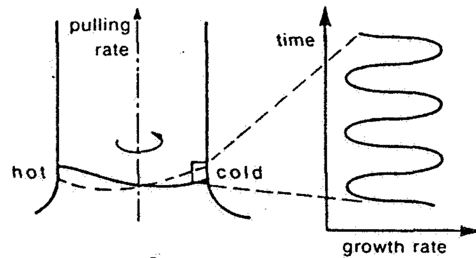
Figure 4. Origin of Microscopic Compositional Inhomogeneities in Melt-Growth Matrices

(a) rotational striations:



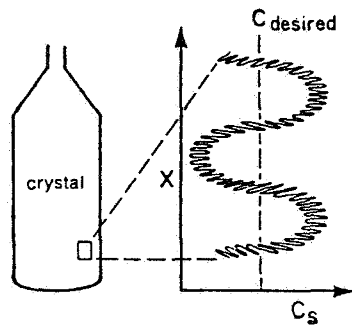
REASON:

crystal rotation in non-asisymmetric thermal environment:

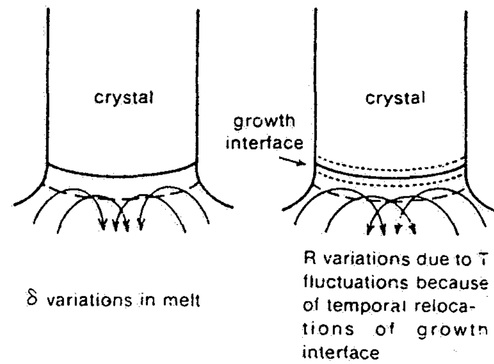


$$C_S = \frac{kC_L}{k+(1-k)e^{-\frac{\delta R}{D}}}$$ ← R varies periodically

(b) non-rotational striations:



due to turbulant convection δ and R vary randomly in high temperature systems:



$$C_S = \frac{kC_L}{k+(1-k)e^{-\frac{\delta R}{D}}}$$ ← δ and R vary randomly

C-2

Figure 5. Cz Grown With Heat Pipe for Radially Symmetric Thermal Field Distribution in Melt

- Effectiveness Limited by Crucible Diameter

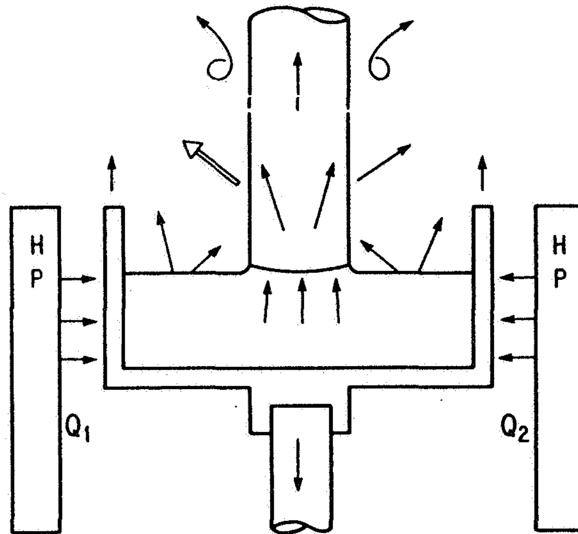
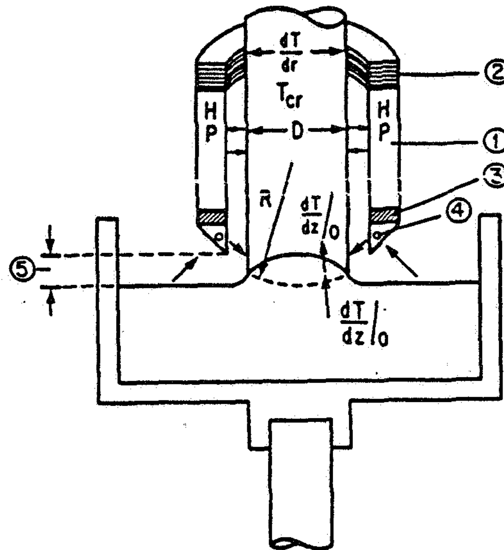


Figure 6. Heat Exchange System for Optimized Control of the Following Interdependent Parameters:

- Crystal temperature (range 500 °C-1100 °C)
- Growth interface morphology
- Temperature gradients about the growth interface
- Radial thermal symmetry in the vicinity of the growth interface
- Radial thermal gradient in growing crystal



① Inconel Heat Pipe with Operating Range from 500 °C - 1100 °C.

② Peltier Heating / Cooling System.

③ Thermal Insulation.

④ Auxiliary Heating Element.

⑤ Axial Position of Heat Exchange System (adjustable)

Figure 7. Effect of Heat Exchange System on Reduction of Stresses at Periphery of a GaAs Crystal

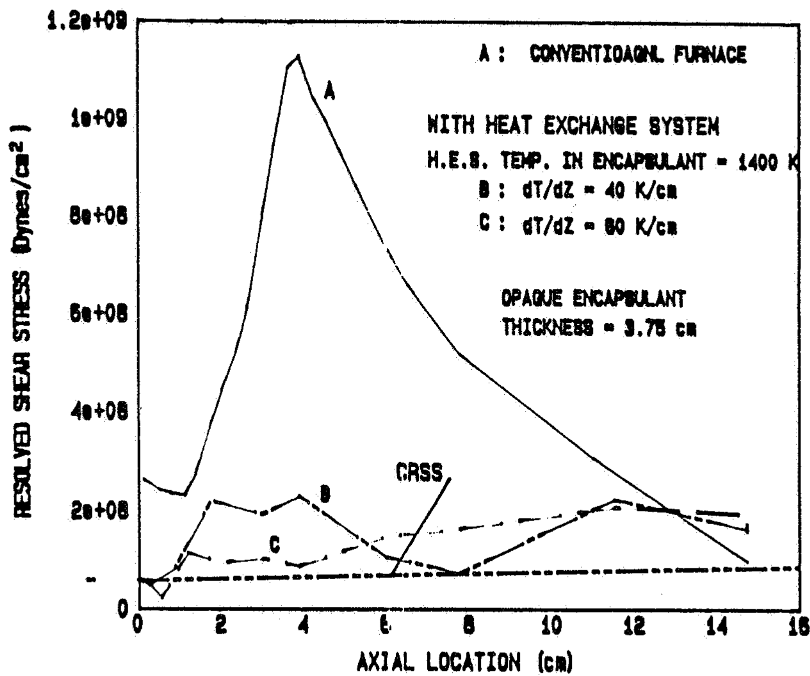
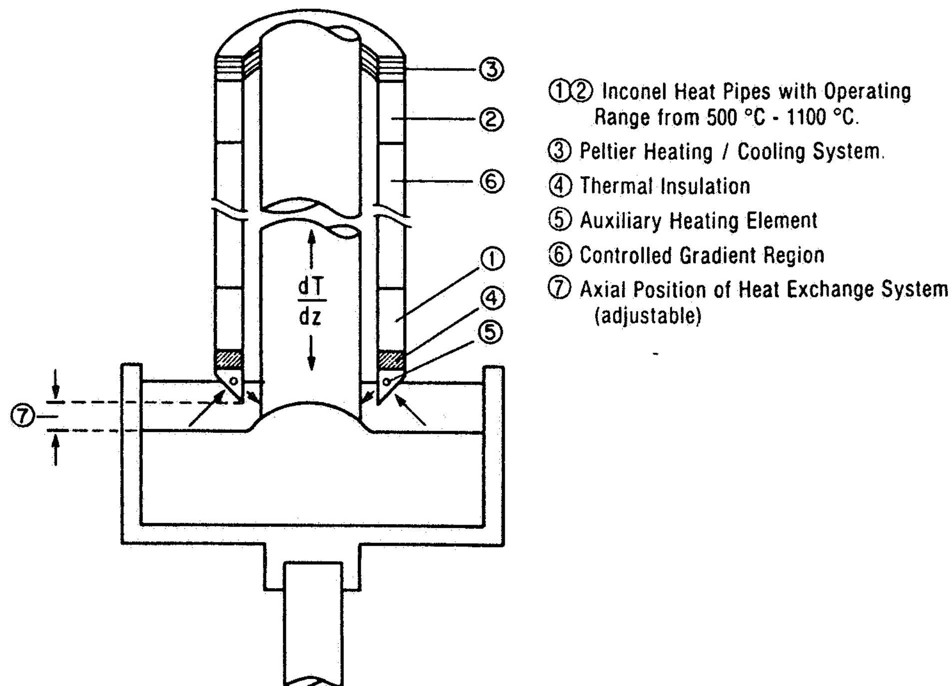


Figure 8. Heat Exchange System for Optimized Control of Axial Temperature Gradient in Growing Crystal



DISCUSSION

WITT: My colleague, Dr. Schwuttke, is convinced that he can get the degree of contamination in Czochralski growth to the level of float-zoning. I am pessimistic about this. If I look at all of the evidence that has been compiled so far, I don't see it.

SCHWUTTKE: We should strive to improve the Czochralski quality in terms of oxygen content to a point that is approaching what we have in float-zone after two passes, and that is around 10^{17}. We can produce Czochralski today with 2×10^{17}, and I think that is not even optimized.

MORRISON: One of the things that makes float-zone attractive, at least from a cost point of view, is the high thermal gradients giving high growth rates. In Czochralski growth all of the newly applied technologies to improve the process talk about adding heat. Adding heat has to slow the growth rate. Are there technologies where we can go the other way?

WITT: You bring out a very valid point. You want to optimize the growth rate. If you do that you have to operate under a very high thermal gradient but if you believe that that will lead to superior material along the lines of point-type defects you are wrong. I think you can stabilize your supersaturated point-type defect so that it does not coalesce or cluster and deteriorate. But on an absolute basis, you then have an inferior material, the more you remove yourself from the equilibrium phase transformation. Therefore, it is my contention that that in principle is the weak point of float-zoning. The complication that I see is the very strange and, in my opinion, non-quantifiable thermal boundary condition associated with the hour-glass type configuration of float-zone growth. I think an attempt at modelling and, therefore, optimizing float-zoning along these lines is not even on the horizon. In my opinion, if you want maximum throughput, you can get it and I think you can increase your throughput in Czochralski very, very significantly with no problem. I think the maximization of growth rates at what I heard today at two inches is far removed from what's theoretically possible. But the question is, do you want to? The material will have very negative side effects when you go to high-temperature processing.

LESK: When you rotate a crystal in a liquid you get a certain amount of pumping action. Is that anywhere near the significant thermal gradient effect?

WITT: Sure, you have two driving forces in that configuration. One of them is natural convection, due to the density gradient, which moves the system outward, up, and in towards the center. Counteracting that you have forced convection due to the crystal rotation, which has a centrifugal force that moves the fluid up and out. Unfortunately, the driving forces in much of the Czochralski system are so high for

convection that in at least the bulk of the matrix I do not see the dominance of forced over natural convection. In addition to that, in many of these systems we are not dealing with an annular ring, as predicted by theory, but rather in one cell a typical consequence of the thermalized symmetry of the system. You are correct, in low-temperature systems. If you go to germanium or indium antimonide at 450° or at 940° then the driving forces are small, and if the volume in addition is small, then you get exactly what you want. You get, at low rotation rates, dominance of natural convection, and at high rotation rates, you get dominance of forced convection due to the seed rotation.

KIM: Your approach to achieve thermal symmetry is very logical, but I wonder if it is practical. Wouldn't it be an experimental nightmare to have six heaters controlled separately?

WITT: Fortunately, we are a university, so the nightmare isn't so great. At this stage we have two different approaches, as I indicated. The first approach is to test the effectiveness of the heat pipe coaxially. This is not a simple approach. If we see the responsiveness of the thermal field due to the location of the heat pipe then there is no longer a need for the radially asymmetric heat input. The second approach we are actively now engaged in is totally modifying the basic heater design. We are very concerned about the vertical gradient control and this is where we are designing our system with three independent ring-type heaters, which will allow us to get a handle on the heat losses on the bottom and on the gradient control, which are partially responsible for the convection.

KIM: Is it correct that you can measure the silicon melt temperature with plus or minus one degree resolution?

WITT: Yes, although absolute calibration is a problem. We are not interested in absolute temperatures in process control. We are interested in temperature changes. Therefore, the need for absolute calibration doesn't arise. If you do thermal imaging, the primary problem you must overcome is internal reflections.

ELWELL: Do you have any feeling or experimental evidence on whether surface tension forces are stronger than the buoyancy in a typical Czochralski growth?

WITT: I have none. I personally do not believe all the indicators, and the indicators that we do have suggest that we have indeed density driven convection. However, theoreticians, particularly in Europe, and several of them in this country, are not convinced that density-driven convections are the cause of our problem rather than surface-tension-driven convections.

SCHWUTTKE: Maybe they should do their experiment in space.

WITT: They have suggested that, but so far there were more failures than results.

N86-19729

MCZ: STRIATIONS IN CZ SILICON CRYSTALS GROWN UNDER VARIOUS AXIAL MAGNETIC FIELD STRENGTHS

(George) K.M. Kim

IBM East Fishkill Labs
Hopewell Junction, NY 12533

Suppression of fluid flow instabilities in the melt by the axial magnetic field in Czochralski silicon crystal growth (AMCZ) is investigated precisely by a high-sensitivity striation etching in conjunction with temperature measurements. The magnetic strength (B) was varied up to 4.0 kG, incremented in 0.5 kG/5 cm crystal length. The convection flow was substantially suppressed at $B \geq 1.0$ kG. A low oxygen level of 2-3 ppma and a high resistivity of 400 ohm-cm is achieved in the AMCZ silicon crystals at $B \geq 1.0$ kG. Details of the striation formation as a function of B will be presented. Computer simulation of the magneto-hydrodynamics of the AMCZ silicon crystal growth will be discussed briefly with regard to the solute, especially oxygen segregation at B=0, 1.0, and 2.0 kG, which has been published recently.(1)

Earlier studies in the inverted Bridgman growth of InSb(2) and Ge(3) are reviewed, which have established the cause and effect relationship between the convection in the melt and the striation formation as well as the suppression of the convections in the melt by transverse magnetic field.(4)

---

(1) Lee, K.J., Langlois, W.E. and Kim, K.M., J. Physico-Chem. Hydrodynam., 5, 135 (1984)

(2) Kim, K.M., Witt, A.F., and Gatos, H.C., J. Electrochem. Soc., 119, 1218 (1972)

(3) Kim, K.M., Witt, A.F., and Gatos, H.C., J. Electrochem. Soc., 125, 475 (1978)

(4) Kim, K.M., J. Electrochem. Soc., 129, 427 (1982)

OVERVIEW

1. Earlier Studies in Inverted Bridgman Growth of InSb and Ge:

   - Convection in the melt and striation formation
   - Suppression of convections by transverse magnetic field

2. MCZ: Suppression of Convection in CZ Silicon by Axial Magnetic Field

   - Axial MCZ (AMCZ) apparatus
   - Magnetic field uniformity
   - Convection and suppression in AMCZ silicon crystal growth:
     - (a) Temperature measurement
     - (b) Striation formation

3. Computer Simulation and Modeling of AMCZ Silicon Crystal Growth

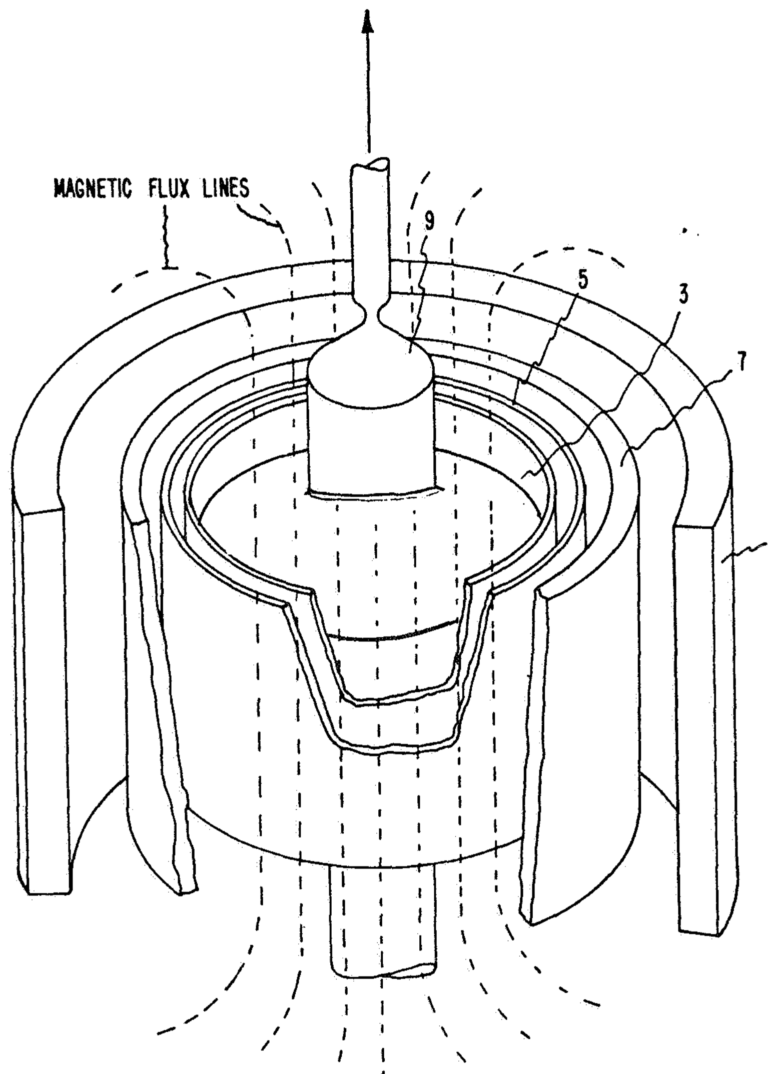
4. Summary

PRECEDING PAGE BLANK NOT FILMED

IBM Technical Disclosure Bulletin Vol. 24 No. 7A December 1981

APPARATUS FOR CZOCHRALSKI SILICON CRYSTAL GROWTH THROUGH AXIAL MAGNETIC FIELD FLUID FLOW DAMPING

K. M. Kim, G. H. Schwuttke and P. Smetana



An arrangement is provided for utilizing axial magnetic fields to suppress the fluid flow in the melt of Czochralski-type silicon crystal growth systems.

© IBM Corp. 1981

FIGURE CAPTIONS

Fig. 1. (a) - Schematic illustration of an AMCZ silicon crystal growth arrangement. (b) magnetic field distribution inside the crystal growth chamber. Note that the field uniformity is within $\pm$ 3% in the silicon melt.

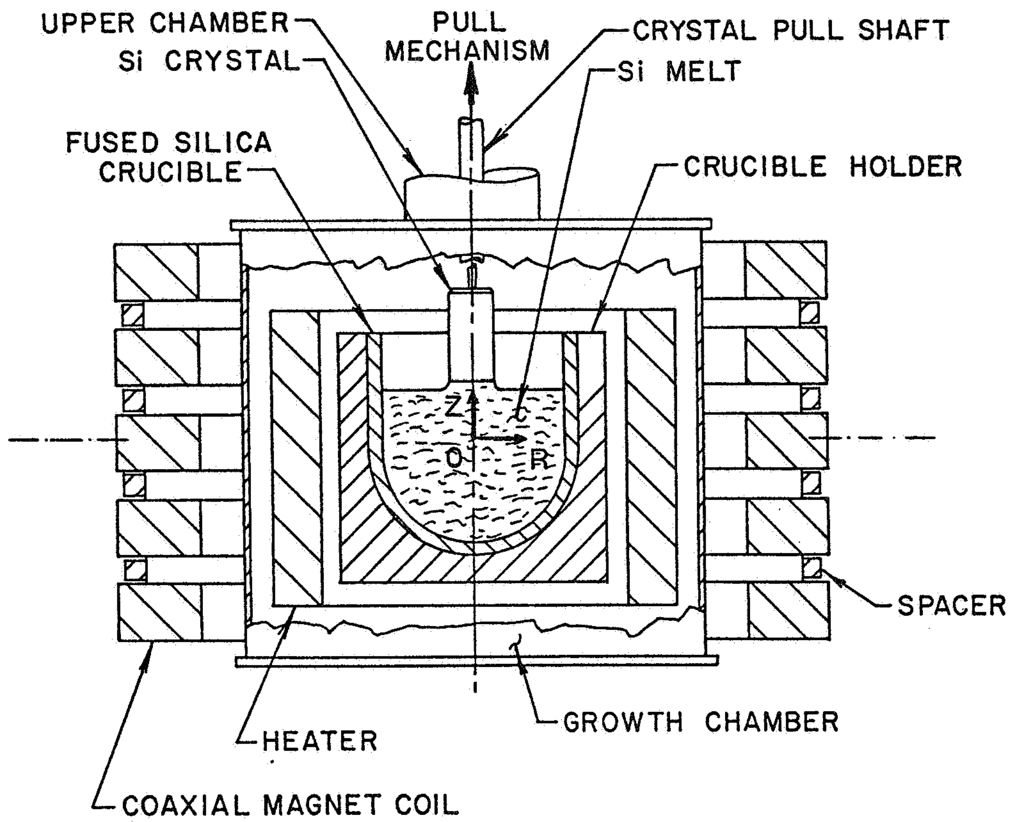
Fig. 2. Measured temperature change and the amplitude of the temperature fluctuations vs. the axial magnetic field strength at a fixed position in the melt at half the crucible radius, 5mm below the melt surface.

Fig. 3. Sketch of the striation pattern of an etched longitudinal crystal section. Random striations at B=0 assumed progressively a periodic pattern at $0.35 \leq B \lesssim 4.0$ kG. Note that the periodic striations have a non-uniform contrast, and some weak localized striations persist near the crystal periphery.

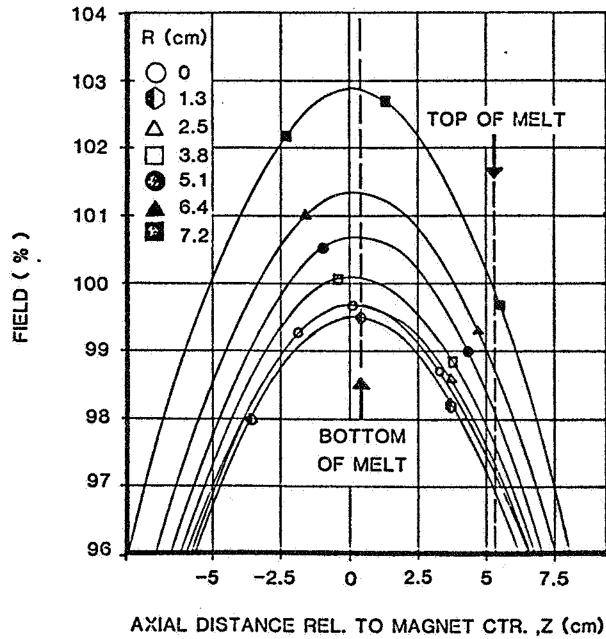
Fig. 4. Photomicrographs of some representative AMCZ crystal sections shown in Fig. 3. (a) B=0, (b) 0.35, (c) and (d) 1.0, (e) and (f) 4.0 kG. Note that the central region of the crystal grown at 4 kG is free of striations. Some dislocation etch pits are present in (f).

Fig. 5. Spreading resistance profile (a)-(f), parallel to the growth axis in typical crystal sections as seen in Fig. 4 (a)-(f), respectively.

Figure 1



(a)



(b)

Figure 2

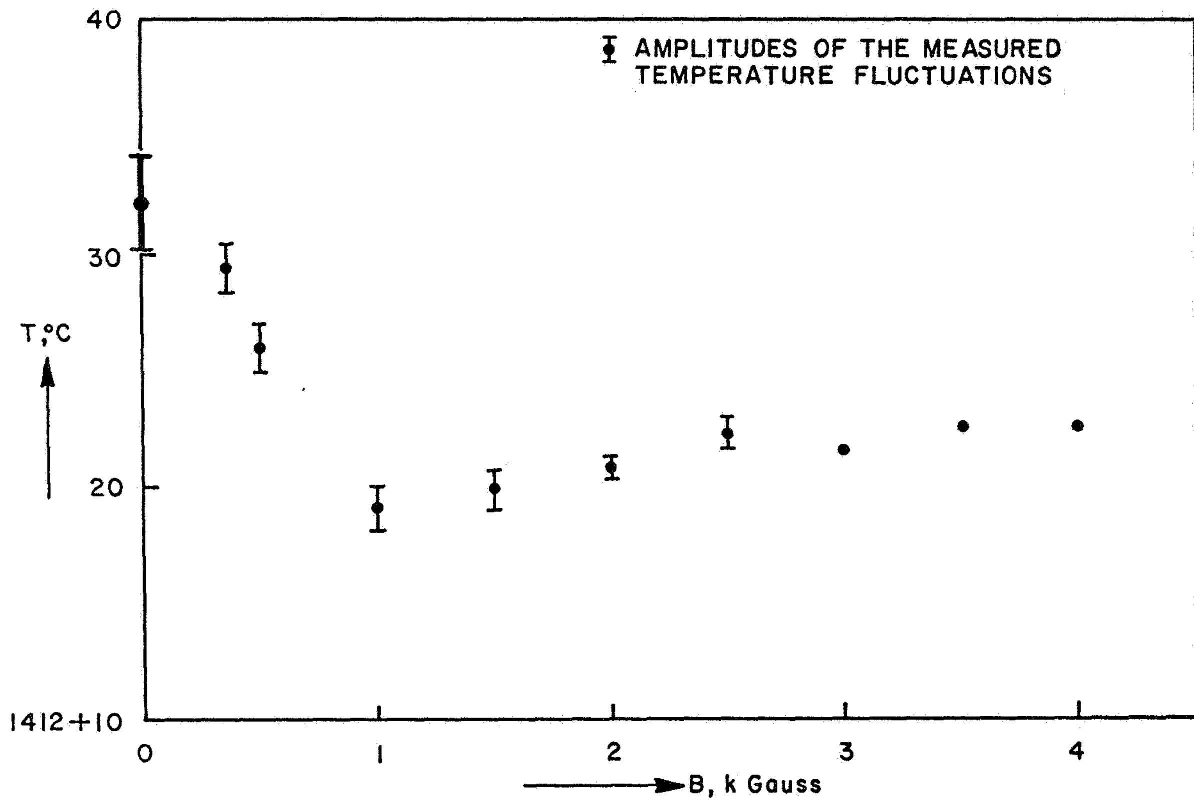


Figure 3

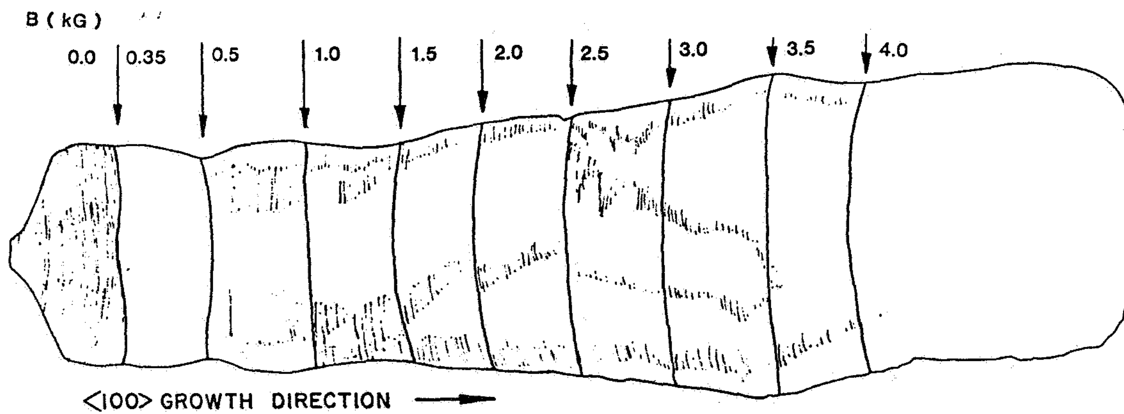
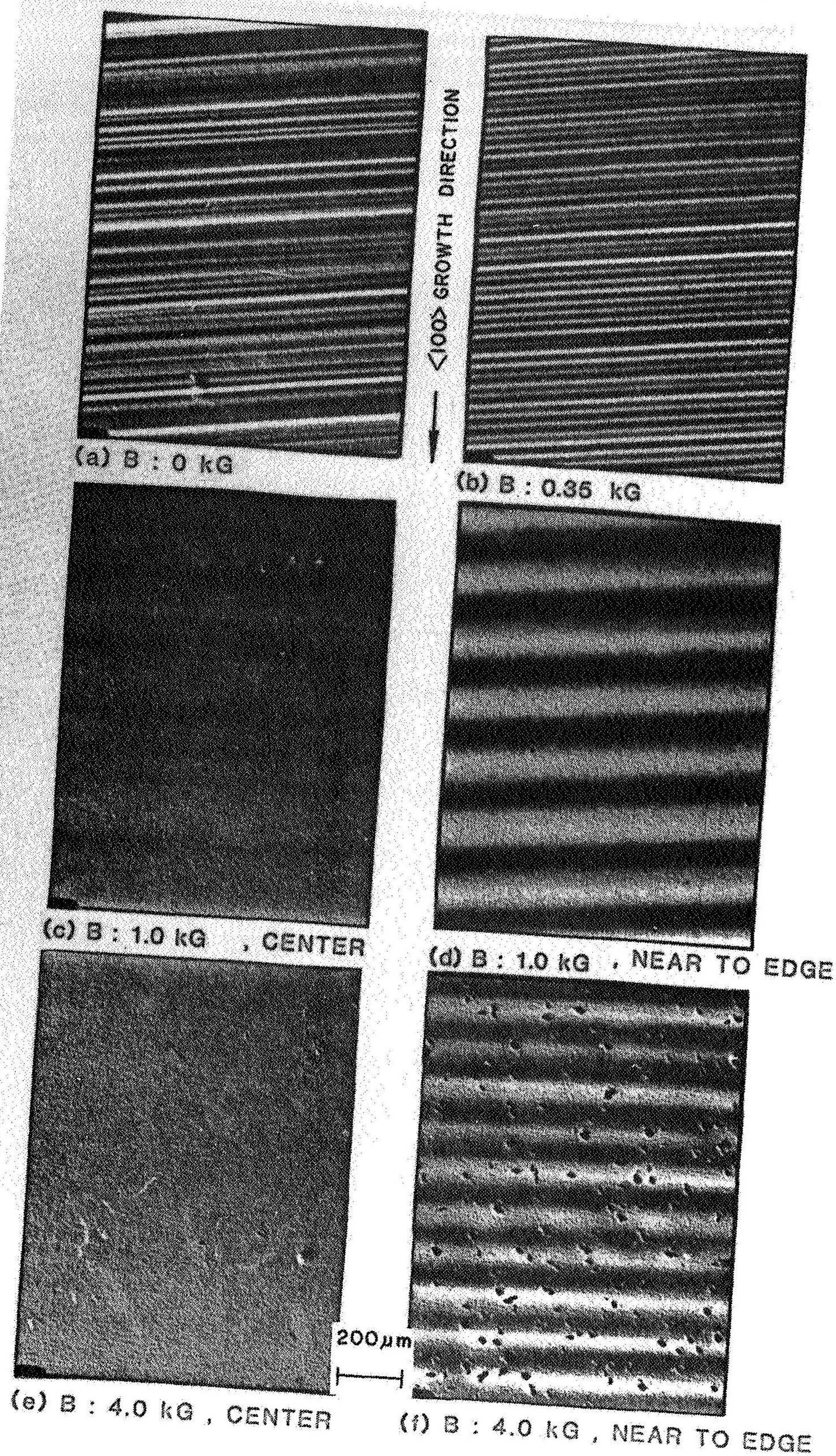


Figure 4

ORIGINAL PAGE IS
OF POOR QUALITY



ORIGINAL PAGE IS OF POOR QUALITY

Figure 5

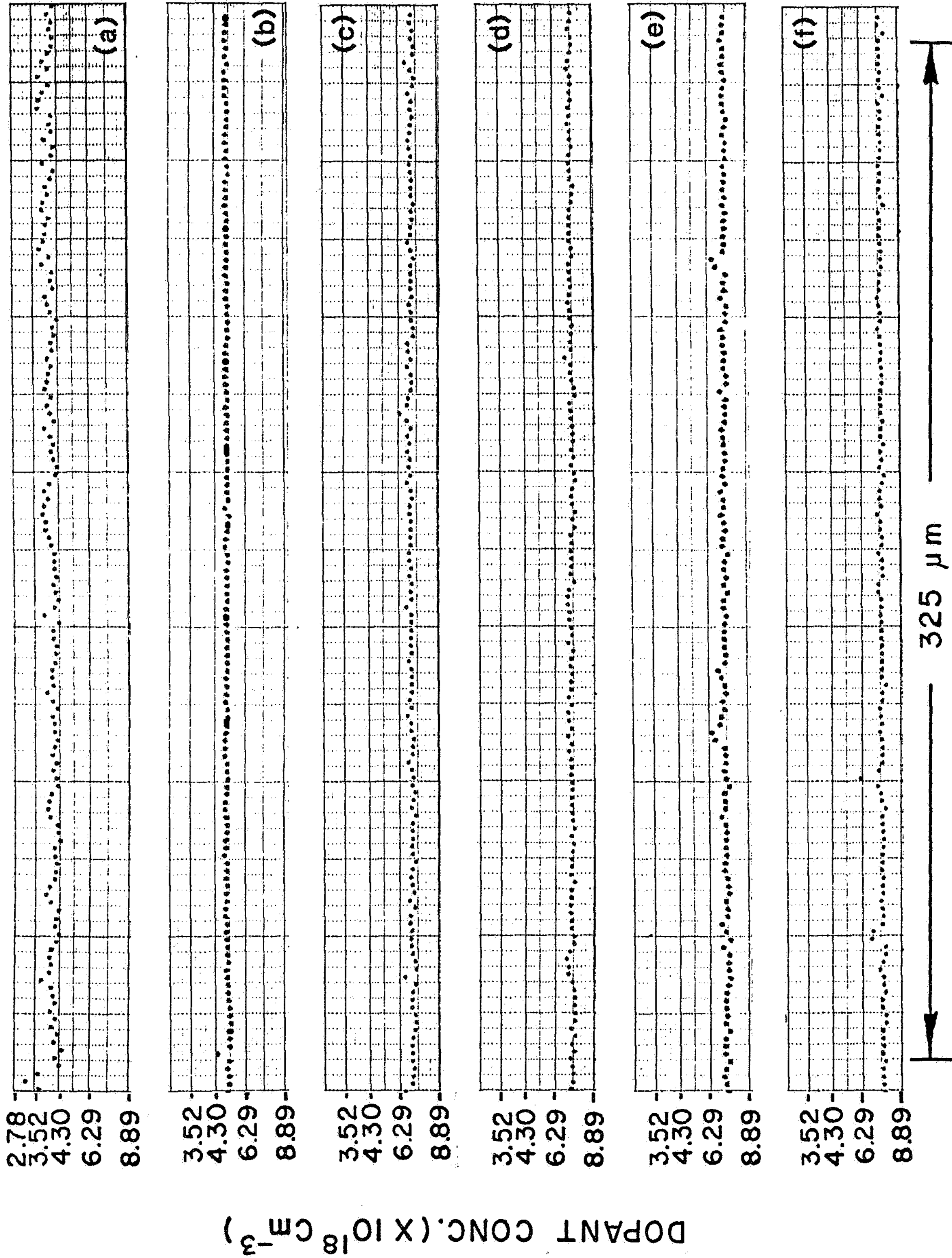


Figure 6

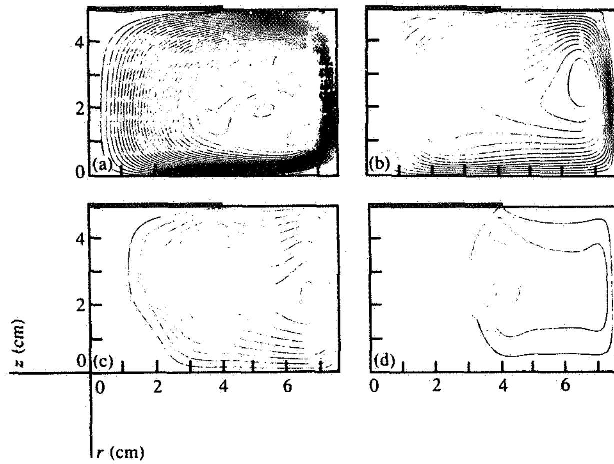
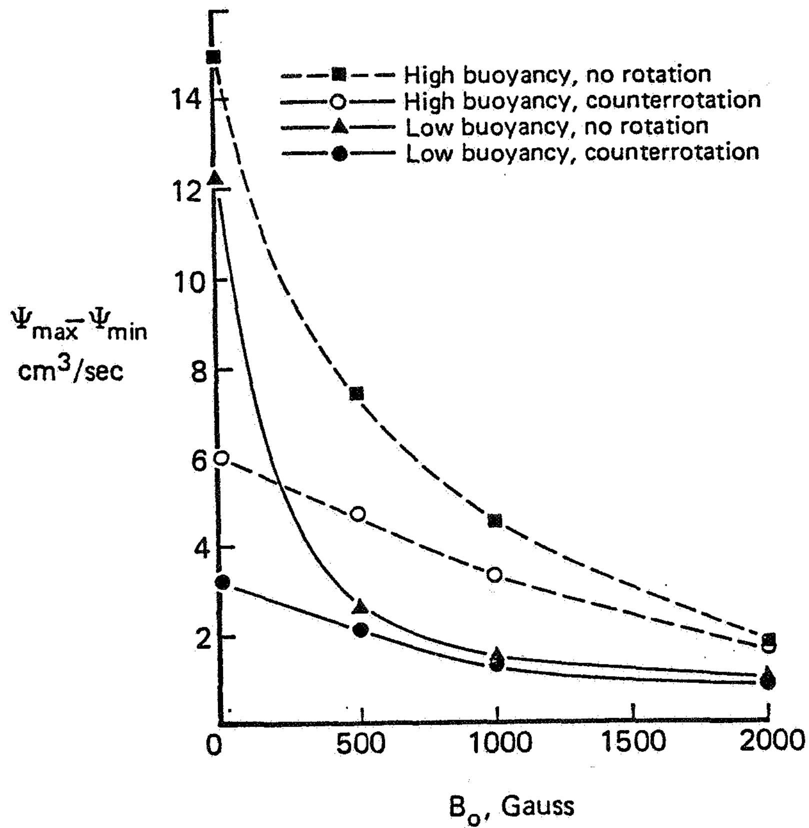


Figure 6 Meridional circulation patterns for the simulations of high-buoyancy flows without rotation: a) $B = 0$; b) $B = 0.05$; c) $B = 0.1$; and d) $B = 0.2$ T. Contour spacing = 0.5 cm^3/s.

Figure 7



Effect of magnetic field intensity on the strength of the meridional circulation.

DISCUSSION

LESK: Why does a magnetic field increase the viscosity?

WITT: According to the three-finger rule, you have the charge moving in one direction, which gives the charge, and you have the normal magnetic field, and then you have the right angles of force. The Lorentz force in this case always acts normal to the direction of propagation and that is interpreted as affecting the viscosity.

LESK: Why not try and force the liquid back where it came from by applying a current?

WITT: If you apply an electric current and you introduce a magnetic field then you get turbulence. You can use that for effective mixing in the melt if you want to.

N86-19730

HIGH PURITY LOW DEFECT FZ SILICON

H. Kimura and G. Robertson

Hughes Research Laboratories
Malibu, CA 91265

The most common intrinsic defects in dislocation-free float zone (FZ) silicon crystals are the A- and B-type "swirl" defects. The mechanisms of their formation and annihilation have been extensively studied by Petroff and de Kock[1], Foell, Goesele and Kolbesen[2], and others. Another type of defect in dislocation-free FZ crystals, found by Roksnoer and van den Boom[3], is referred to as a D-type defect. Concentrations of these defects can be minimized by optimizing the growth conditions and the residual swirls can be reduced by the post-growth extrinsic gettering process.

Czochralski (Cz) silicon wafers are known to exhibit higher resistance to slip and warpage due to thermal stress than do FZ wafers. Sumino and Yonenaga[4] examined various conditions under which dislocation-free Cz crystals have higher mechanical strength than dislocation-free FZ crystals. They observed no difference in the yield strength when external damage had been removed by chemical etching. The Cz crystals containing dislocations are more resistant to dislocation movement than dislocated FZ crystals because of the locking of dislocations by oxygen atoms present in the Cz crystals. Nitrogen doping of FZ wafers at concentrations as low as 1.5×10^{15} cm^{-3} was found by Sumino, et al.[5] to make such wafers less susceptible to slip and warpage than undoped Cz and FZ wafers containing dislocations.

Recently we have applied a transverse magnetic field during the FZ growth of extrinsic silicon.* The objective was the study of the spatial distribution of the major dopant, under the assumption that the magnetic field would reduce fluctuations in the flow occurring in the melt and thus in the dopant concentration. Important changes in spatial distribution of the dopant were indeed observed, but the level of fluctuations was not substantially decreased. The observed flow patterns, as revealed by striation etching and spreading resistance in Ga-doped silicon crystals, indicate strong effects of the transverse magnetic field on the circulation within the melt. At fields of 5500 gauss, the fluid flow in the melt volume is so altered as to affect the morphology of the growing crystal. For crystals grown without rotation, the cross section of the crystal becomes elliptical, with the major axis of the ellipse aligned along the field direction. Melt flow in the directions parallel and perpendicular to the field are distinctly different. We believe that the magnetic field offers a unique experimental tool to help elucidate the mass and energy transport occurring in the float zone process.

* This work has been supported in part by the U.S. Air Force Materials Laboratory.

PRECEDING PAGE BLANK NOT FILMED

References:

(1) Petroff, P.M. and de Kock, A.J.R., J. Crystal Growth 35, 4-10 (1976).

(2) Foll, H., Gosele, U. and Kolbesen, B.O., J. Crystal Growth 40, 90-108 (1977).

(3) Roksnoer, P.J. and van den Boom, M.M.B., J. Crystal Growth 53, 563-573 (1981).

(4) Sumino, K. and Yonenaga, I., Japanese J. Appl. Physics, 20, L685-L688 (1981).

(5) Sumino, K. and Yonenaga, I., Imai, M., and Abe, T., J. Appl. Physics 54, 5016 (1983).

Introduction

- FLOAT ZONE (FZ) Si CRYSTAL GROWTH
- CRYSTALLINE DEFECTS
- DEFECT GETTERING
- MECHANICAL STRENGTH OF FZ CRYSTALS

Growth of <100> Dislocation-Free FZ Si Crystals

PARAMETERS AFFECTING THE DISTRIBUTION AND CONCENTRATION OF INTRINSIC DEFECTS

- PULL RATE
- ROTATION RATE OF CRYSTAL
- AMBIENT ATMOSPHERE
- COOLING RATE OF CRYSTAL
- MAGNETIC FIELD

Observable Imperfections in Dislocation-Free FZ Si Crystals

- STRIATIONS
- "SWIRLS"
- STACKING FAULTS

Swirls

DENSELY PACKED DISCRETE DEFECTS

A-, B-, AND D-TYPE DEFECTS IN FZ DISLOCATION-FREE CRYSTALS

A-TYPE

- DISLOCATION LOOPS OR CLUSTERS OF DISLOCATION LOOPS WHICH ARE FORMED BY AGGLOMERATION OF Si SELF-INTERSTITIALS
- DISTRIBUTED IN STRIATED PATTERN NEAR BANDS OF IMPURITIES WITH DISTRIBUTION COEFFICIENT LESS THAN ONE
- SIZE: $\sim 1 - 40\,\mu m$
- CONCENTRATION: $10^7 - 10^9\ cm^{-3}$ (H. FÖLL, et al.)
- PULL RATES OF CRYSTAL FOR FORMATION OF DEFECTS: 0.2 - 4.5 mm/min (23 mm diam)

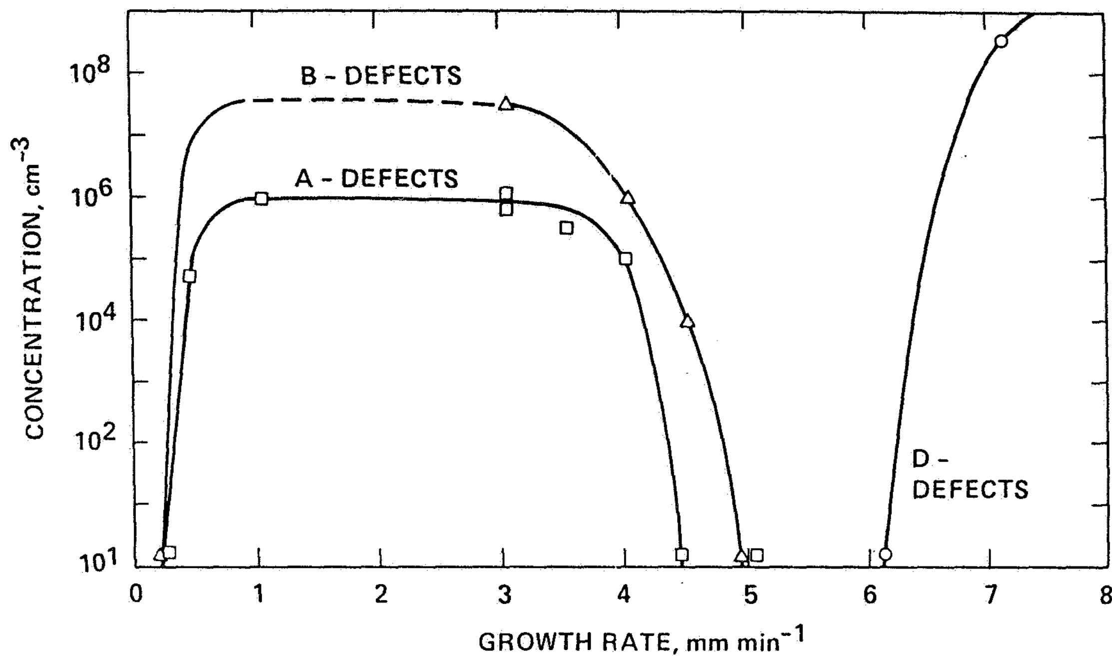
B-TYPE

- THREE DIMENSIONAL AGGLOMERATES OF Si SELF-INTERSTITIALS AND IMPURITY ATOMS, PARTICULARLY C
- DISTRIBUTED IN STRIATED PATTERN SIMILARLY TO A-TYPE SWIRLS
- SIZE: ≤ 30 nm
- CONCENTRATION: $<\sim 10^{11}\ cm^{-3}$ (H. FÖLL, et al.)
- PULL RATES OF CRYSTAL FOR FORMATION OF DEFECTS: 0.2 - 5 mm/min (23 mm diam)

D-TYPE

- CONDENSATION OF POINT DEFECTS (VACANCIES), WHICH DO NOT PRECIPITATE ON CARBON NUCLEI
- HOMOGENEOUSLY DISTRIBUTED IN THE CRYSTAL
- SIZE: 30 nm - $1\,\mu m$
- CONCENTRATION: $10^9\ cm^{-3}$ (P. J. ROKSNOER, et al.)
- PULL RATES OF CRYSTAL FOR FORMATION OF DEFECTS: >6 mm/min

Swirl Concentration vs Growth Rate



FROM: P. J. ROKSNOER AND M. M. B. van den BOOM
J. OF CRYSTAL GROWTH 53 (1981) 563 - 573

Extrinsic Gettering of Swirl Defects

ABRASION GETTERING (C. L. REED AND K. M. MAR)

- MATERIAL

  <111>, P-DOPED, FZ Si CRYSTAL WITH SWIRL DEFECTS

  WAFERS 305 $\pm$ 13 μm THICK

  SPECULAR DAMAGE-FREE FRONT SURFACE

  CHEMICALLY ETCHED STRAIN-FREE BACK SURFACE

- ABRASION

  BACK SIDE DAMAGE APPLIED BY MECHANICALLY LAPPING WITH 2 - 15 μm SIZE DIAMOND AND ALUMINA PARTICLES

- OXIDATION AND CHEMICAL ETCHING

  OXIDIZED AT 1150°C TO ACTIVATE DEFECTS AND WRIGHT ETCHED TO REVEAL DEFECTS

- RESULTS

  ABRASION GETTERING REDUCED THE ETCH PIT DENSITY FROM 5×10^5 TO $< 5 \times 10^2$ cm^{-2}

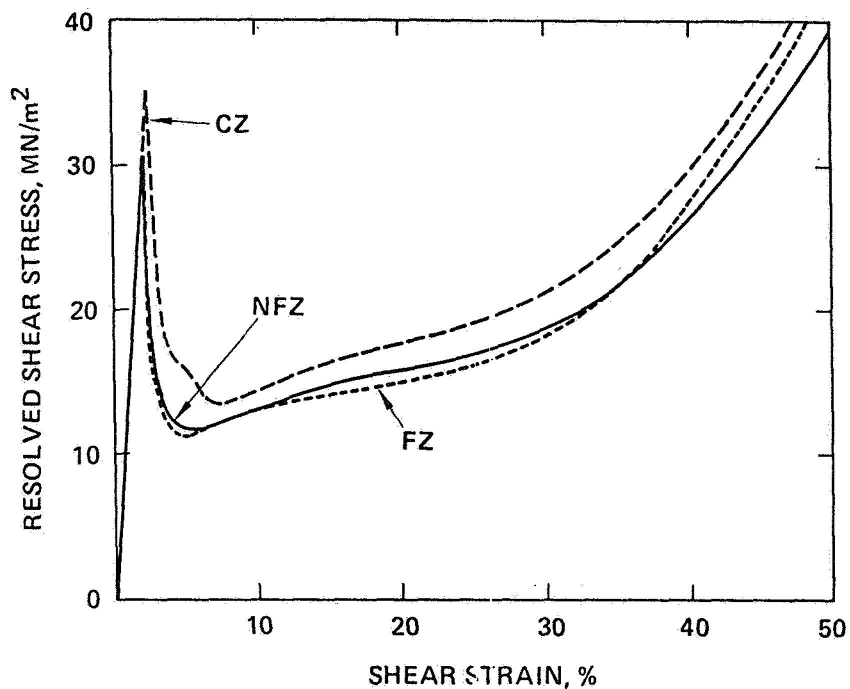
Mechanical Strength of FZ and Cz Si Crystals
(K. Sumino et al, 1981)

- YIELD STRENGTH SAME FOR DISLOCATION-FREE CHEMICALLY POLISHED FZ AND CZ WAFERS
- DIFFERENCE IN MECHANICAL STRENGTH DUE TO DISLOCATION PRIOR TO DEFORMATION
- DISLOCATIONS NOT GENERATED IN CZ FOR STRESSES $\tau < \tau_c$
- DISLOCATIONS GENERATED IN FZ FOR VERY LOW τ

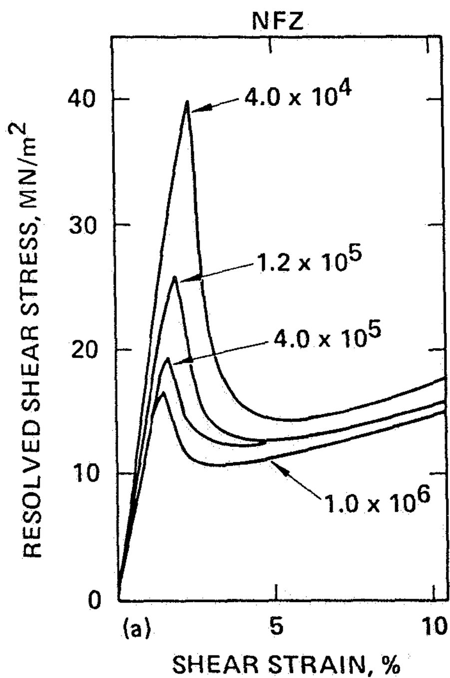
Effect of Nitrogen on Mechanical Strength of FZ Crystals
(K. Sumino et al, 1983)

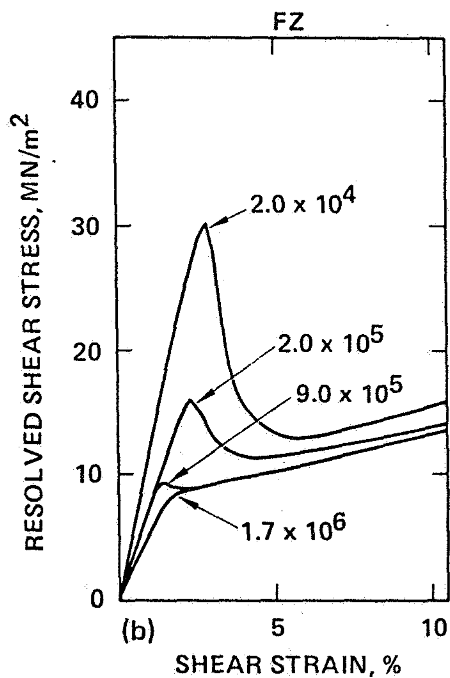
- 1.5×10^{15} cm^{-3} N-DOPED FZ LESS SUSCEPTIBLE TO SLIP
- N ELECTRICALLY INACTIVE IN Si. OCCUPIES INTERSTITIAL SITE
- DISLOCATION-FREE FZ, CZ HAVE SIMILAR STRESS-STRAIN CHARACTERISTICS
- DISLOCATED FZ N-DOPED HAVE HIGH UPPER YIELD STRESS
- DISLOCATIONS IN FZ N-DOPED IMMOBILIZED UNDER LOW STRESSES AT ELEVATED TEMPERATURES

Resolved Shear Stress vs Shear Strain



FROM: K. SUMINO, et al.
J. APPL. PHYS. 54 (9) SEPT 1983





FROM: K. SUMINO, et al.
J. APPL. PHYS. 54 (9) SEPT 1983

Introduction

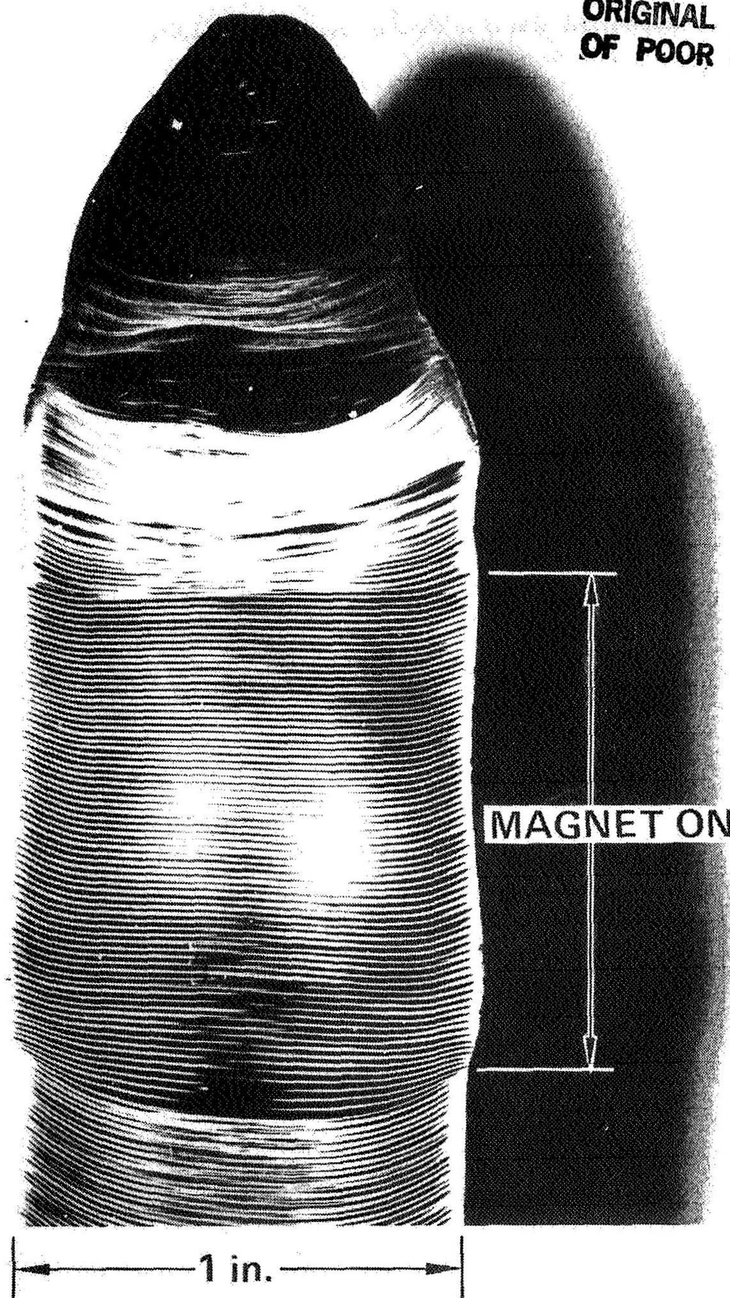
- EXPERIMENTAL APPARATUS FOR APPLYING TRANSVERSE MAGNETIC FIELD TO FZ MOLTEN ZONE
- TYPICAL RESULTS FROM ROTATING CRYSTALS
- UNUSUAL RESULTS FOR NON-ROTATING CRYSTALS
- SIGNIFANCE OF RESULTS

Experimental Parameters

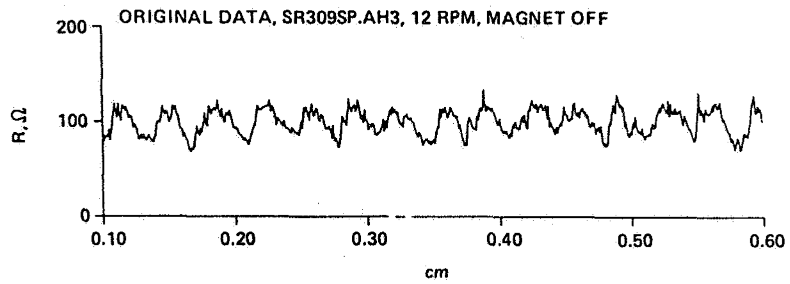
Parameter		Value
• CRYSTAL ORIENTATION	–	⟨100⟩ AND ⟨111⟩
• CRYSTAL DIAMETER	–	UP TO 30 mm
• PULL RATES	–	2 TO 4 mm/min
• ROTATIONAL RATES	–	0 TO 12 rpm
• MAGNETIC FIELD STRENGTH	–	0 TO 5500 G

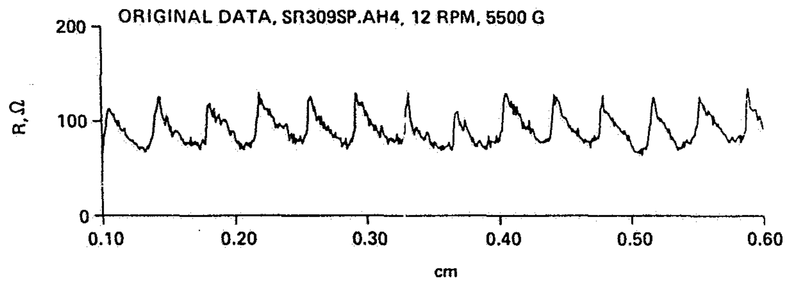
Striation Etch Pattern, Crystal Z309; 5000 Gauss Transverse Magnetic Field (12 rpm Section)

ORIGINAL PAGE IS OF POOR QUALITY

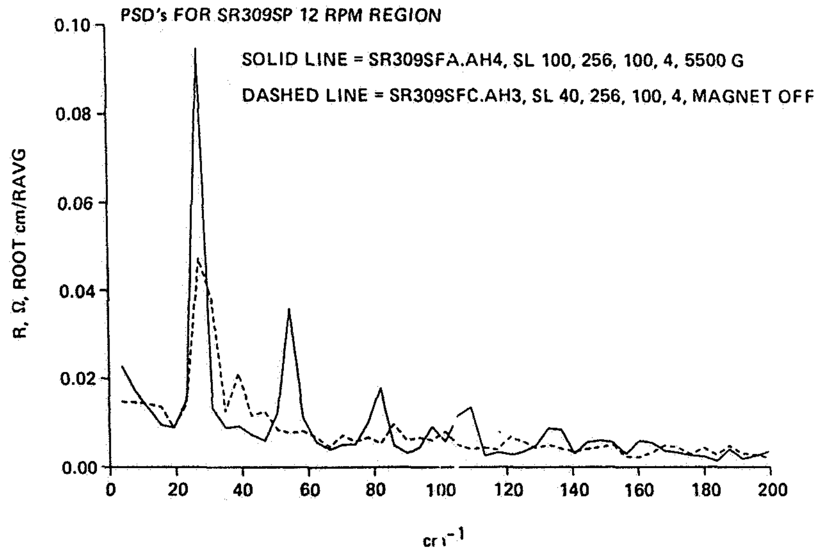


Typical Spreading Resistance Data





Power Spectral Densities

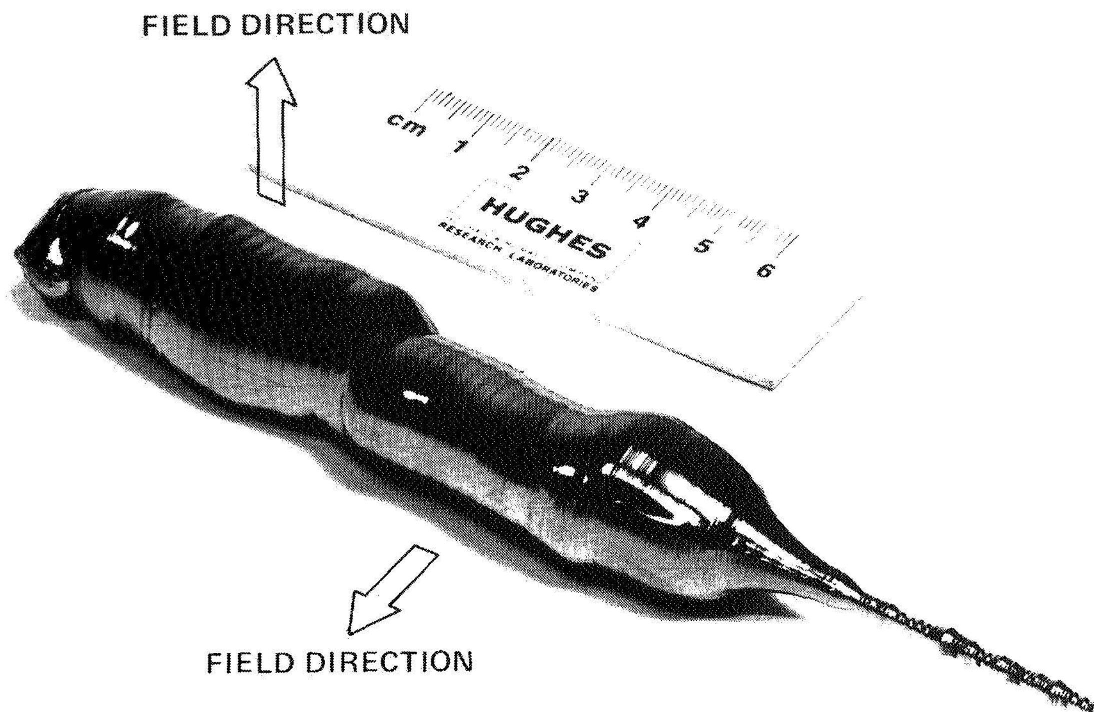


ORIGINAL PAGE IS
OF POOR QUALITY

5500-Gauss Field Applied to Rotating Crystal

OBSERVATION	HYPOTHESIZED CAUSE
• GROWTH INTERFACE "FLATTENS"	ALTERED HEAT FLOW PATTERNS
• CRYSTAL DIAMETER INCREASES	FLATTENING OF INTERFACE
• DOPANT CONCENTRATION INCREASES	THICKENED DIFFUSION BOUNDARY LAYER
• ROTATIONAL STRIAE ENHANCED	REDUCED FLUCTUATIONS
• FINE STRIAE ALTERED	REDUCED "TURBULENCE"

Crystal Grown With No Rotation in 5000 Gauss Transverse Field (Z321)



5500-Gauss Field Applied to Non-Rotating Crystal

OBSERVATION	HYPOTHESIZED CAUSE
• DOPANT CONC INCREASES	THICKENED DIFFUSION BOUNDARY LAYER
• ROTATIONAL STRIAE ABSENT	AS EXPECTED FOR 0 RPM
• FINE STRIAE ALTERED	REASON NOT CLEAR YET
• SR FLUCTUATIONS REDUCED FOR F $< 300\ cm^{-1}$ ($\sim$2 Hz)	INCREASED MELT "VISCOSITY"
• CROSS SECTION → ELLIPTICAL	B x V EFFECTS
• GROWTH INTERFACE → CYLINDRICAL	ALTERED HEAT TRANSFER

Summary

- MAGNETIC FIELD IMPACTS CIRCULATION PATTERNS IN THE MOLTEN ZONE
- FORCES FROM FIELD ARE LARGE ENOUGH TO PRODUCE USEFUL EFFECTS
- FOURIER ANALYSIS OF SPREADING RESISTANCE MAY REVEAL FLUCTUATION SPECTRA IN MELT
- MAGNETIC FIELD PROVIDES NEW TOOL TO STUDY THE FZ GROWTH PROCESS

DISCUSSION

NEITZEL: I've heard the word turbulence mentioned a couple of times today and I think we have to be very careful when we mention the word turbulence because it implies something definite, in a fluid dynamic sense, that I don't think is occurring in your geometry for your region of parameter space.

ROBERTSON: Do you have some good reason for saying it's not occurring?

NEITZEL: I would guess it's not. We did a rough calculation for the maximum rotational Reynolds number that you should see in your configuration. It's probably on the order of 1000. For the transition to turbulence, the transitional Reynolds number is 3×10^5.

ROBERTSON: All I can tell you is that the flows in that melt volume are very strong. They are being driven by electromagnetic forces. They are not being driven by convective forces or Marangoni surface-tension forces or the rotational forces. Those are all there, but superimposed on that is a circulation pattern from the electrodynamic forces. Professor Muhlbauer has just published information that indicates that that force is 50 to 100 times stronger than these other forces. If you look at particles in that melt zone, for example, they are in violent motion.

NEITZEL: I don't doubt that, but I just want to say that it's possible to have very oscillatory laminar flows that are not turbulent flows.

N86-19731

DEFECTS IN SILICON EFFECT ON DEVICE PERFORMANCE AND RELATIONSHIP TO CRYSTAL GROWTH CONDITIONS

L. Jastrzebski

RCA Laboratories
Princeton, NJ 08540

A relationship between material defects in silicon in performance of electronic devices will be described. A role which oxygen and carbon in silicon play during defects generation process will be discussed.

Electronic properties of silicon are a strong function of the state in which oxygen is in silicon. This various states control mechanical properties of silicon efficiency of internal gettering and formation of defects in device active area. In addition to: temperature, time, ambient, cooling/heating rates of high temperature treatments the oxygen state is a function of crystal growth process. It is well documented that incorporation of carbon and oxygen into silicon crystal is controlled by geometry, and rotation rates applied to crystal and crucible during crystal growths. Also, formation of nucleation centers for oxygen precipitation is influenced by growth process, although there is still a controversy which parameters play a major role.

All these factors will be reviewed with the special emphasis on the area which are still ambiguous and controversial.

PRECEDING PAGE BLANK NOT FILMED

Introduction

DEFECT REDUCTION IN DEVICE ACTIVE AREA

PROBLEMS:

SOFT JUNCTIONS - LEAKAGE

LOW LIFETIME - LEAKAGE, DIFFUSION LENGTH DEGRADATION

DEFECTS:

CRYSTALLOGRAPHIC:

- DISLOCATIONS
- STACKING FAULTS
- PRECIPITATES

} ELECTRIC ACTIVITY ⇕ DECORATION (HEAVY METALS)

POINT:

- GENERATION/RECOMBINATION CENTERS ⇕ (HEAVY METALS)

MECHANICAL STRENGTH

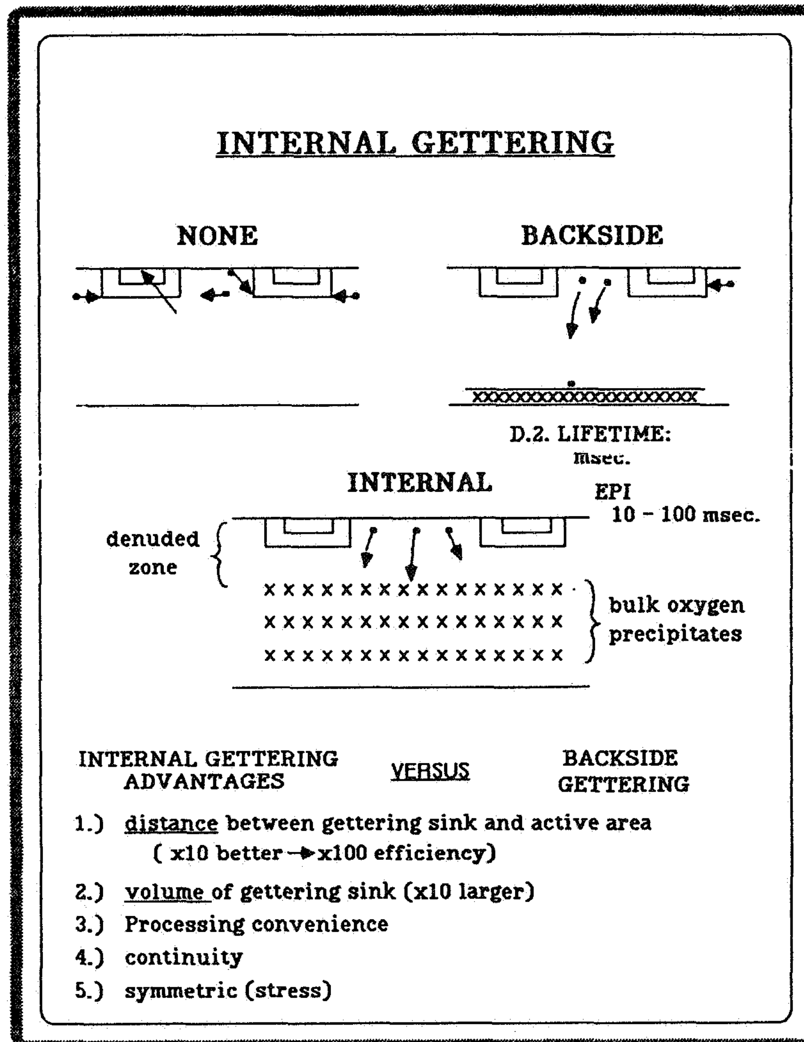
PRECEDING PAGE BLANK NOT FILMED

Goal

ESTABLISH RELATIONSHIP BETWEEN:

1. INTERNAL GETTERING EFFICIENCY AND CHARACTERISTICS OF OXYGEN PRECIPITATES

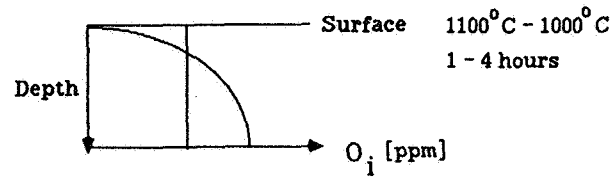
2. CHARACTERISTICS OF SUPPLIED WAFERS AND OXYGEN PRECIPITATION (FOR A GIVEN PROCESS)



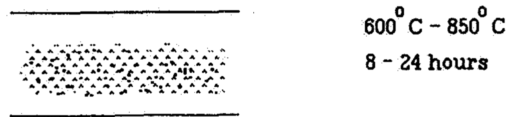
ORIGINAL PAGE IS
OF POOR QUALITY

INTERNAL GETTERING PROCEDURE

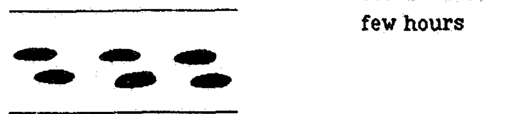
1.) Outdiffusion of oxygen from surface region.



2.) Nucleation step.



3.) Precipitate growth.



Internal Gettering (Bipolar Process)

1. EFFECT ON CIRCUIT PERFORMANCE/YIELD FOR BIPOLAR
2. MECHANISM OF INTERNAL GETTERING/EFFICIENCY
3. OXYGEN PRECIPITATION KINETICS/CHARACTERISTICS OF AS-GROWN WAFERS

ACCORDING TO PUBLISHED RESULTS

INTERNAL GETTERING EFFICIENCY

- DEPTH OF DENUDED ZONE
- AMOUNT OF PRECIPITATED OXYGEN

PRECIPITATION KINETICS ⟷ STARTING WAFERS CHARACTERISTICS

- INTERSTITIAL OXYGEN CONCENTRATION
- CARBON CONCENTRATION
- COOLING RATE OF CRYSTAL BULL

NAKANISHI....

JAP. J. APPL. PHYS. (1980)

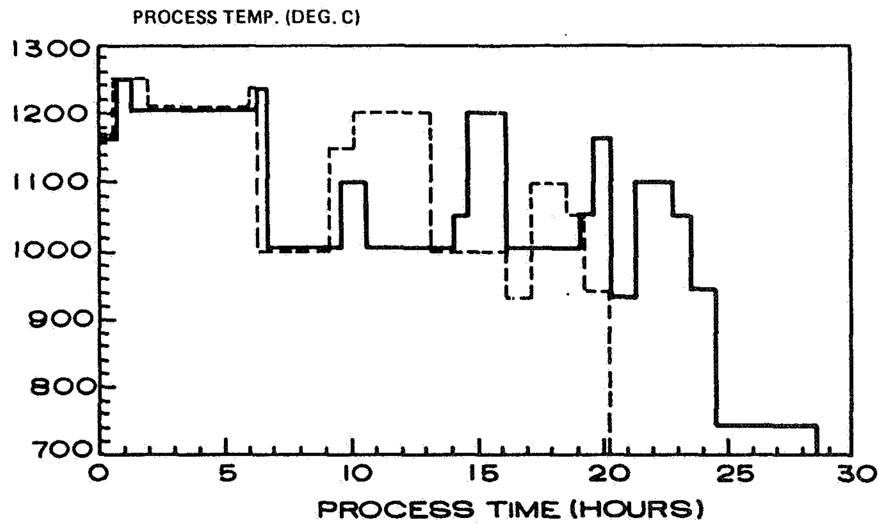


FIG. 1 TIME VS TEMP OF I^2L (SOLID LINE) AND ANALOG (DASHED LINE) PROCESSES.

Efficiency of Internal Gettering

FUNCTION OF:

- DEPTH OF DENUDED ZONE
- AMOUNT OF PRECIPITATED OXYGEN
- PRECIPITATES MORPHOLOGY
- PRECIPITATION KINETICS

EACH PROCESS (BIPOLAR, CMOS, CCD) HAS DIFFERENT REQUIREMENTS:

- DEVICE SENSITIVITY
- TIME/TEMPERATURE
- EQUIPMENT

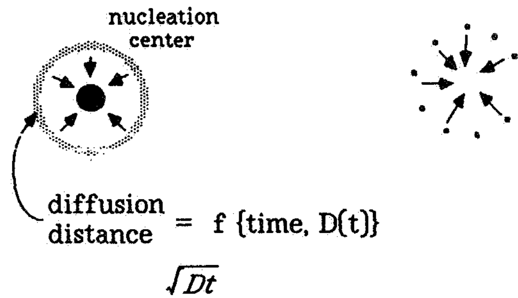
RELATIONSHIP OF I.G. TO STARTING CHARACTERISTICS OF SILICON WAFERS:

- INTERSTITIAL OXYGEN CONCENTRATION
- CARBON CONCENTRATION
- NONINTERSTITIAL OXYGEN CONCENTRATION
- POINT DEFECTS ⇄ COOLING, ???

GROWTH VELOCITY FLUCTUATIONS? → POINT DEFECTS

(heterogeneous)

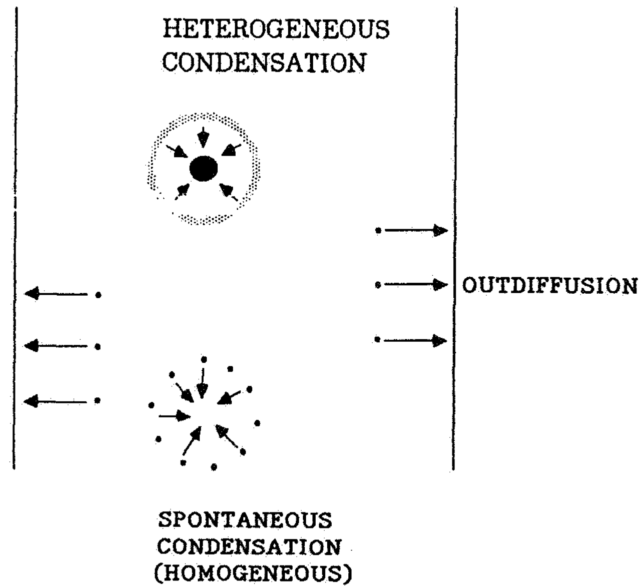
spontaneous
nucleation
(homogeneous)



Heterogeneous and homogeneous nucleation can take place in the same time.

Contribution of each of them will change with temperature.

Point-Defect Condensation During Cooling of Silicon Ingot



Crystal Growth

1. INCORPORATION OF OXYGEN FROM SiO_2 CRUCIBLE INTO THE SILICON MELT

2. INTERFACIAL PHENOMENA--EFFECT OF GROWTH KINETICS:

   EFFECT OF *TEMPERATURE* FLUCTUATIONS:
   - INCORPORATION OF OXYGEN INTO THE SOLID
   - FORMATION OF HETEROGENEOUS NUCLEATION *CENTERS*
   - FORMATION OF POINT DEFECTS

   ABE "SEMICONDUCTOR SILICON 1981"

3. COOLING AFTER GROWTH:

   - CONDENSATION OF POINT DEFECTS
   - INITIAL STAGE OF OXYGEN PRECIPITATION

   850° - 650°C TEMPERATURE RANGE

   NAKANISHI...JAP. J. APPL. PHYS. (1980).

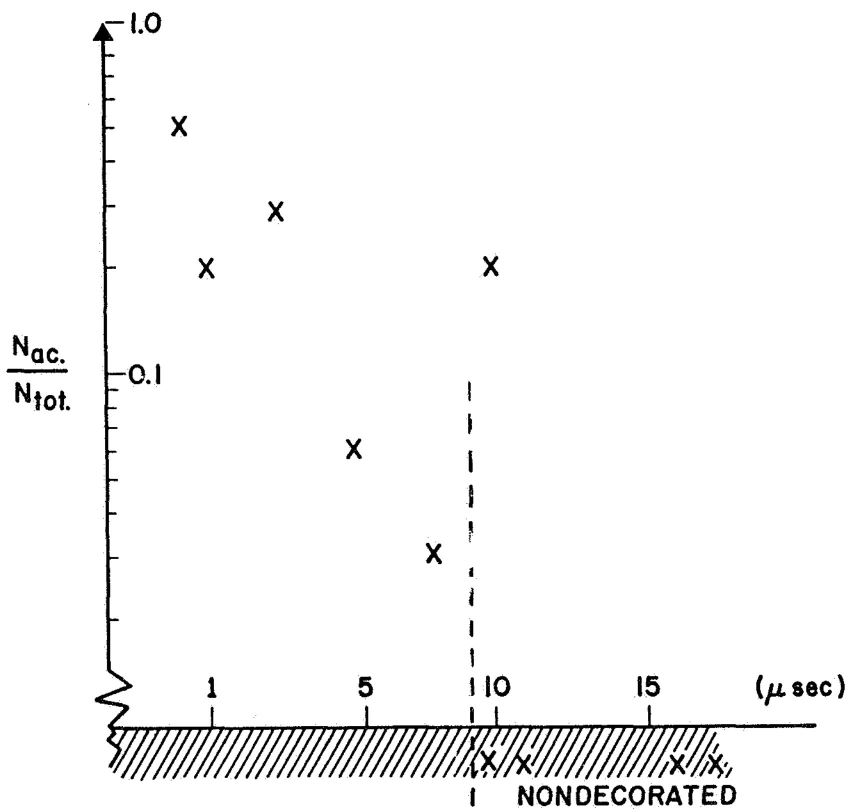
Comparison Between Oxygen Precipitation Models

	Driving Force	Kinetic Limiting Step	Precipitation Centers
Homogeneous	Critical value value of super-saturation	Condensation or diffusion of oxygen	None
Heterogeneous	Oxygen super-saturation (interstitial oxygen concentration minus oxygen solubility)	Diffusion of oxygen	Impurities clusters: carbon, donors, acceptors. Point clusters: small vacancy complexes. Noninterstitial oxygen

Depth of Denuded Zone

SAME FOR ALL SUPPLIERS

1-1	35 [μm]
1-2	30
2-1	32
3-1	28
3-2	35
4	30
5-1	30



Probability of Decoration ($\frac{\text{Electrically Active}}{\text{Total}}$ Defects) as a Function of Lifetime.

ORIGINAL PAGE IS
OF POOR QUALITY

Table I. Parameters of As-Grown Wafers

Group(*)	Interstitial Oxygen (ppm) 20 30 40	Non-Interstitial Oxygen in As Grown (ppm)	Carbon Concentration (ppm)
1-1(**)		None	1-3.5
1-2		≈1.5	1-3.5
2-1		None	None
2-2		None	0.3-0.6
3-1		≈2	0.6-1.0
3-2		≈3	<2(***)
4		None	0.3-0.8
5-1(****)		None	None
5-2		None	None

(*) First number corresponds to supplier.

(**) According to supplier 1 group 1-2 had higher precipitation rate than 1-1.

(***) Two subgroups: (1) carbon less than 0.5 ppm; (2) carbon 1-2 ppm.

(****) Group 5-1 had 3 μm backside damage, 5-2 had 10 μm backside damage.

Table II. Efficiency of Internal Gettering; Yield Improvement (See Text) and the Amount of Precipitated Oxygen During I^2L and Analog Processes

Group	Preheat Treatment Yes	Preheat Treatment No	Initial Interstitial Oxygen (PPMA)	Yield Loss Due to Leakage — Analog: % Experiment / % Standard	Analog: Normalized to Lowest Loss Observed	I^2L: Normalized to Lowest Loss	Precipitated Oxygen: Analog	Precipitated Oxygen: I^2L
1-1-I	 X	X	30-34	.46 .31	2.7 1.8	1.12	19 20	19 22
1-1-II		X	30-34	.93	1.15			
1-2	 X	X	30-35	1.1 .6	3.5 6.1		21 22	21 24
2-1	 X	X	22-25	1.1	2.0		2 9	6 10
2-2	 X	X	24-28	1.4	2.7		3 14	5 16
3-1	 X	X	22-26	1.4	2.5	1.46 3.4	6 11	11 14
3-2	 X	X	27-29	.83 .73	1.6 1.3	1.22 3.1	15 15	18 18
4	 X	X	37-42	1.2 .54	2.2 1.0	 1.0	10 23	8 23
5-1	 X	X	30-33	.84	1.3		8 16	12 19
5-2	 X	X	30-32	1.05	1.65	1.25	13 16	11 17

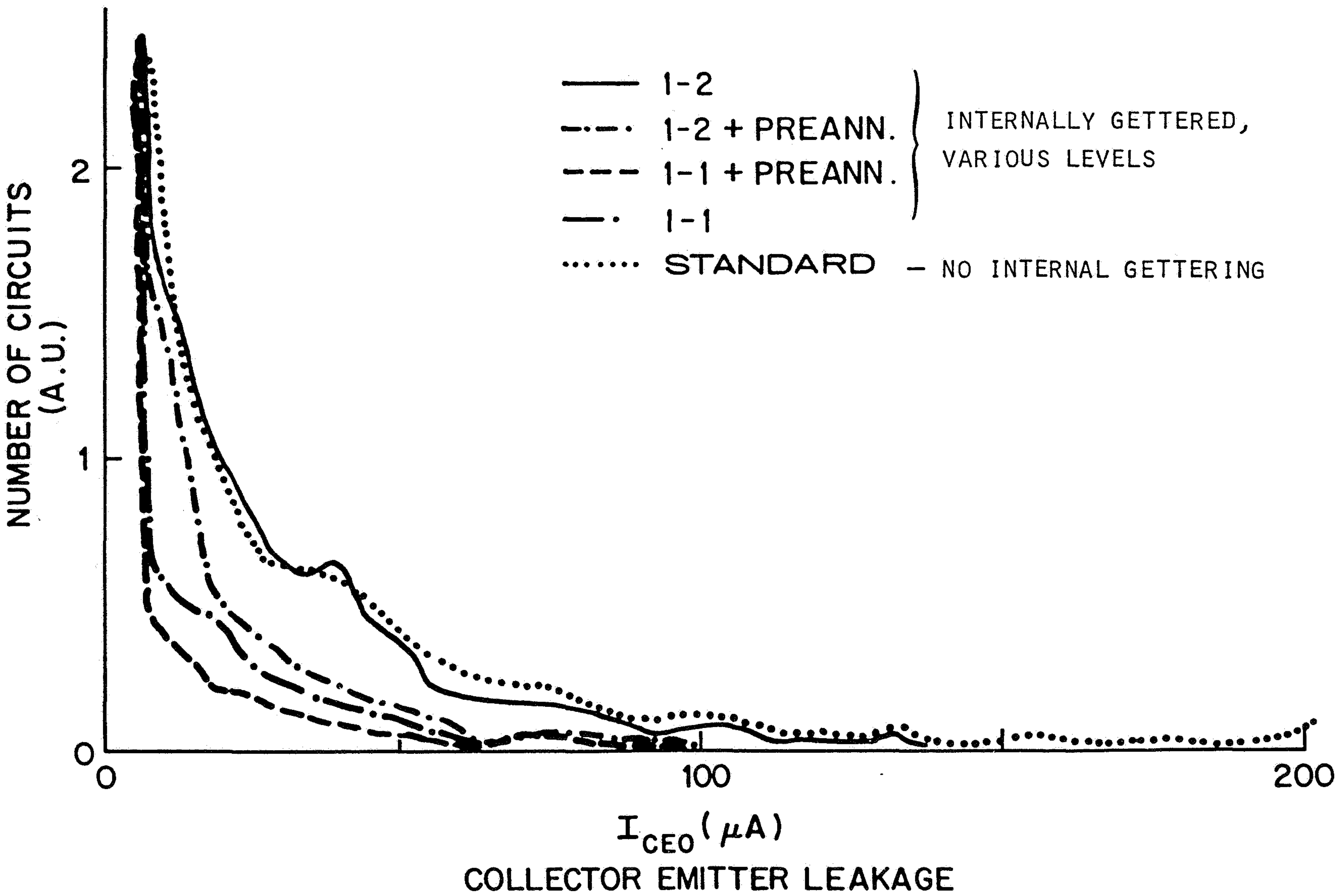


Figure 2. Leakage Distribution for Analog Circuits Made on Standard and Internally Gettered Wafers (1-1, 1-2)

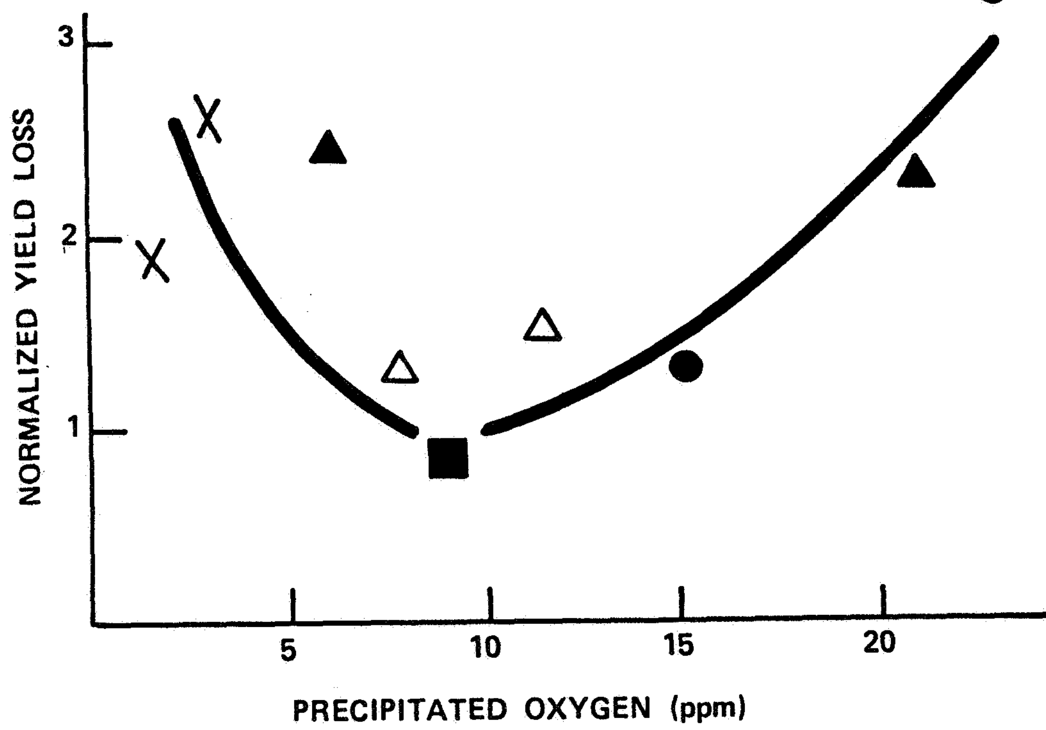


Figure 4. Normalized Yield Loss as a Function of Amount of Precipitated Oxygen After Completion of the Analog Process (Wafers Without Preannealing) O - Group 1, X - Group 2, - Group 3, - Group 4

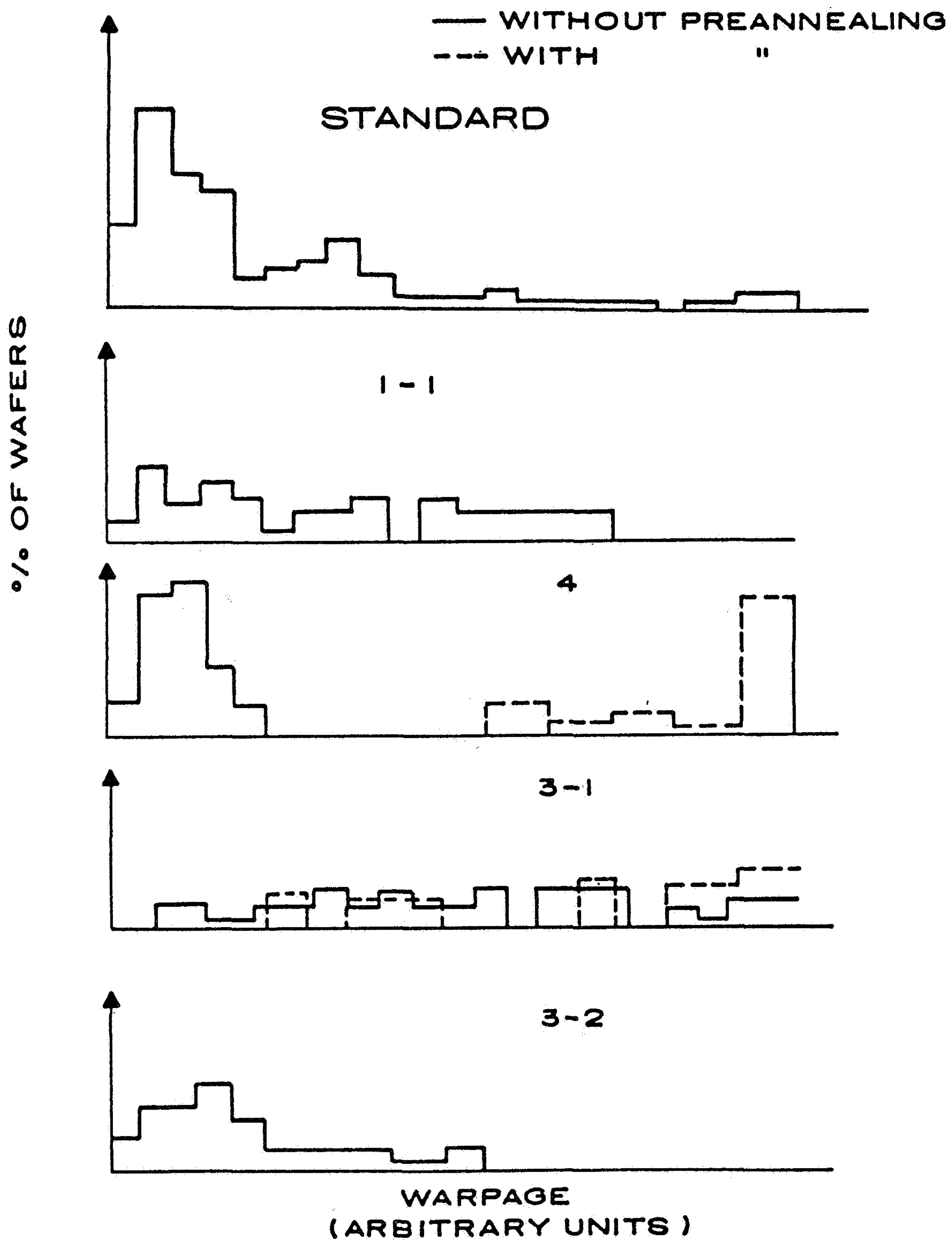


Figure 6. Histogram of Warpage in the Wafers from Different Groups After Completion of Analog Process

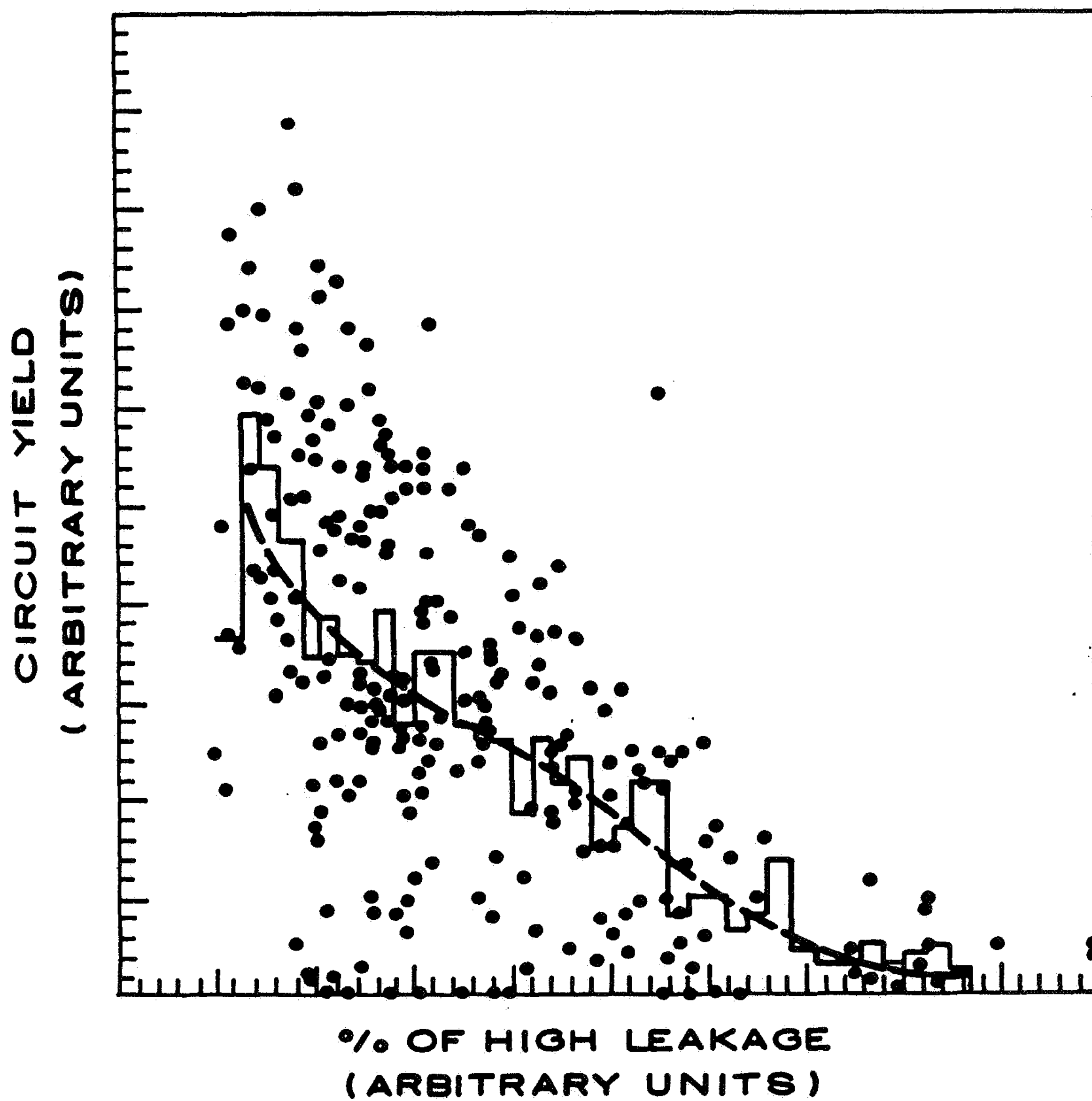
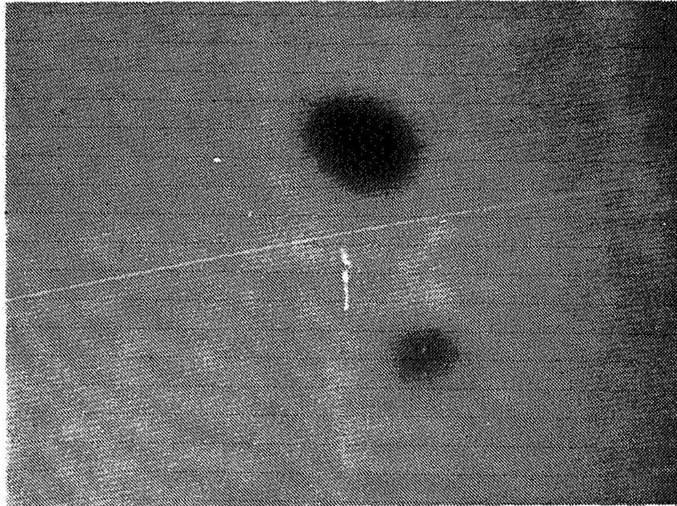


Figure 3. I^2L Circuit Yield Versus % of Highly Leaky Circuits

ORIGINAL PAGE IS
OF POOR QUALITY



EBIC

Dash Etch

15 μm

Decoration of Crystallographic Defects by Heavy Metals.
Only two out of four defects are electrically active.

ORIGINAL PAGE IS
OF POOR QUALITY

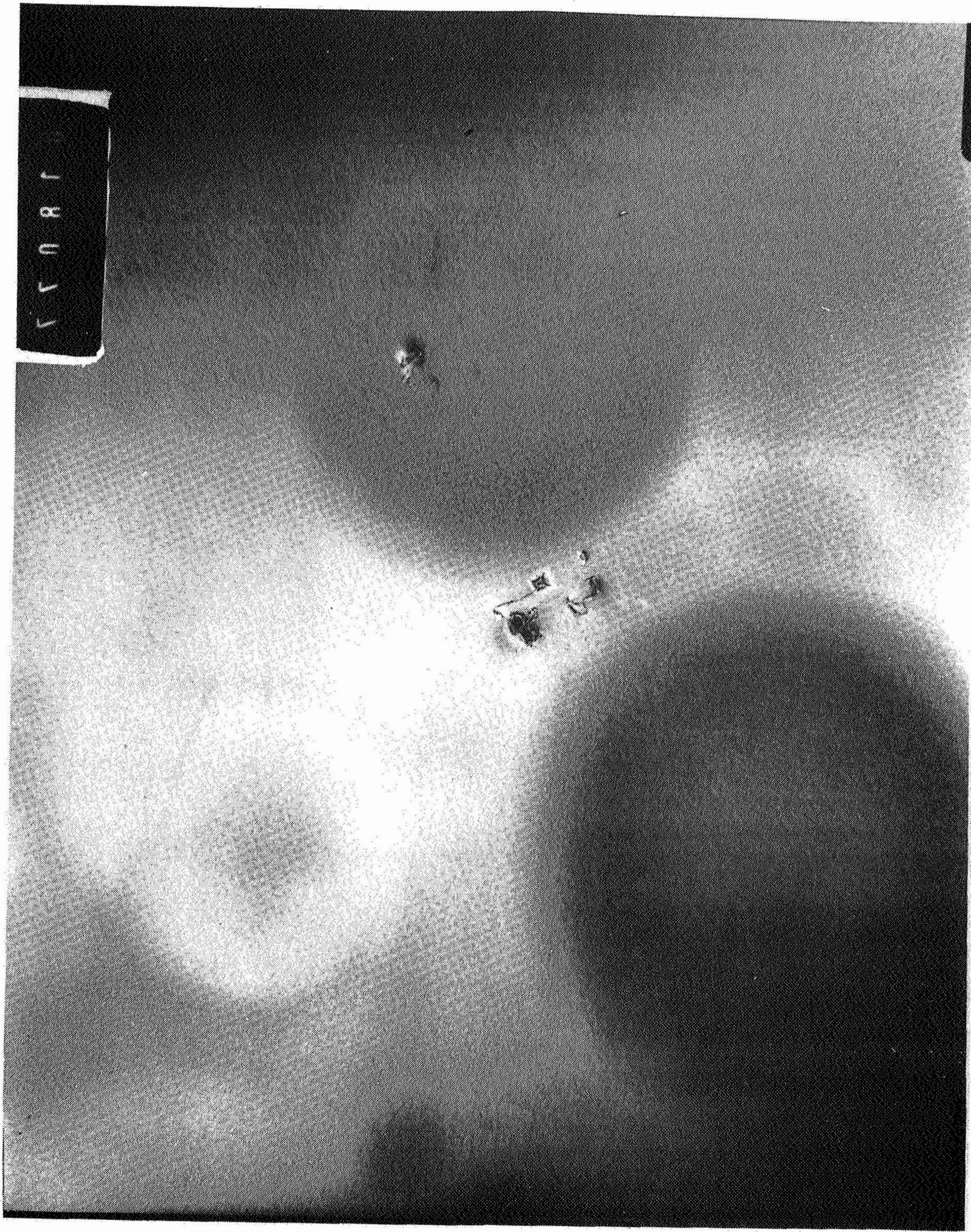
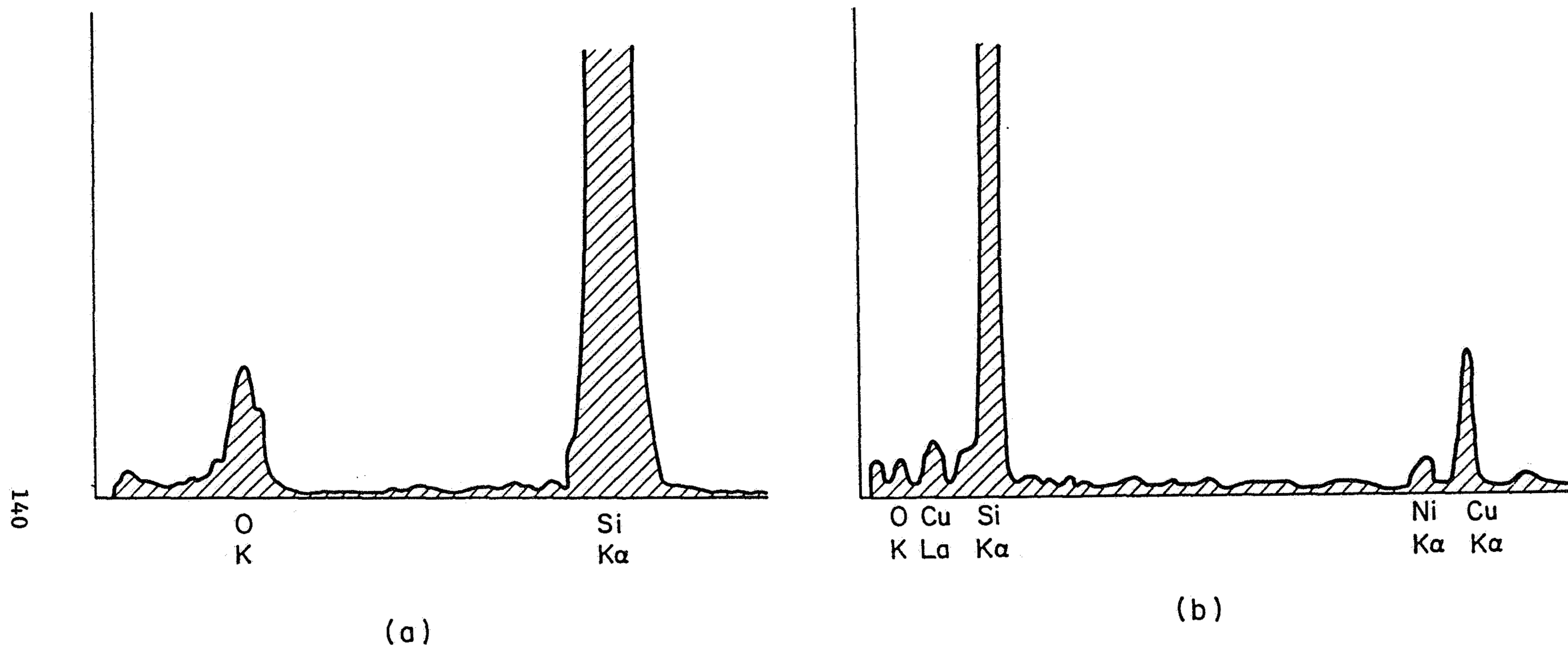


Figure 13. Plate-like Precipitates Observed in "3-2" and "4" Wafers



EDAX Composition Analysis Taken From Plate-like Precipitate (a)--
Notice Only Si and O- and (b) Precipitate on Stacking Fault From
Group 4 (Figure 12b)--Notice Presence of Heavy Metals

DISCUSSION

WITT: Do you have to invoke heterogeneous and homogeneous nucleation to explain the difference in behavior? I'm asking because it is certainly possible to have different types of nuclei for which the activation energy for growth differs very, very significantly. There are many who seriously doubt your curves of homogeneous nucleation, in principle.

JASTRZEBSKI: In general, I agree with you. Homogeneous nucleation will probably never take place, but it is a question of how close are we to homogeneous nucleations. The homogeneous type of nucleations that I'm referring to are a certain type of precipitation process of the oxygen. This precipitation process of oxygen has helped in a way. You can think of it as a kind of decay time. When this time is as high as we were ever able to see, we called this homogeneous. Probably the baseline will change in the future. I believe we have different types of heterogeneous centers, for it's very difficult to measure this in any direct way.

DYER: Do you know of any way in which the internal gettering of the type that you have been speaking of could be a benefit to a typical solar cell?

SCHWUTTKE: May I comment on this? Using internal gettering the way it is being used for MOS processing is not a good approach for solar cells. We are dealing with recombination lifetimes. You will kill the cell if you precipitate, as it is done for MOS processing, to get a denuded zone. I believe you [Jastrzebski] have chosen about the most difficult experiment you can do to follow the kinetics of oxygen, namely a bipolar process. You just can't use a bipolar process to study oxygen kinetics. You should get out of the high-oxygen-concentration regime and concentrate on low oxygen.

MORRISON: How might co-doping of metallic impurities be affecting a heterogeneous deposition process in your material, and the process you are describing?

JASTRZEBSKI: Stacking faults are related to the presence of metallic impurities. Homogeneous nucleation of stacking faults isn't very likely. Metallic impurities will act as nucleation centers and you will have heterogeneous nucleation of stacking faults around this metallic impurity precipitate.

RAO: You showed oxygen precipitates in two samples. If you have the same type of precipitate, then you should find the defect generation around that, which is the result of the lattice parameter mismatch of the interface. If that is the case, why are you getting a decorated stacking fault in one case and a non-decorated stacking fault in the other, and what was the character of the two stacking faults that you had seen, the one that was decorated and the one that was not decorated?

JASTRZEBSKI: You have defects around the precipitate that are punch-out dislocation loops. I can only speculate why you have a difference. My working hypothesis is that you have a difference when, in the process, impurities are coming from this formation of the stacking faults and cristobalites. I suspect that in one case we're having a different driving force from the nucleation that is a heterogeneous type of precipitation. Different precipitation rates will give you different defect densities, and cause a different gettering action. I believe that this is the reason you are seeing a difference between precipitate gettering by stacking faults. The clean stacking faults usually form later in the process because of a difference in the oxygen supersaturation in the precipitation.

WOLF: You said the problem is really the heavy metals you introduce during the processing. That means that your final heat treatment that does the gettering has to come after all the high-temperature processes.

JASTRZEBSKI: No. This is the dispute of internal gettering. You can have gettering in the stages when you form the precipitates. In oxygen, for example, the precipitation is taking place during processing, so you have gettering throughout all the processing steps. For example, with phosphorus you can only have gettering when you introduce the phosphorus through the back of the wafer.

WOLF: You are saying that each time you go to a high temperature the heavy metals move towards the getters. Evidently they must be moving very fast.

JASTRZEBSKI: Not really, it depends on what kind of impurity you have. You are talking about something between 10 and 25 µm for these heavy metals.

ELWELL: The original model of internal gettering was that the precipitate would punch out dislocation loops which would be decorated by the heavy metals. The efficiency of this process should depend on how fast you precipitate. Do you believe in that as a classical model or do you have data that would make us think that is a long way off?

JASTRZEBSKI: No, I don't. The comparison of different-morphology precipitates has not been proven.

ELWELL: You take whatever microdefects are present in the "as grown" crystal and, you don't do any heat treatment. Is that correct?

JASTRZEBSKI: We do not have any microdefects in the as-grown crystal, at least according to the classical sense of microdefects that you find by etching.

ELWELL: There could be 50 Å precipitates.

JASTRZEBSKI: Definitely no. This is why you sometimes have oxygen in non-interstitial states, which causes this completely different change in the precipitation kinetics.

SCHWUTTKE: For the record, I don't believe that we are dealing with cristobalites. Our measurements of the denuded zone using transmission electron microscopy indicate that we are dealing with amorphous silicon. The dislocation loops are punched out due to the volume strain generated by the growth of the amorphous silicon.

WITT: Do I understand it that there are two types of precipitates, one of them with gettering capabilities and the other one not?

JASTRZEBSKI: That is correct.

WITT: If that is so, have you been able through, say, STEM, to identify the gettering action or the presence of heavy metals on some and the absence on others?

JASTRZEBSKI: Yes, we have. Using STEM we see heavy-metal precipitates on this particular stacking fault when we normally did not see any heavy-metal precipitates. In another case, when it was a very quick precipitation rate, it was the opposite.

SESSION III

L. DYER, CHAIRMAN

PRECEDING PAGE BLANK NOT FILMED

N86-19732

SIMULATION OF THE TEMPERATURE DISTRIBUTION IN CRYSTALS GROWN BY CZOCHRALSKI METHOD

M.P. Dudukovic and P.A. Ramachandran

Washington University
St. Louis, MO 63130

Production of perfect crystals, free of residual strain and dislocations and with prescribed dopant concentration, by the Czochralski method is possible only if the complex, interacting phenomena that affect crystal growth in a Cz-puller are fully understood and quantified. Natural and forced convection in the melt, thermocapillary effect and heat transfer in and around the crystal affect its growth rate, the shape of the crystal-melt interface and the temperature gradients in the crystal.(1) In this work we have concentrated on describing the heat transfer problem in the crystal and between the crystal and all other surfaces present in the crystal pulling apparatus.

This model and computer algorithm are based on the following assumptions: i) only conduction occurs in the crystal (experimentally determined conductivity as a function of temperature is used), ii) melt temperature and the melt-crystal heat transfer coefficient are available (either as constant values or functions of radial position), iii) pseudo-steady state is achieved with respect to temperature gradients, iv) crystal radius is fixed, v) both direct and reflected radiation exchange occurs among all surfaces at various temperatures in the crystal puller enclosure.

This is the first model to replace the simple Stefan's law for radiation from the melt and crystal surface to the ambient with the Gebhart's enclosure theory which accounts for both direct and reflected radiation. Available emissivities were used. The position of the melt-crystal interface is not assumed _a priori_ but is computed as part of the solution as a locus of points where the flux continuity (heat flux from the melt plus the rate of release of the heat of crystallization is balanced by heat conduction into the crystal) is satisfied at the melting point isotherm.

Galerkin finite elements with triangular basic cells and linear trial functions are used to reduce the problem to a set of nonlinear algebraic equations. These are solved by an iterative scheme both for the temperatures and the melt-crystal interface position.(2)

Using 10 elements in the radial direction and 30 in the axial proved adequate to achieve the desired accuracy and resulted in 352 unknowns. Doubling the number of nodes did not affect the results. One minute of CPU time on a DEC20 computer was required per iteration. Convergence was obtained usually in less than 8 iterations.

The model calculates the axial and radial temperature profiles in the crystal and the position of the melt-crystal interface as a function of the input parameters (melt temperature, crucible wall temperature, temperatures of

PRECEDING PAGE BLANK NOT FILMED

various surfaces in the enclosure, pulling rate, crystal radius). Comparison with the results in the literature[2] which used Stefan's law to describe radiative heat transfer show that these underpredict the axial temperature profile and the radial temperature gradients. Thus, proper accounting for reflected radiation seems important. The model also indicates that an increase in pulling rate at other fixed parameters would tend to make the melt-crystal interface more concave to the crystal (i.e. melt protrudes into the crystal). The same trend is caused by an increase in melt or crucible temperature.

These final predictions regarding the melt-crystal interface need further verification. This can only be done by incorporating the thermocapillary effect, to describe the meniscus at the crystal-melt-gas line of contact, and by evaluating the convective patterns in the melt to obtain proper melt temperature and heat transfer coefficient profiles. This work is currently in progress.

---

(1) Kobayashu, N., Heat Transfer in Cz Crystal Growth (W.R. Wilcox, ed.), Marcel Dekker, Inc. (1981).

(2) Ramachandran, P.A. and Dudukovic, M.P., "Simulation of Temperature Distribution in Crystals Grown by Czochralski Method," J. Crystal Growth (accepted for publication, 1984).

(3) Williams, G. and Rousser, P.E., J. Crystal Growth, 64, 448 (1983).

Oxygen Content in Silicon

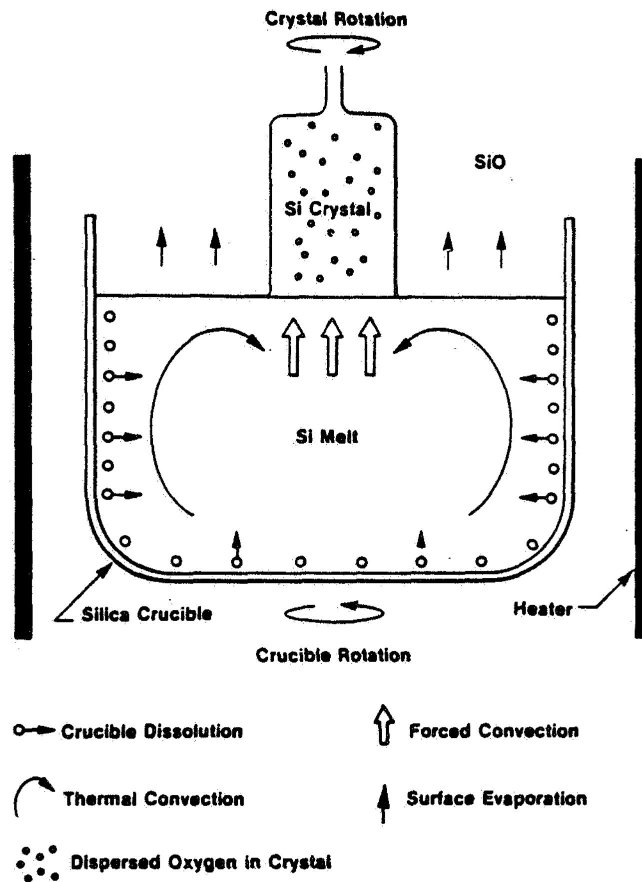


Fig. 3—Schematic drawing illustrating the spatial relationship of separate factors that affect oxygen content in silicon during crystal growth. (After a drawing in Benson, et al. [25].)

R. R. Huff, Solid State Technology, Feb. '83

Problem Complexities

1. Temperature distribution in melt and crystal are coupled.

2. Complex flow patterns in melt

    1. forced convection

    2. natural convection

    3. thermocapillary effect

3. Floating boundary, interface shape cannot be fixed a priori

4. Radiation interactions

Variables Affecting Cz Growth

i) geometric variables including crucible shape, enclosure shape, heater position and shape, etc.;

ii) controllable operating variables such as pulling rate, crystal rotation rate, crucible rotation rate, gas flow rate, furnace power;

iii) process variables such as melt depth, crystal diameter, etc.

Due to the complex interaction among many variables their interrelationship cannot be understood in a quantitative sense through any number of experiments unless experimental results are interpreted through an appropriate model of the system.

Ultimate Objective Is to Produce a Perfect Crystal

CRYSTAL

- FREE OF RESIDUAL STRAIN
- FREE OF DISLOCATIONS
- UNIFORMLY DOPED

ONCE A PROPER MODEL IS ESTABLISHED AND VERIFIED THE EFFECT OF CHANGES IN VARIOUS VARIABLES ON CRYSTAL QUALITY CAN BE ASSESSED MORE READILY WITH FAR FEWER EXPERIMENTS. OPTIMIZATION OF THE OPERATION BECOMES POSSIBLE.

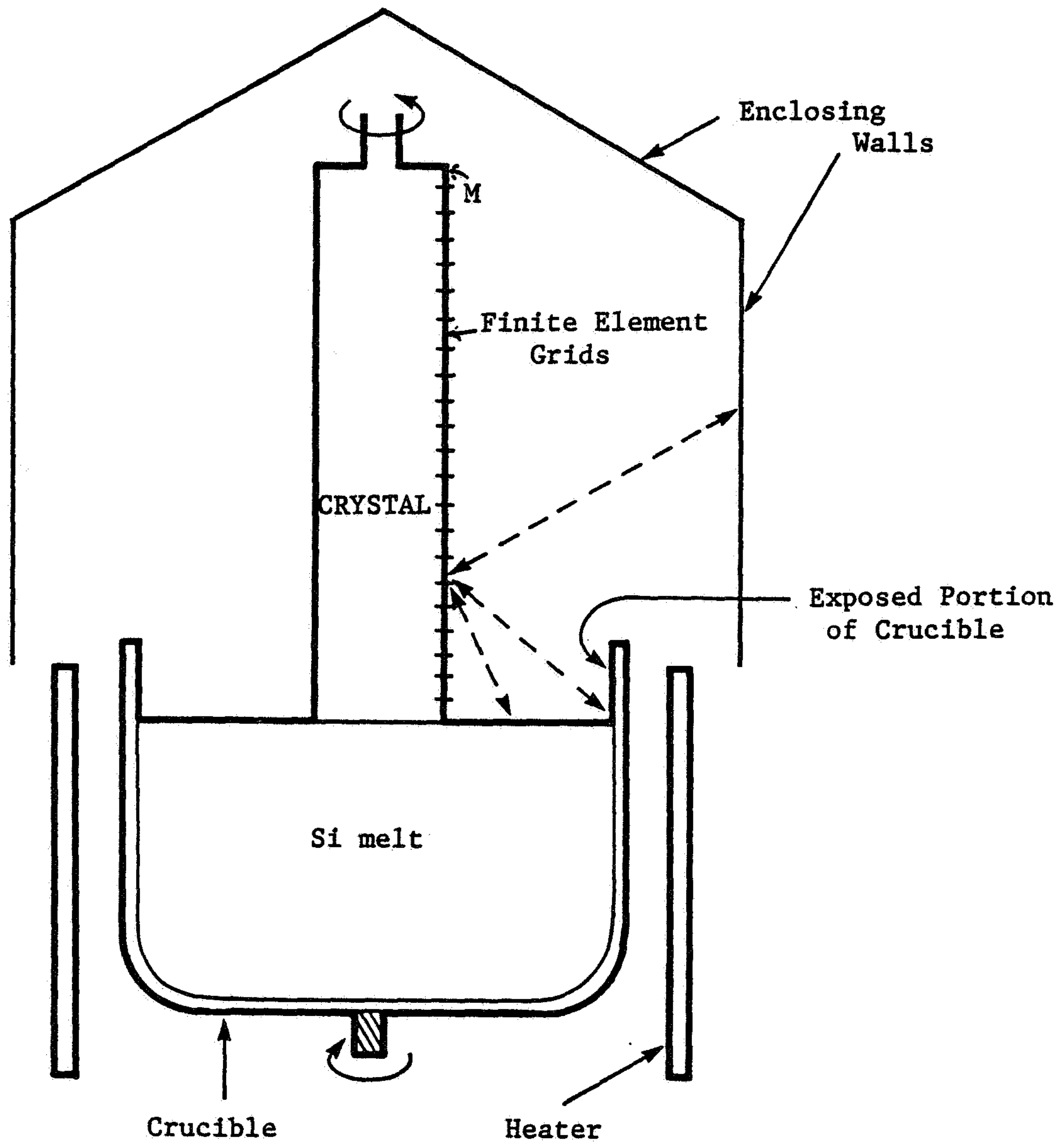
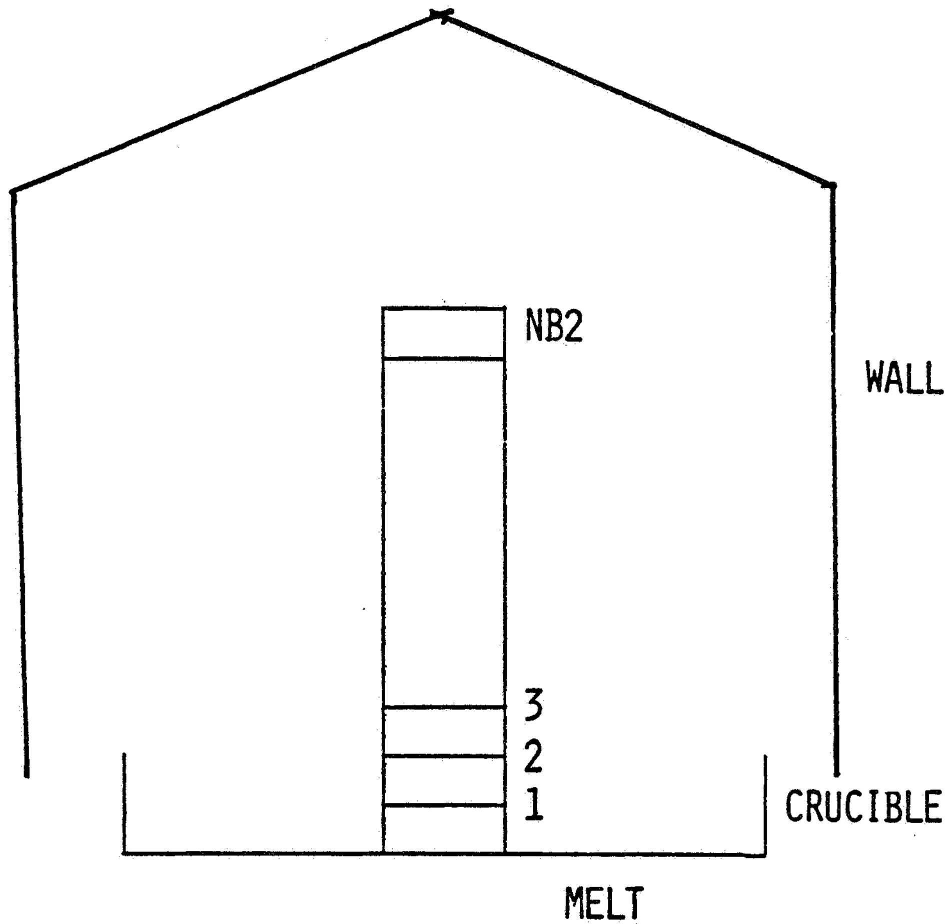


Figure 1. Schematic of Czochralski single crystal pulling apparatus,
--- indicates radiation interaction between various surfaces

Enclosures for Crystal Problem



CRYSTAL IS DIVIDED INTO NB2 ELEMENTS. THESE PROVIDE NB2 SURFACES. THREE ADDITIONAL SURFACES ARE CONSIDERED AS SHOWN ABOVE

$$N = NB2 + 3$$

Model Equations

$$\frac{1}{r}\frac{\partial}{\partial r}\left(k_e\, r \frac{\partial T}{\partial r}\right) + \frac{\partial}{\partial z}\left(k_e \frac{\partial T}{\partial z}\right) - v\,\rho\, C_p \frac{\partial T}{\partial z} = 0$$

Cylindrical Surface

$$k_e\left(\frac{dT}{dn}\right)_R + h_c(T - T_a) + q_R = 0$$

Top Surface

$$k_e\left(\frac{dT}{dz}\right)_L + h_c(T - T_a) + q_R = 0$$

Calculation of Radiation Flux

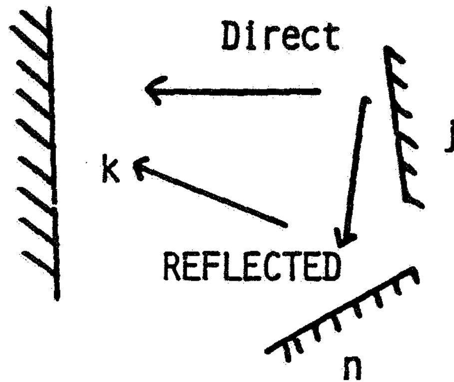
GEBHART METHOD IS USED

CONSIDER AN ENCLOSURE WITH N SURFACES, EACH SURFACE BEING AT TEMPERATURE T_k. THE HEAT LOSS FROM SURFACE k IS

$$Q_k = A_k \epsilon_k \sigma T_k^4 - \sum_{j=1}^{N} A_j \epsilon_j \sigma T_j^4 G_{jk}$$

$$q_k = \frac{Q_k}{A_k}$$

CALCULATION G_{jk} (j = 1 TO N) FOR ANY GIVEN SURFACE k



SURFACE k RECEIVES BOTH DIRECT AS WELL AS REFLECTED RADIATION FROM SURFACE j. DIFFUSE REFLECTION IS ASSUMED.

DIRECT RADIATION (j to k)

$$\epsilon_j \sigma T_j^4 A_j F_{jk} \epsilon_k$$

REFLECTED RADIATION (j to n to k)

$$(\epsilon_j \sigma T_j^4 A_j F_{jn})(\rho_n)(G_{nk})$$

(j to n) (REFLECTION) (n to k)

TOTAL RADIATION FROM j

$$\epsilon_j \sigma T_j^4 A_j$$

G_{jk} FACTOR

$$G_{jk} = F_{jk}\epsilon_k + \sum_{n=1}^{N} F_{jn} \rho_n G_{nk}$$

$$F_{ij} = 0 \text{ for } i \leq NB2$$

and

$$j \leq NB2$$

HENCE THE CALCULATION OF G_{jk} CAN BE SIMPLIFIED.

$$\begin{pmatrix} \underline{g_1} \\ \\ \underline{g_2} \end{pmatrix} = \begin{pmatrix} \underline{0} \\ \\ \underline{p} \end{pmatrix} + \begin{pmatrix} \underline{\underline{0}} & \underline{\underline{B_2}} \\ \\ \underline{\underline{B_3}} & \underline{\underline{B_4}} \end{pmatrix} \begin{pmatrix} \underline{g_1} \\ \\ \underline{g_2} \end{pmatrix}$$

LINEARIZED FORM OF BOUNDARY CONDITION

$$k_e \left(\frac{dT}{dr}\right)_R + h_c(T - T_a) + \underbrace{\varepsilon_k \sigma \left(T_k^{\,4} - \frac{1}{\varepsilon_k A_k} \sum_{j=1}^{N} A_j \varepsilon_j \sigma \, T_j^{\,4} \, G_{jk}\right)}_{h_R \, (T - T_{eff})} = 0$$

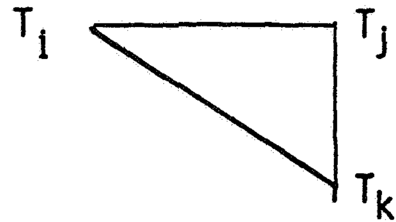
AN EFFECTIVE TEMPERATURE FOR RADIATION CAN BE DEFINED

$$T_{eff,R} = \left[\frac{1}{\varepsilon_k A_k} \sum_{j=1}^{N} A_j \varepsilon_j \sigma \, T_j^{\,4} G_{jk}\right]^{1/4}$$

$$q_R = \varepsilon\sigma \, (T^4 - T_{eff}^4) = h_R \, (T - T_{eff})$$

$$h_R = \varepsilon\sigma \, (T^2 + T_{eff}^2) \, (T + T_{eff})$$

Finite-Element Equations



$$\underline{\underline{K}} \begin{Bmatrix} T_i \\ T_j \\ T_k \end{Bmatrix} = \underline{P}$$

$\underline{\underline{K}}$ and $\underline{P}$ depend on nodal coordinates, physical properties, and the boundary conditions imposed on the element.

Equations for each element can be assembled and the resulting global matrix can be solved for all the nodal temperatures.

TO START ITERATION SCHEME USE ONE-DIMENSIONAL MODEL

WITH FINITE PECLET NUMBER

(Wilcox & Duty, J. Heat Transfer, 1966)

$$\frac{T(z) - T_a}{T_m - T_a} = \theta = \exp\left\{ \frac{\frac{V\rho C_p R}{k} - \sqrt{\left(\frac{V\rho C_p R}{k}\right)^2 + \frac{8hR}{k}}}{2} \frac{z}{R} \right\}$$

WHERE WE TAKE

$$h \approx 3\ h_{convection}$$

PULLING RATE EFFECT NEGLIGIBLE

(SMALL PECLET NUMBER) WHEN

$$\left(\frac{V\rho C_p R}{k}\right)^2 << \frac{8hR}{k}$$

Program Structure

1. INPUT

2. NODE AND ELEMENT NUMBERING

3. ASSUME TRIAL VALUES FOR TEMPERATURES FOR FIRST ITERATION

3a. CALCULATE G FACTORS

3b. CALCULATE

$T_{eff,R}$, h_r, q_c, etc.

4. SOLVE FINITE ELEMENT EQUATIONS FOR NODAL TEMPERATURES

5. CHECK FOR CONVERGENCE

6. $T_{New} = W_1 \, T_{calculated} + (1 - W_1) \, T_{assumed}$

7. LOCATE Z POSITIONS WHERE TEMPERATURE IS EQUAL TO TO MELTING POINT (INTERFACE SHAPE).

8. REPEAT CALCULATIONS TILL CONVERGENCE IS OBTAINED.

Special Features

- INTERFACE SHAPE CALCULATED AND NOT ASSUMED
- TWO DIMENSIONAL MODEL
- ENCLOSURE THEORY PERMITS DETAILED ANALYSIS OF RADIATION HEAT TRANSFER
- EFFECTS OF ADDITIONAL HEATING AND COOLING SURFACES CAN EASILY BE SIMULATED
- PHYSICAL PROPERTIES ASSUMED AS A FUNCTION OF TEMPERATURE

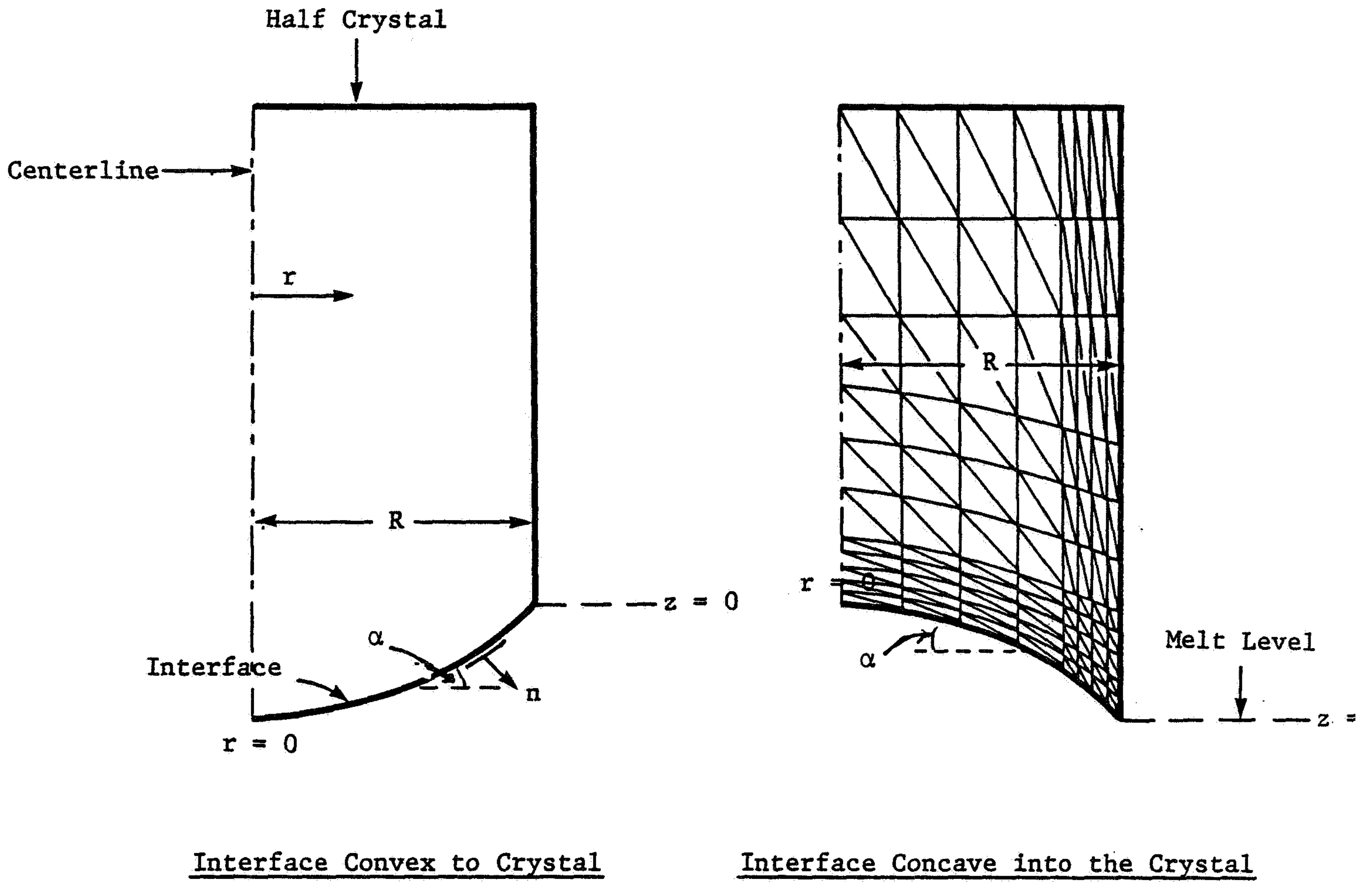


Figure 2. Interface shapes commonly encountered; also defines the various geometric parameters and indicates the schematic of finite element meshes used

Table 2. Parameter Values Used in Illustrative Application Example

radius of crystal	4 cm
height of crystal	17 cm
crystal pulling rate	0.002 cm/s
crucible radius	10 cm
height of exposed crucible	3 cm
wall area	1500 cm^2
wall temperature	100°C
melt temperature	1470°C
crucible temperature	1480°C
average argon temperature	250°C
effective temperature for radiation (Stefans model)	327°C
convective heat transfer coefficient	$1.2433 \times 10^{-4} (\Delta T)^{1/3}$ W/cm^2K
melt to crystal heat transfer coefficient	0.3265 W/cm^2K
thermal conductivity	$0.98892408 - 9.4286595 \times 10^{-4} T + 2.889 \times 10^{-7} T^2$, W/cm K (T in Kelvin)
emissivity of silicon crystal	$\varepsilon = 0.64$ if $T < 1000$ K $= .9016 - 2.616 \times 10^{-4} T$ if $T > 1000$ K
emissivity of melt	0.3
emissivity of crucible	0.59
emissivity of wall	0.59

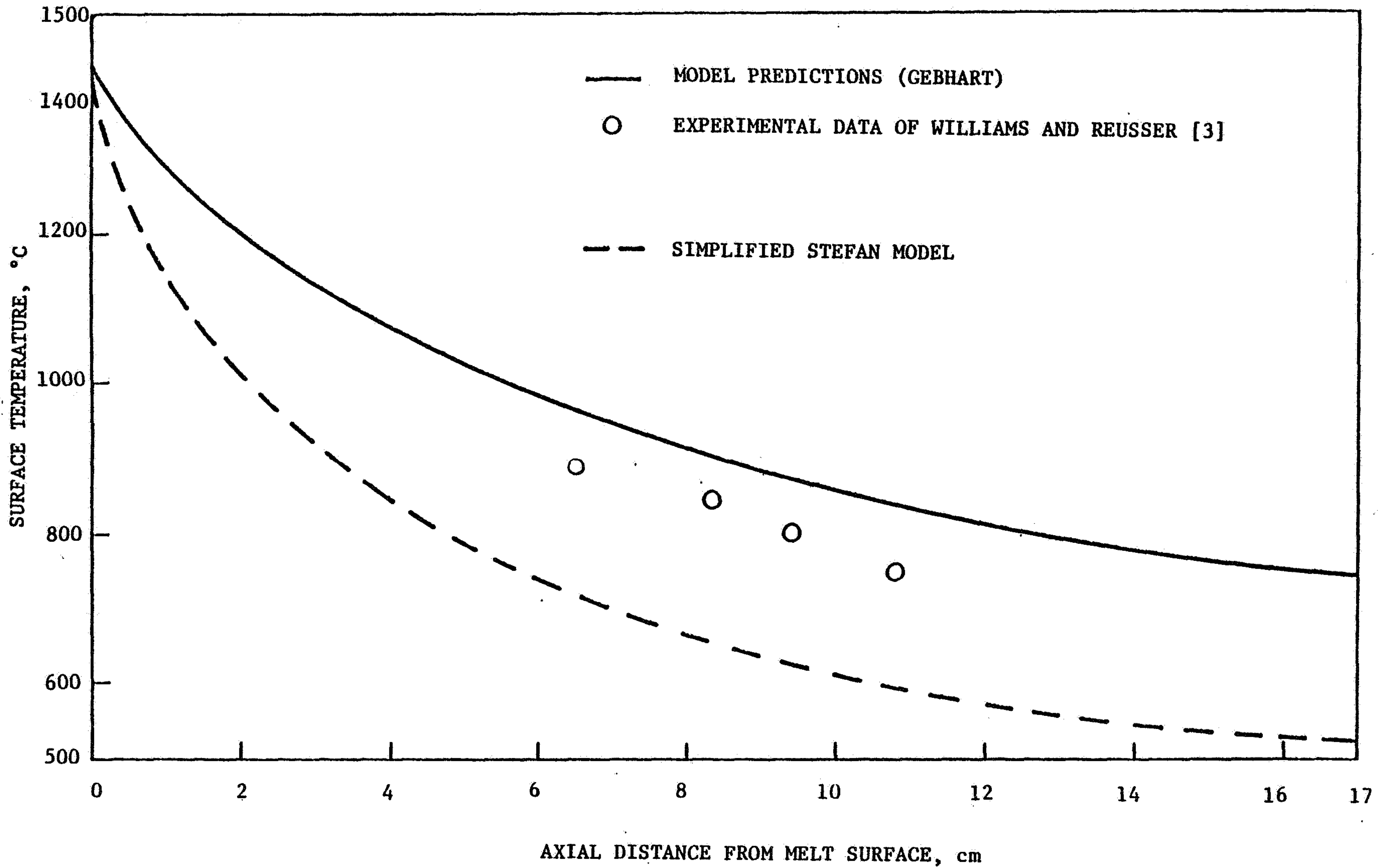


Figure 5. Predicted crystal surface temperatures based on Gebhart and Stefan models and experimental results of Williams and Reusser [3]

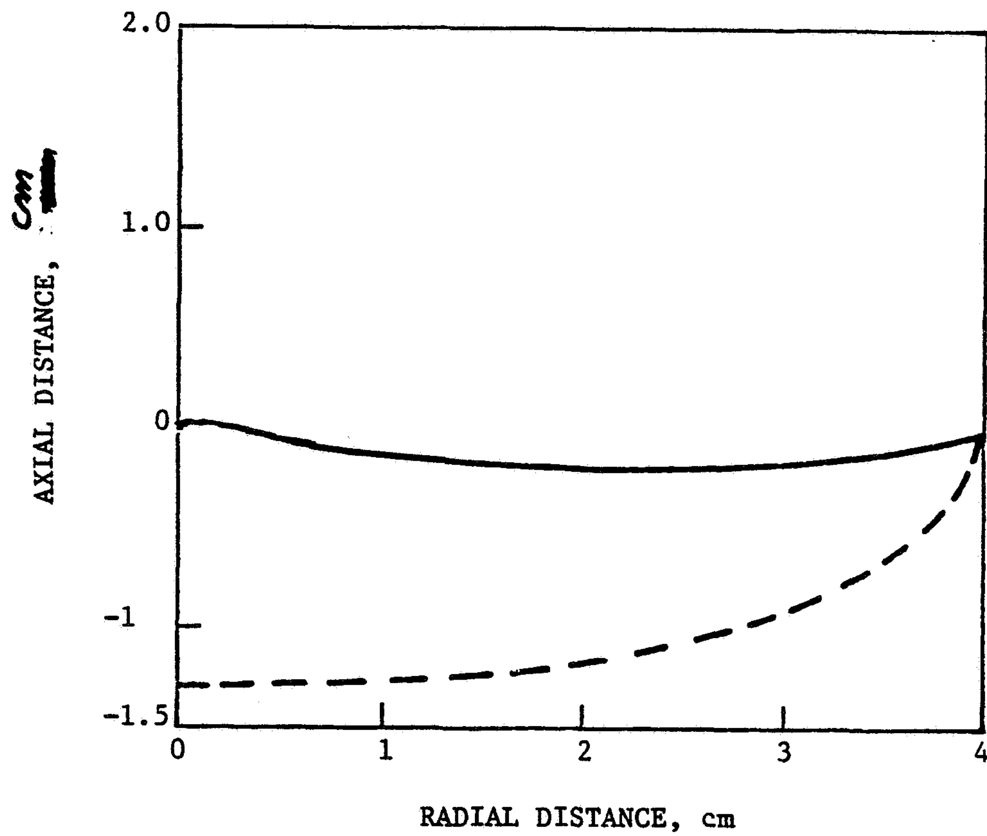


Figure 6. Interface shape calculated for the data of Table 2. — Gebhart analysis for radiation, --- Stefan model

Summary

A FINITE ELEMENT ALGORITHM HAS BEEN DEVELOPED FOR EVALUATION OF THE TEMPERATURE PROFILES IN THE CRYSTAL AND FOR PREDICTION OF THE POSITION OF THE CRYSTAL-MELT INTERFACE.

IT IS SHOWN THAT ACCOUNTING PROPERLY FOR RADIATION EFFECTS CAN INFLUENCE CONSIDERABLY THE PREDICTIONS FOR THE TEMPERATURE PROFILE AND MELT-CRYSTAL INTERFACE.

THE DEVELOPED ALGORITHM, AT PRESENT, INCORPORATES THE FOLLOWING SIMPLIFYING ASSUMPTIONS

- pseudo-steady state
- symmetry
- constant melt temperature
- constant heat transfer coefficient at melt-crystal interface
- no thermo capillary effect
- fixed crystal radius

COUPLING OF THIS MODEL WITH A REALISTIC HYDRODYNAMIC AND THERMOCAPILLARY MODEL IS NECESSARY AND IS CURRENTLY IN PROGRESS.

COMPARISON WITH EXPERIMENTAL DATA AND PARAMETER SENSITIVITY STUDIES ARE ALSO ESSENTIAL.

Recommendations

OUR UNDERSTANDING OF THE COMPLEXITIES OF THE CZ (OR LECZ) PROCESS IS FAR FROM COMPLETE.

UNIVERSITY PERSONNEL AT A NUMBER OF LOCATIONS MUST BE ENCOURAGED (AND FUNDED) TO CONTINUE THE WORK IN THIS AREA.

COMPETITION AND OVERLAP OF COVERAGE OF CERTAIN TOPICS IS HELPFUL. INADEQUATE COVERAGE AND NEGLECT OF THESE PROBLEMS CAN ONLY HURT OUR COMPETITIVENESS IN THE FUTURE.

DISCUSSION

WITT: I would like you to treat the inverse problem. Namely, we need an establishment of the boundary conditions, or the range of boundary conditions, under which in the desired thermal configuration the crystal in the melt can be achieved, rather than quantitative verification through modeling of adverse thermal configurations. I recognize that the inverse problem is infinitely more difficult to solve. What I think industry needs to know is, what are the required boundary conditions necessary to achieve optimized silicon growth? Not verification of the complexity of the heat transfer conditions through modeling.

DUDUKOVIC: Your point is well taken, but I think the two really go together. I don't see it at all incompatible in the process of learning the complexities, that you show that one should be thinking about some other configurations in which asymmetry will not be a problem. Even if you go to those other configurations, it's still nice to have a quantitative rigorous model for well-defined situations.

WITT: I'm only trying to preserve realism, and the realism is that you can only sell the effort to industry if industry sees the direct impact. I think industry wants concrete input to systems design and the connection from what we are doing to that is obscure.

SCHWUTTKE: It looks like you are trying to calculate the position of the train after it left the station. The crystals are already grown and nothing happens anymore that I am concerned about. I need to know how to shape my interface.

DUDUKOVIC: In order to know where the interface shape is -- you are not going to get there just by knowing the meniscus. We also need to know the radiative heat fluxes and the conductive heat fluxes.

One has to start from someplace. Once you have solved the crystal problem right you can now couple that with any level of approximation for the meniscus and for the melt that you want. The three are coupled. You can not arrive at a one-line formula by which you can resolve the interface shape just by considering one of those effects.

MORRISON: I know for a fact that industry has been interested in your modeling. I think that when the models are built and verified you can go back and use the models as a tool to build a station.

Have you compared the interfaces of the terminations of grown crystals with the interface shapes that your model is generating?

DUDUKOVIC: That would be the wrong thing to do, because it would just demonstrate the effect of one factor on the position of that interface. This is exactly the trap that industrial people often fall into. They run out and say it doesn't match my experimental

observations. One can make sense of complex phenomena by putting them together and the only way that putting them together can be done is through mathematics. There is no other way. Everything else is just handwaving.

N86-19733

CONVECTIVE EFFECTS IN FLOAT-ZONE AND CZOCHRALSKI MELTS

G. P. Neitzel

Arizona State University
Tempe, AZ 85287

The hydrodynamics of crystal-growth melts is a relatively new research area. Numerical modeling of these processes is necessary, considering the hostile environment from the standpoint of laboratory experimentation. The work discussed herein is in two parts: numerical simulations are being conducted of the flow in a Czochralski melt and also of that in a float zone. In addition, for the float-zone case, energy stability theory will be used to determine stability bounds for the onset of oscillatory thermo-capillary flow.

Convective effects in crystal-growth melts arise from a variety of mechanisms. Temperature gradients both in the direction of gravity and normal to it give rise to convection due to buoyancy effects. Rotation of the crucible and/or crystal causes a forced convection which may augment or oppose the buoyancy-driven flow. Finally, thermo-capillary forces (due to the variation of surface tension with temperature) drive surface motions which in turn generate convection in the bulk fluid. All of these mechanisms are present in either Czochralski or float-zone growth.

The research objective of the Czochralski modeling is to develop an accurate numerical simulation of the flow in a Czochralski silicon melt and to investigate the effects of various parameters on the flow properties. Like some earlier investigations, we intend to simulate the effects of buoyancy, forced, and thermo-capillary convection, including unsteady effects. Unlike earlier work, the ultimate aim is to be able to include the effects of a variable free surface and freezing interface and, possibly incorporate non-axisymmetric effects.

Model experiments by Preisser, Schwabe and Scharmann and also Chun have demonstrated the importance of thermo-capillary convection on the float-zone process. In particular, the work of the former group has concluded that it is an instability of thermo-capillary convection which leads to the onset of oscillatory convection which may be responsible for striations observed in some crystals. This phenomenon will be especially important in applications of the float-zone process in a microgravity environment.

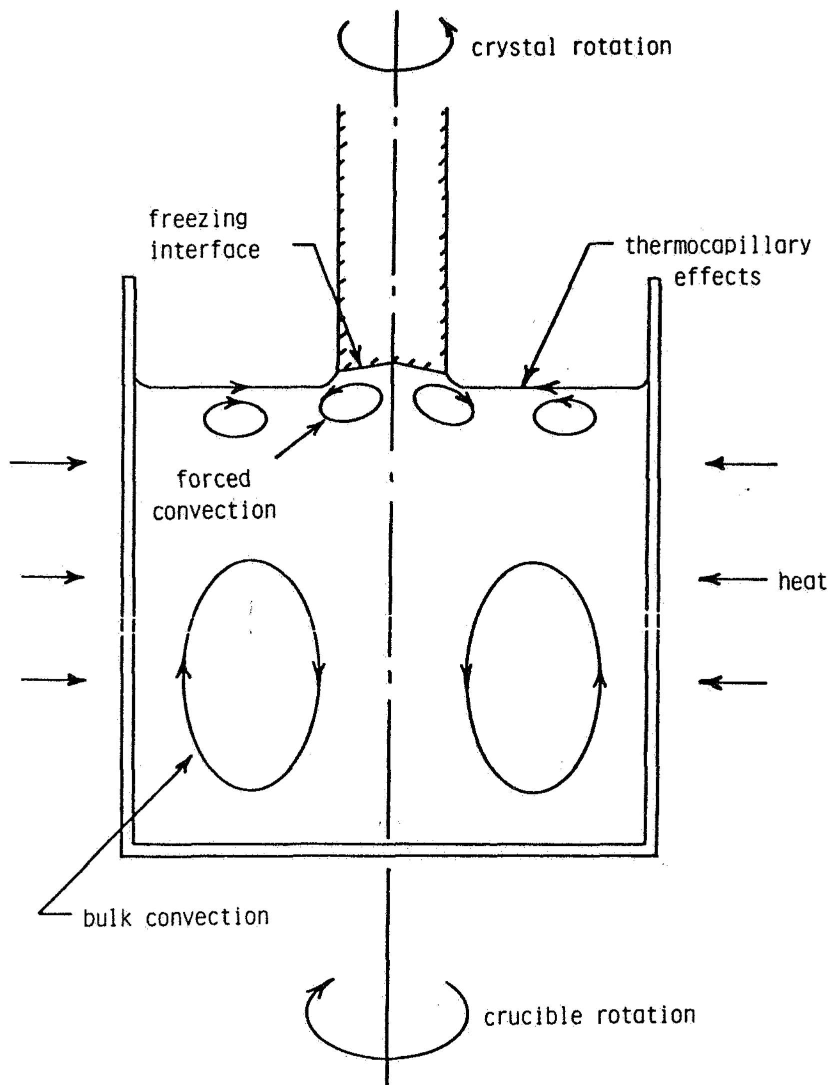
Computations of float-zone basic states will concentrate on three model problems. The first of these will neglect free-surface deformation and consider flat melting and freezing interfaces. The second will relax the restriction on free-surface deflection, but maintain flat crystal/melt interfaces. Finally, the third model problem will attempt to compute basic states for which these interfaces are determined as part of the problem.

PRECEDING PAGE BLANK NOT FILMED

A stability analysis will be performed on each of these basic states using energy stability theory. Energy theory yields a sufficient condition for stability, i.e., a "critical" value of a dimensionless parameter below which disturbance growth will not take place. For some types of instability mechanisms, the sufficient condition for stability provided by energy theory is quite conservative, i.e., small. For instabilities driven by surface tension, however, there is reason to believe that this will not be the case. Hopefully, the results of the study will provide results which will allow the growth of striation-free crystals by the float-zone process.

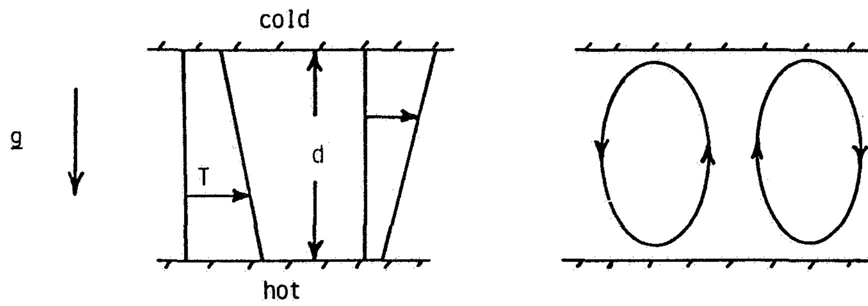
The computations will be performed for each of the basic states discussed above under conditions of variable gravity to examine the possibilities for space processing by this technique. The consideration of the proposed basic states will allow comparisons with previous analytical work by Davis and his coworkers and the model experiments of Preisser et al. mentioned above. These will assist greatly in the development and verification of the model.

Czochralski Process



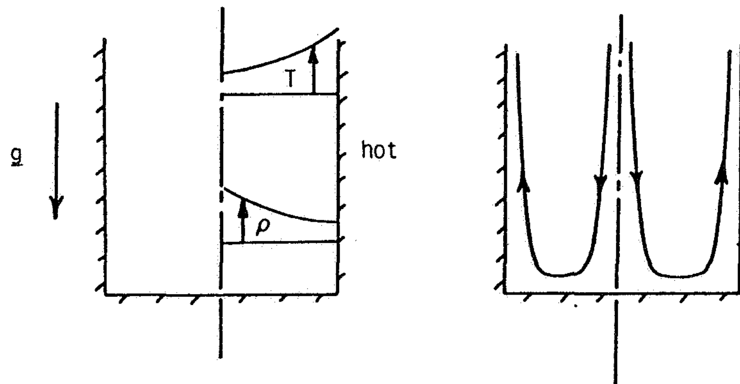
Convection Mechanisms in Cz Crystal Growth

I. Buoyancy

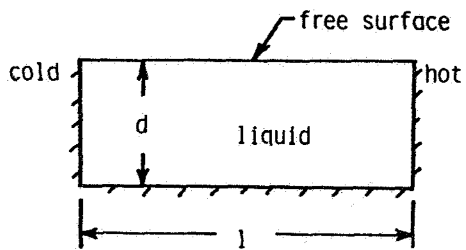


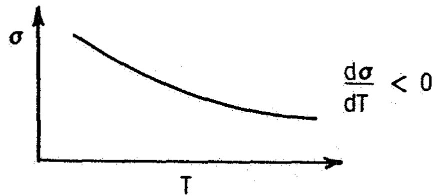
Rayleigh number $\quad R = \frac{\alpha \Delta T g d^3}{\kappa \nu}$

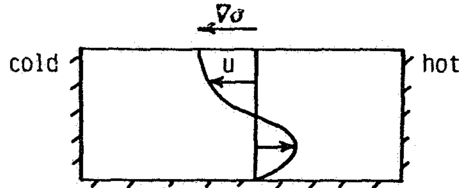
Prandtl number $\quad Pr = \frac{\nu}{\kappa}$



Thermocapillary Effects







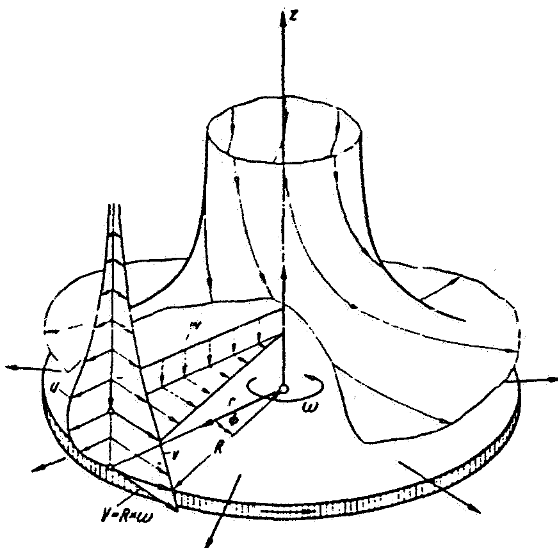
Aspect ratio $A = d/l$

Marangoni number $M = \frac{-d\sigma/dT \; A \Delta T \; d}{\mu \kappa}$

Capillary number $C = \frac{-d\sigma/dT \; A \Delta T}{\sigma}$

Forced Convection

Flow "above" a rotating disc:



Reynolds number $\quad Re = \dfrac{\Omega R^2}{\nu}$

Research Objective

Numerical simulation of the flow and temperature fields occurring during Czochralski growth of silicon.

Investigation of the influence of various parameters (e.g., rotation, aspect ratio) on the results.

Ultimate Computational Abilities

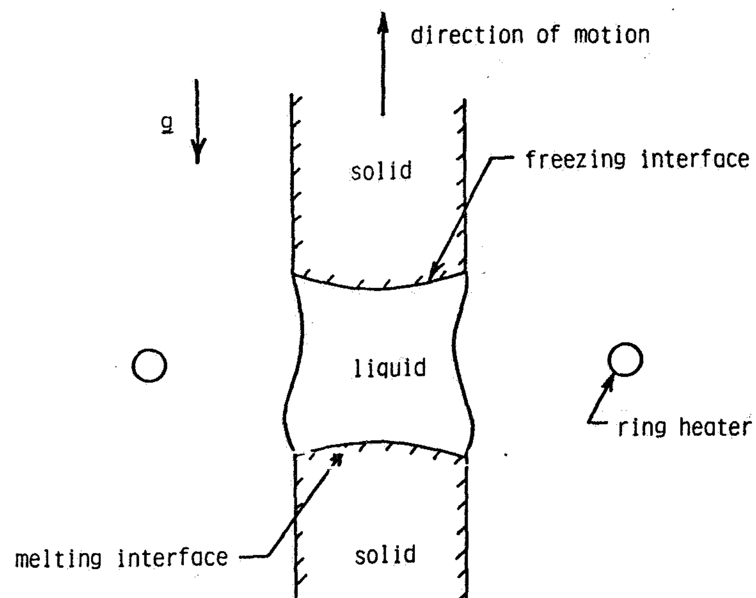
Effects of buoyancy, forced, and thermocapillary-induced convection.

Time-dependent simulation.

Variable free-surface and freezing interface.

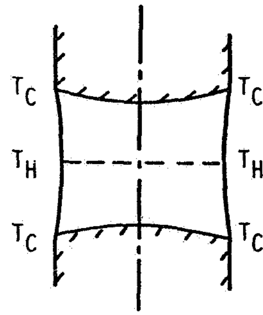
Non-axisymmetric simulation ? ?

Float-Zone Process



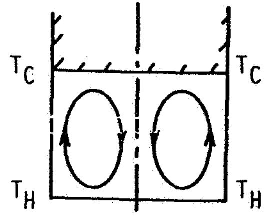
Advantage: containerless process

Float zone



Top half:

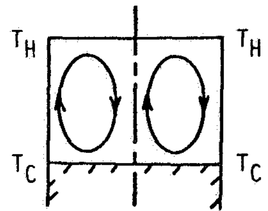
destabilizing radial & axial temp gradients
buoyancy



surface tension gradient
thermocapillary

Bottom half:

destabilizing radial temp gradient
stabilizing axial temp gradient
buoyancy

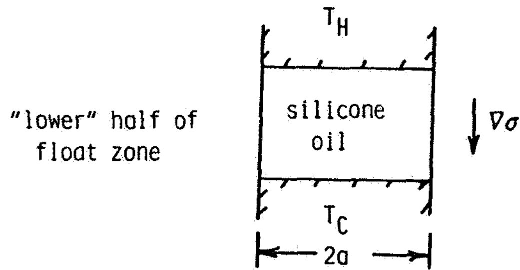


surface tension gradient
thermocapillary

Model Experiments

Preisser, Schwabe & Scharmann have performed model experiments

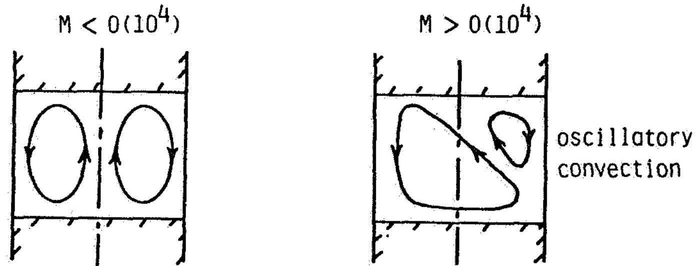
in which the dominant convection mechanism is thermocapillarity:



Relevant dimensionless parameter:

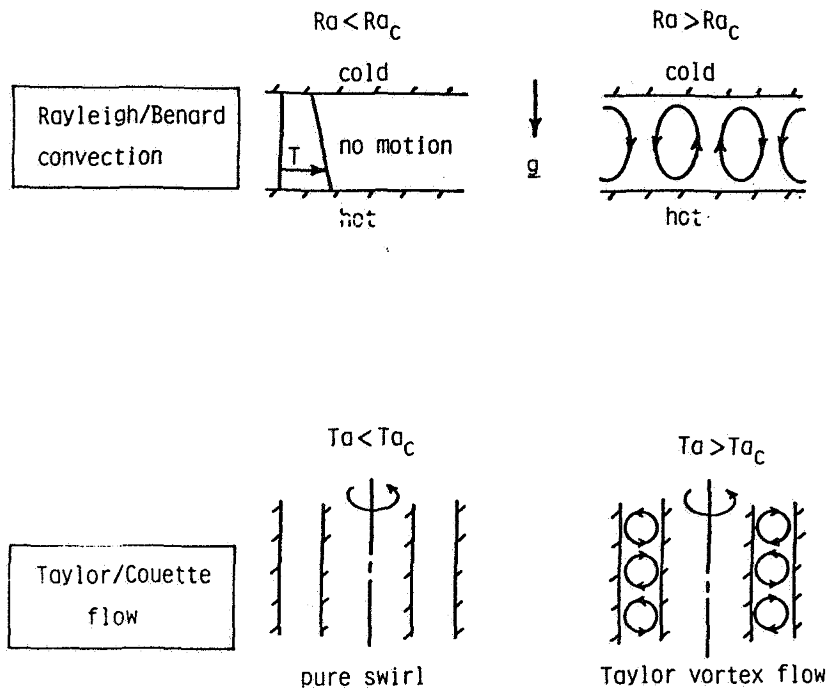
Marangoni number $$M = \frac{\rho c_p |d\sigma/dT| \cdot |dT/dz| a^2}{\mu k}$$

Results:

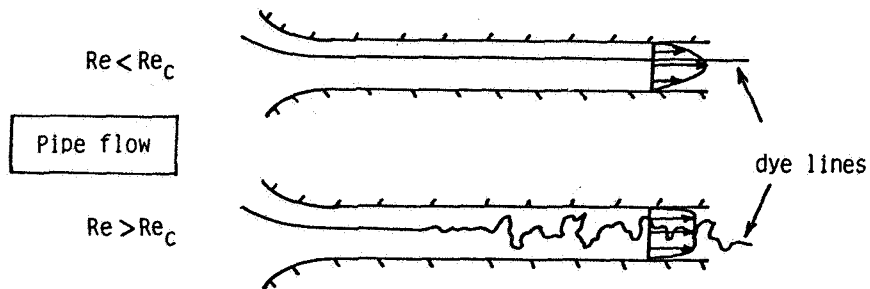


Hydrodynamic Stability

Like other dynamical systems, under certain situations, some fluid flows can be unstable to the inevitable disturbances which are present. In some cases, the instability of a given basic state results in the establishment of another laminar state:



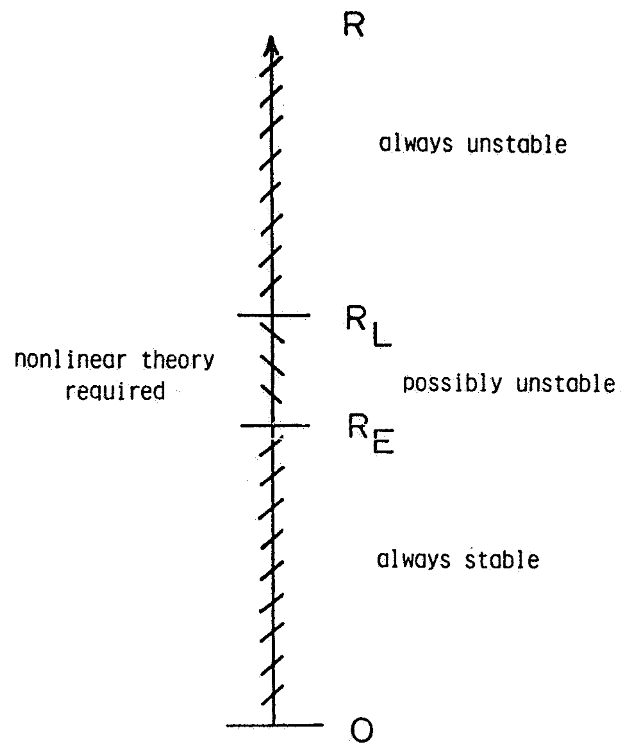
In other cases, the instability can lead directly to a chaotic, turbulent state:



In each case, there is a relevant dimensionless parameter; when it exceeds a "critical" value, the flow becomes unstable.

The goal of the present research is to examine the stability of thermocapillary convection in models of the float-zone crystal growth process in terrestrial and microgravity environments.

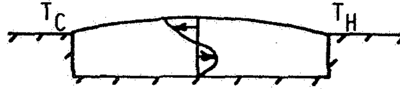
Stability Criteria



Previous Related Work (Linear Stability Theory)

Sen & Davis, Smith & Davis

2-D slot



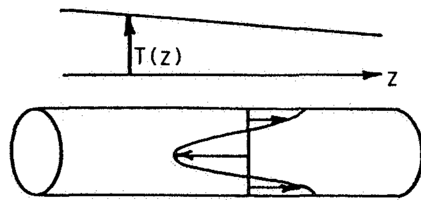
2-D layer with
surface shear stress

Instability mechanisms studied:

- classical shear flow
- surface waves
- convective instabilities

  rolls

  "hydrothermal waves"



basic state requiring return flow

The preferred instability was found to be a hydrothermal wave.

- Similar azimuthal dependence as the oscillatory convection seen in model float-zone experiments

- Much lower critical Marangoni number than that observed experimentally.

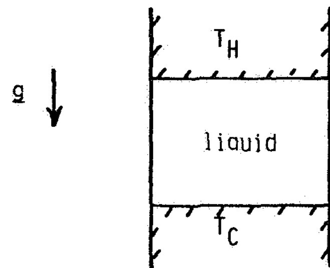
  Reasons (speculated):

  finite length is a stabilizing feature.

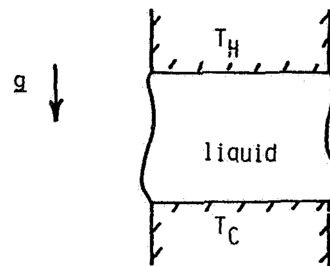
  buoyancy forces in the model half-zone experiment are stabilizing.

Problem Sequence

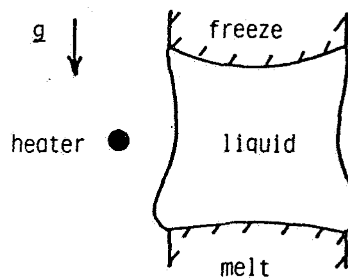
Features



- model half zone
- specified planar endwalls
- non-deformable free-surface
- variable body force



- model half zone
- specified planar endwalls
- deformable free-surface
- variable body force



- float-zone configuration
- unspecified melt/freeze interfaces
- deformable free-surface
- variable body force

DISCUSSION

MATLOCK: In silicon float-zone crystal growth, the heating is always done with radio frequencies, where there is significant RF levitation. Have you considered the possibilities of what that will do to the validity or invalidity of the directions that you are going?

NEITZEL: We have considered the possibilities but there is also some work being done on focused light melting, so we feel that the exclusion of the RF effects might not be unrealistic for that type of a case.

MATLOCK: Do you have any general thoughts about what the RF situation would do to what you are doing?

NEITZEL: No, not really. It's an additional complication that adds to an already very complicated problem.

As an aside, I would like to emphasize that there is a great need for these hydrodynamic simulation experiments because one can't make fluid dynamical measurements in molten silicon. It's a very hostile environment. It's optically opaque. If we have a model experiment in which certain other relevant dimensionless parameters might be matched, then that allows us to have something to compute analytically or numerically. And then, if we can verify a numerical model against that model experiment, that gives us some justification for extrapolating to other values or parameters that might be more appropriate to Czochralski growth.

KIM: Thermal conductivity is completely different, but you may simulate fluid dynamics like a Marangoni flow. If you include axial non-symmetric flow, can you still use a 2-D simulation or do you have to go to a 3-D simulation?

NEITZEL: One does have to make a three-dimensional simulation. The equations are not separable. You cannot just take an $e^{im\Theta}$-type dependence because of the fact that you have non-linearities. You have to do a three-dimensional simulation, but there have been advances recently in numerical fluid dynamics and in the use of structural methods that seem to hold great promise for doing this kind of computation. So it's not out of the realm of possibility.

ELWELL: Do you have a good number for $d\sigma/dT$ for silicon?

NEITZEL: No, there are several numbers in the literature, but I don't think there is any universal agreement as to what the $d\sigma/dT$ is. I'm not sure there is universal agreement as to what σ is.

KALEJS: I believe there is a recent measurement by Hardy that Bob Brown mentioned at NBS that is about 0.2 or so. It is found in an internal NBS publication.

C-2

WITT: We tried elements of what you have tried to do in a reduced-gravity environment. We did indium antimonide and the theoretical predictions were that the driving forces for Marangoni flow exceed by a factor of 10 each of the driving forces for buoyancy-driven convection. It means that the phenomenon is strictly and exclusively due to Marangoni-type convection. We did the experiment in space and there was zero evidence for any Marangoni-type flow. I'm not saying that the theory is wrong. I am throwing an enormous amount of doubt on the available $d\gamma/dT$ data, because if you look at the sensitivity of the surface tension to contamination, it's fierce. Not only that, we also have absolutely no numbers for the gradients in the vicinity of the growth interface itself. So you are confronted with non-availability of thermo-physical data and an absolute lack of quantitative verification of thermal gradients and then you have to attempt to interpret the data. Finally, I wanted to say that in your system you have radial thermal gradients and then regardless of your stabilizing axial gradient, you will have serious convection.

NEITZEL: The magnitude of this convection is probably swamped by thermocapillary effects.

WITT: If you do it in confinement then your surface-tension-driven convection falls down to almost nothing. In the Bridgman configurations, we find that the momentum boundary layer is in the micron range stabilized with minimized radial gradients. It cannot get much less.

NEITZEL: You are not talking about a model experiment with silicon oil. You are talking about a crystal-growth experiment with radial gradients.

WITT: No, you are now making a dangerous conclusion, by drawing from one system conclusions to another. The surface-tension sensitivity in silicon oil cannot be compared to that of metallic melts. Therefore, the conclusions to be drawn are very, very dangerous, because you have no surface-tension data. I don't think anybody will question the soundness of your argument that there are surface-tension forces and they give rise to convection. However, the magnitude of the driving forces is in many instances in competition with other driving forces. Then the question is what becomes the primary mode. That's where I think we have a problem.

NEITZEL: That's right, but all we can do with our modeling is to try to predict those types of instabilities that occur where we know what's going on. That silicon oil experiment is a very good example of that. The data are very well known there. The material properties are well known, and if we can succeed in giving a stability boundary for that type of flow, then we have some confidence that maybe we could predict, if given the right material properties, what would happen in a float-zone silicon melt.

DYER: Is the wall pumping in the Czochralski arrangement included in your model? Being of a larger area and the fact that they are rotating,

possibly counter-rotating, this would seem to be an overwhelming effect compared with the small size of the crystal.

NEITZEL: What's really important to the crystal-growth process is what's going on in the vicinity of the freezing interface. Whereas that may be a very small effect in the overall bulk convective motion, it might be a very important effect with regard to the transport of scale of properties, oxygen, heat and whatsoever in the vicinity of the freezing interface. The side walls don't really do any pumping in the sense that the end walls do pumping and that the crystal-freezing interface does pumping.

SESSION IV

J. KALEJS, CHAIRMAN

N86-19734

THERMAL-CAPILLARY MODEL FOR CZOCHRALSKI GROWTH OF SEMICONDUCTOR MATERIALS

J.J. Derby and R.A. Brown

Department of Chemical Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139

Introduction and Methodology

Over 80 per cent of the silicon used by the electronics industry is grown from the melt by the Czochralski (CZ) crystal growth process, which is depicted schematically in Fig. 1. A single crystal boule is slowly pulled from a pool of melt maintained by heating the outside of the crucible. Surface tension acts against the force of gravity to form a meniscus connecting the the growing crystal to the surface of the melt pool. The precise temperature gradient needed to sustain the solidification of nearly perfect crystalline solid is maintained by a cooler ambient above the crucible. The crystal and crucible are rotated to minimize thermal asymmetry in the system. In addition, as the melt level drops during growth, the crucible is raised by movement of the pedestal so that the solidification front remains in a specified region of the heater.

Capillarity and heat transfer determine the shape and stability of crystals grown by the Czochralski method. We describe the solution of the first quasi-steady, thermal-capillary model of the CZ growth process which directly predicts the dependence of the crystal radius, melt-solid interface, and melt/gas meniscus on growth parameters and thermal boundary conditions in the furnace. The equations governing heat transfer are presented in Fig. 2., and the expressions for determining the radius and interface location are shown in Fig. 3. We model heat transfer in the system as conduction-dominated and include latent heat generation at the solidification interface. Radiation and convection accounts for heat exchange between the melt and crystal and the thermal surroundings. The thermal boundary conditions used in the calculations presented here represent an idealized, but qualitatively realistic thermal environment for CZ crystal growth. The heating of the melt through the crucible is modeled by specifying the temperature of the melt adjacent to the crucible wall as a constant without coupling this value to the actual power input to the crucible from the surrounding heater. Heat flows out of the melt through the bottom of the crucible, according to a specified heat transfer coefficient set to model energy loss to the pedestal and the surroundings. By itself, this heat transfer system represents a slightly nonlinear conductionradiation problem and its solution would be straightforward except that the shape of the melt and crystal are unknown and are aprt of the solution.

The locations of the interfaces are coupled to the heat transfer in the system by setting the shapes of the regions for conduction and by determining the surface areas for radiative and convective exchange with the ambient.

PRECEDING PAGE BLANK NOT FILMED

The melt/solid interface is determined by the location of the melting point isotherm. The shape of the melt meniscus is found from the Young-Laplace equation of capillary statics, the condition for three-phase contact at the melt/solid/gas tri-junction, the wetting condition at the crucible wall, and by the specification of the instantaneous volume of the melt. The radius of the crystal is determined so that the three-phase (melt/crystal/gas) equilibrium contact angle for growth is satisfied (Surek and Chalmers 1975).

These relations form a complete set of coupled partial differential equations for this complex nonlinear free-boundary problem. Only Ettouney et al. (1983) have solved a thermal-capillary model with a similar degree of complexity. As detailed in Fig. 4., We solve the field and boundary equations simultaneously by a finite-element/Newton scheme for the temperature field in melt and crystal, the shapes of the meniscus and melt-solid interface, and the radius of the crystal. Besides giving quadratic convergence in each of these unknowns, the Newton method is the basis for computer-implemented analyses of parametric sensitivity and stability (Yamaguchi et al. 1984). The details of the finite element algorithm are presented in a recent manuscript (Derby et al. 1985) for the modeling of liquid encapsulated Czochralski growth of gallium arsenide.

Results

Results for the thermophysical properties characteristic of CZ Silicon growth in a small-scale system are shown in Fig. 5. along with a specified ambient temperature distribution. On the left representative isotherms are shown for the melt and crystal. Note that heat flows into the melt from the crucible wall and exits the melt both upward through the surface of the melt and through the crystal and downward out of the bottom of the crucible. The shape of the meniscus is shown along with the melt/solid interface which is concave into the crystal. For this set of parameters, the resultant crystal radius was 3.8 cm. On the right, the ambient temperature distribution for this case is shown. The almost step decrease in the surrounding temperature field that occurs above the top of the hot crucible was modeled by the ambient temeperature profile shown in Fig. 5. The hot crucible has an increasingly important effect on the crystal size as the melt level drops and the outer crystal surface directly views this distribution. Similar ambient temperature distributions were used for the decreasing melt volume calculations of Figs. 10., 11., and 12.

The response of the system to changes in the steady-state growth rate is detailed in Fig. 6. as the pull rate, represented by the dimensionless Peclet number, is varied from 0-20 cm/hr ($0 \leq Pe \leq 0.4$). All other parameters were held constant and the ambient distribution was taken to be uniform at 1262K. The crystal radius decreased with increasing pull rate because of the increased latent heat release at the interface. This effect has been observed experimentally. The release of latent heat also was responsible for the increasing curvature of the solidification interface. At higher growth rates the interface became increasingly concave into the crystal.

Some computational aspects of these calculations are presented in Figs. 7 and 8. The converged finite-element meshes for each of the calculations

are shown in Fig. 8. Meshes with 76 element were used in all calculations presented in this report. The mesh follows the shape and position of the changing interfaces for each case. Since the mesh was based on the location of the free-boundaries, it converged as part of the entire solution with every iteration. The iteration histories for these runs is detailed in Fig. 8. The convergence was quadratic, as expected for full Newton's method; see Ettouney and Brown (1983).

Calculations are presented in Fig 9. for different equilibrium growth angles for the wetting of the crystal by the melt. The angle is varied from the reported 11 degree value for silicon to 45 and 90 degrees. There were two major effects: the crystal radius decreased with increasing angle, and the shape of the melt-solid interface changed from concave into the crystal to convex into the melt as the angle increased from 11 to 90 degrees. The last case for an equilibrium angle of 90 degrees corresponded to the assumption used by most previous investigators of a flat melt surface joining the crystal at right angles. This simplification obviously lead to erroneous results. Accurate modeling of heat flow in this region necessitates inclusion of the melt meniscus and the proper equilibrium angle.

The next series of figures represents the interaction of the temperature field and interfaces with the melt volume. Several effects are present as the melt level drops. The amount of heat entering the melt from the crucible sides decreased because the surface area in contact with the wall decreased. Also, the heat loss out of the bottom of the crucible was increasingly important in the shallower melt, and the hot crucible wall was exposed. The exposed wall allowed for radiative heat transfer from the hot crucible wall directly into the growing crystal. First, we examine only the effect of the dropping melt level without the complicating effects of radiative heat transfer. The case of decreasing melt volume with an axially uniform ambient temperature of 1262 K is shown in Fig. 10. Since the amount of heat entering the melt decreased as the melt level drops, the radius of the crystal increased. The effect of the heat loss through the bottom of the crucible was manifested in a change of the interface shape from concave to sigmoidal. This transition is known as interface flipping and commonly has been attributed to transitions in the natural convection within the melt. Since our calculations are for a conduction-dominated system, interface flipping was caused solely by conductive heat losses through the melt and the changing shape of the melt pool. Another related effect of the crucible heat loss was the formation of a section of undercooled melt at the bottom of the crucible for the shallow melt depth (V_m=0.5π). In practice, this region would be a small cap of solid silicon at the bottom of the crucible which can grow large enough with decreasing melt depth to touch the upper melt/solid interface. This is occasionally observed in practice, and is known as "crystal bumping".

When we add radiation from the exposed wall in the form of the specified axial temperature distribution discussed previously, we get the situations depicted in Figs. 11. and 12. Even though the heat flow into the melt decreased with the dropping melt, the radiative transfer of heat from the exposed wall into the crystal can prevent the growth in the radius of the crystal as the melt level dropped. This effect is seen for the case with melt volume V_m=0.5π for the shallow crucible in Fig. 11. and for both cases

for the deep crucible in Fig. 12. Radiation from the crucible wall to the crystal is so overpowering for the deeper crucible case of Fig. 12 that a non-zero crystal radius did not exist for the V_m=0.5π case. Radiative interchange between wall and crystal also magnified the interface flipping effect. With heat entering the side of the crystal, the melt/solid interface was pushed even further into the melt. The solid cap at the bottom of the crucible was present for the melt volume V_m=0.5π shown in Fig. 11.

The changes in radius for decreasing melt volume are shown together in Fig. 13. For the uniform ambient, the crystal radius increased steadily with decreasing melt volume. When an ambient temperature distribution was introduced to include the crucible wall the increasing effect of radiation from the exposed wall the radius show either a maximum with decreasing volume or decreased monotonically, depending on the depth of the crucible. For the shallow crucible, the crystal radius initially increased as the melt dropped, but decreased as more of the crucible wall was exposed to the view of the crystal. This effect is even more dramatic for the deep crucible: the radius decreased from the start and rapidly melted away so that no steady-state growth was possible after some minimum volume was reached. This last effect is often seen in practice where the crystal becomes very difficult to grow as the melt level drops below some critical value.

Summary

We have demonstrated the success of efficiently calculating the temperature field, crystal radius, melt mensicus, and melt/solid interface in the Czochralski crystal growth system by full finite-element solution of the governing thrmal-capillary model. The model predicts realistic response to changes in pull rate, melt volume, and the thermal field. The experimentally observed phenomena of interface flipping, bumping, and the difficulty maintaining steady-state growth as the melt depth decreases are explained by model results. These calculations will form the basis for the first quantitative pitcure of CZ crystal gowth. The accurate depiction of the melt meniscus is important in calculating the crystal radius and solidification interface. The sensitivity of our results to the equilibrium growth angle place doubt on less sophisticated attempts to model the process without inclusion of a the meniscus.

Quantitative comparison with experiments should be possible once more representation of the radiation and view factors in the thermal system and the crucible are included. Extensions of our model in these directions are underway.

References

Derby, J.J., Brown, R.A., Geyling, F.T., Jordan, A.S., and Nikolakopoulu, G.A., **J. Electrochem. Soc.** to appear, Feb. (1985).

Ettouney, H.M. and Brown, R.A., **J. Computat. Phys. 49,** 118 (1983).

Ettouney, H.M., Brown, R.A., and Kalejs, J.P., **J. Crystal Growth 62,** 230 (1983).

Surek, T. amd Chalmers, B., **J. Crystal Growth 29** 1 (1975).

Yamaguchi, Y., Chang, C.J., and Brown, R.A., **Philos. Trans. R. Soc. Lond. 312** 520 (1984).

Nomenclature

Bi_j, Biot number = $\hat{h}_j R_c / k_s$ for surface j;

Bo, Bond number = $g R_c^2 \rho / \sigma$;

Cp, heat capacity [J/kgK];

$\underline{e_z}$, unit axial vector;

g, gravitational constant [m/s^2];

$\hat{h}_j$, heat transfer coefficient for surface j [W/m^{2}K];

$\tilde{H}_i$, height of interface i from bottom of crucible [m];

h_i, dimensionless interface heights = $\tilde{h}_i / R_c$;

k, thermal conductivity [W/mK];

K_i, temperature-dependent thermal conductivity ratio = k_i / k_s for region i;

$\underline{n_i}$, normal vector to surface i;

Pe, Peclet number = $V_p R_c \rho_s Cp_s / k_s$;

$\tilde{r}$, radial coordinate measued from center of crucible [m];

r, dimensionless radial coordinate = $\tilde{r} / R_c$;

$\tilde{R}$, crystal radius [m];

R, dimensionless crystal radius = $\tilde{R} / R_c$;

R_c, crucible radius [m];

Ra_i, Radiation number = $\sigma^* {}_i R_c T_f^3 / k_s$ for surface i;

S, Stefan number = $H_f / Cp_s T_f$;

T, temperature [K];

T_f, solidification temperature [K];

$\tilde{V}_m$, volume of melt [m^3];

V_m, dimensionless volume of melt = $\tilde{V}_m / R_c^3$;

V_p, steady-state crystal pull rate [m/s];

$\tilde{z}$, axial coordinate measured from bottom of crucible [m];

z, dimensionless axial coordinate = $\tilde{z} / R_c$;

Greek symbols

H_f, heat of fusion [J/kg-mole];

ρ, density difference across melt meniscus;

$_j$, emissivity of surface j;

λ_i, dimensionless reference pressure = $p_{i,datum}/ \rho_i g R_c$;

ϕ, equilibrium wetting angle;

ρ, density [kg/m^2];

σ, surface tension [J/m];

σ^*, Stefan-Boltzmann constant [W/m^2K^4];

Θ, dimensionless temperature = T/T_f;

Subscripts

a, ambient;

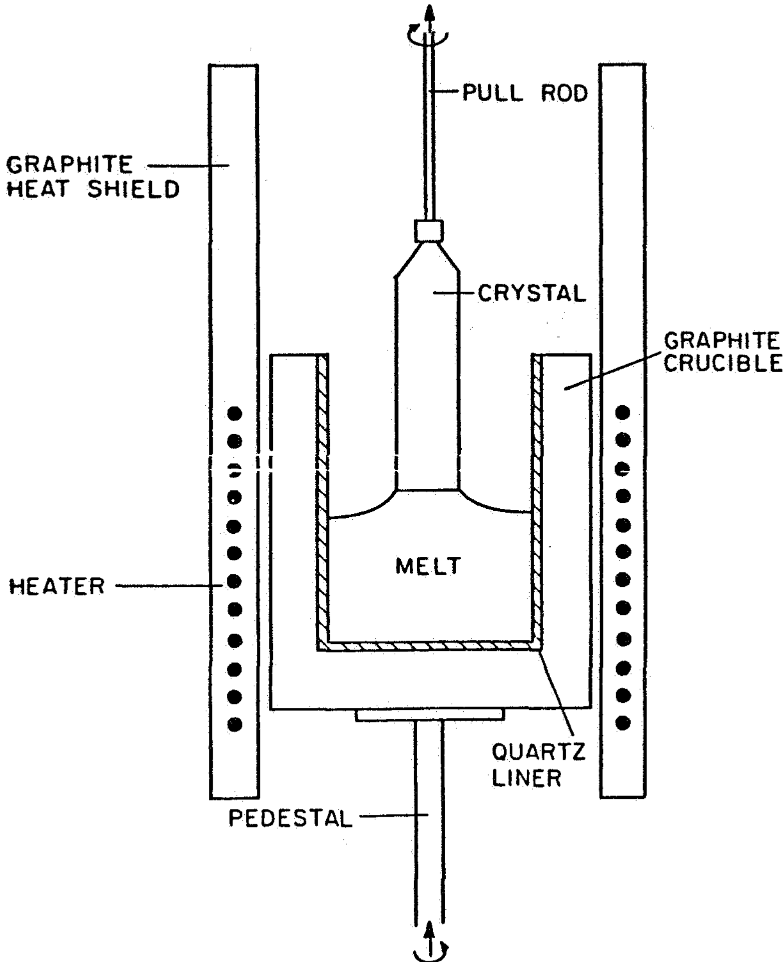
c, crucible;

i,j, numerical indeces denoting surface, domain, or equation;

m, melt;

s, solid.

Czochralski Crystal Growth



Steady-State Thermal-Capillary Model

AXISYMMETRIC CONDUCTION-DOMINATED HEAT TRANSFER

$$\nabla \cdot K_m(\theta)\nabla\theta = 0 \qquad \text{(Melt)}$$

$$\nabla \cdot K_s(\theta)\nabla\theta - Pe(\underline{e}_z \cdot \nabla\theta) = 0 \qquad \text{(Crystal)}$$

THERMAL BOUNDARY CONDITIONS

at melt-solid interface

$$\theta_s = \theta_m = 1$$

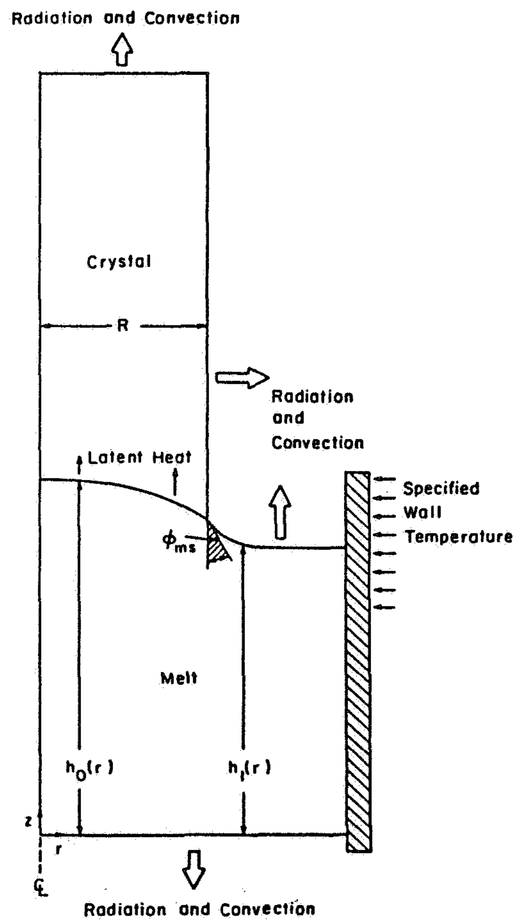
$$K_m(\underline{n} \cdot \nabla\theta_m) - K_s(\underline{n} \cdot \nabla\theta_s) = PeS(\underline{n} \cdot \underline{e}_z)$$

at external surfaces

$$-K(\underline{n} \cdot \nabla\theta) = Bi(\theta - \theta_a) + Ra(\theta^4 - \theta_a^4)$$

at crucible inner wall

$$\theta(r, z) = \theta_c(r, z)$$

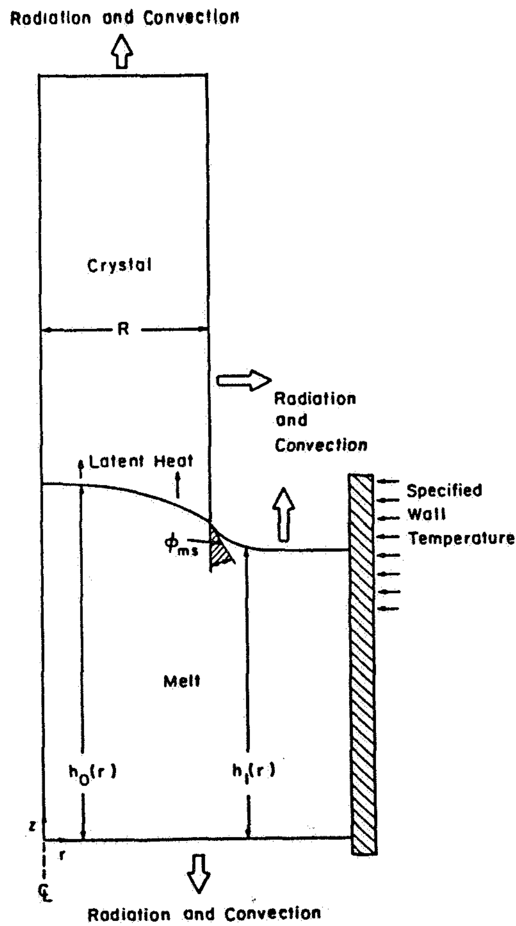


melt-solid interface $\quad B(r, h_0(r)) = 1$

meniscus
$$\frac{\frac{d^2h_1}{dr^2}}{[1+(\frac{dh_1}{dr})^2]^{3/2}} + \frac{\frac{dh_1}{dr}}{r[1+(\frac{dh_1}{dr})^2]^{1/2}} = Bo(h_1(r)-\lambda)$$

radius
$$\left.\frac{dh_1}{dr}\right|_R = \tan(\phi_{ms} - 90°)$$

volume constraint
$$\int_0^R h_0(r)\,r\,dr + \int_R^1 h_1(r)\,r\,dr = V_m/2\pi$$



FINITE ELEMENT/NEWTON METHOD

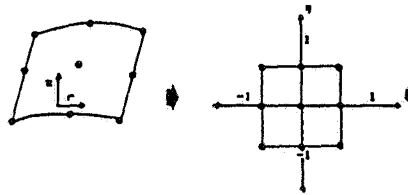
- Piecewise-continuous polynomials used to approximate temperature field (2d) and interface shapes (1d)

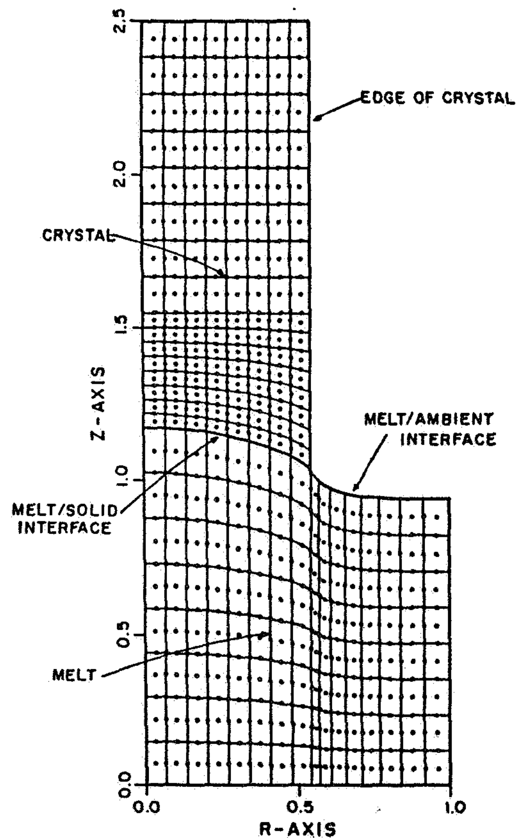
- Adaptive mesh defined by free boundaries

- Galerkin method and elemental isoparametric mapping used to generate set of nonlinear algebraic equations

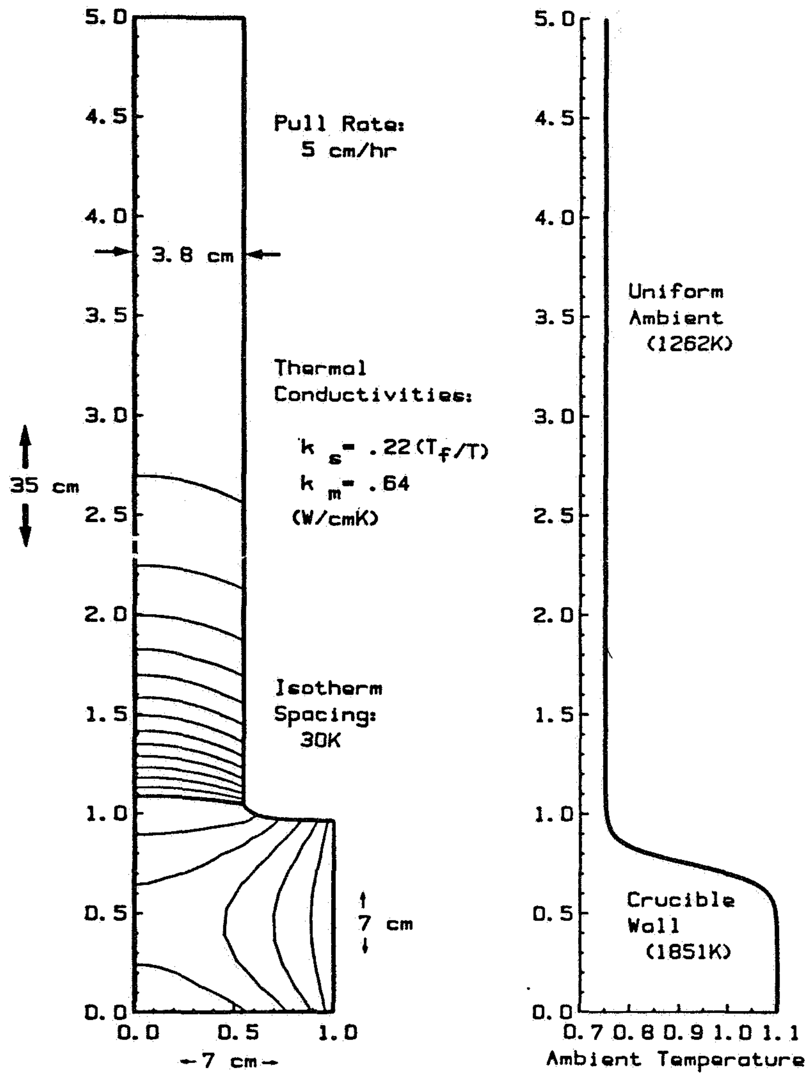
- Newton's method used to solve equation set, giving quadratic convergence to solution

ISOPARAMETRIC MAPPING

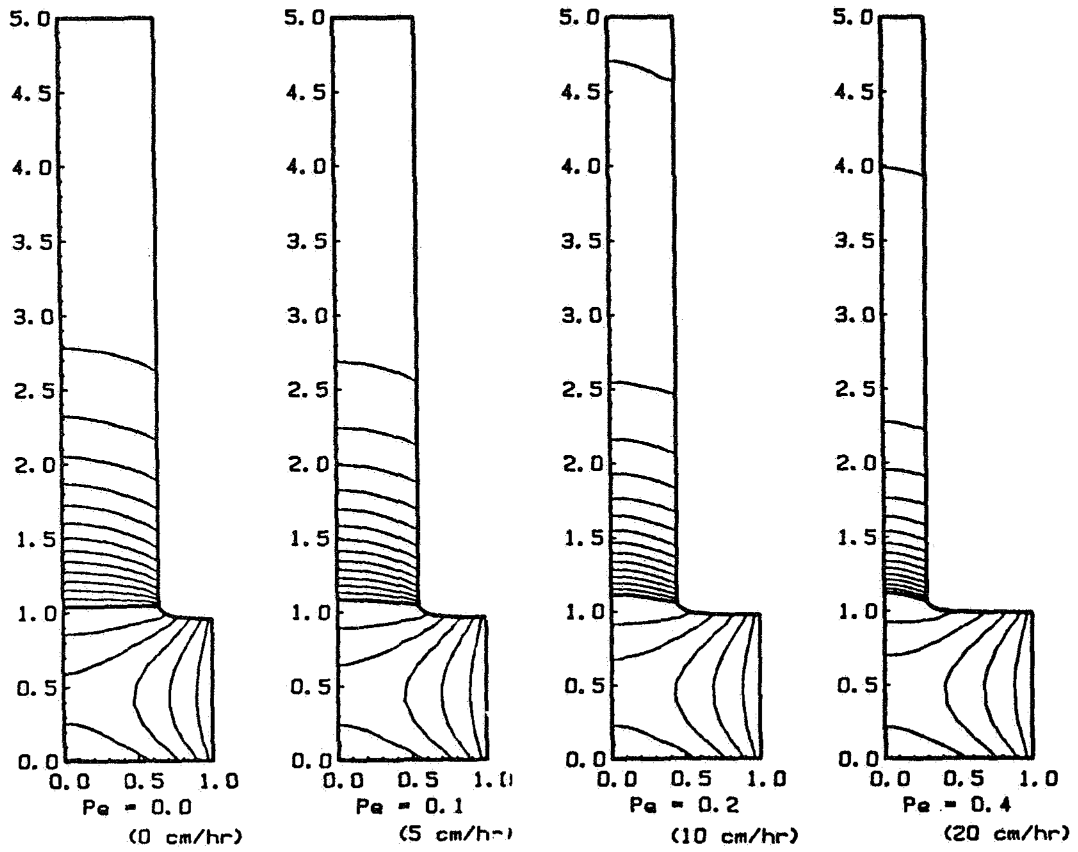




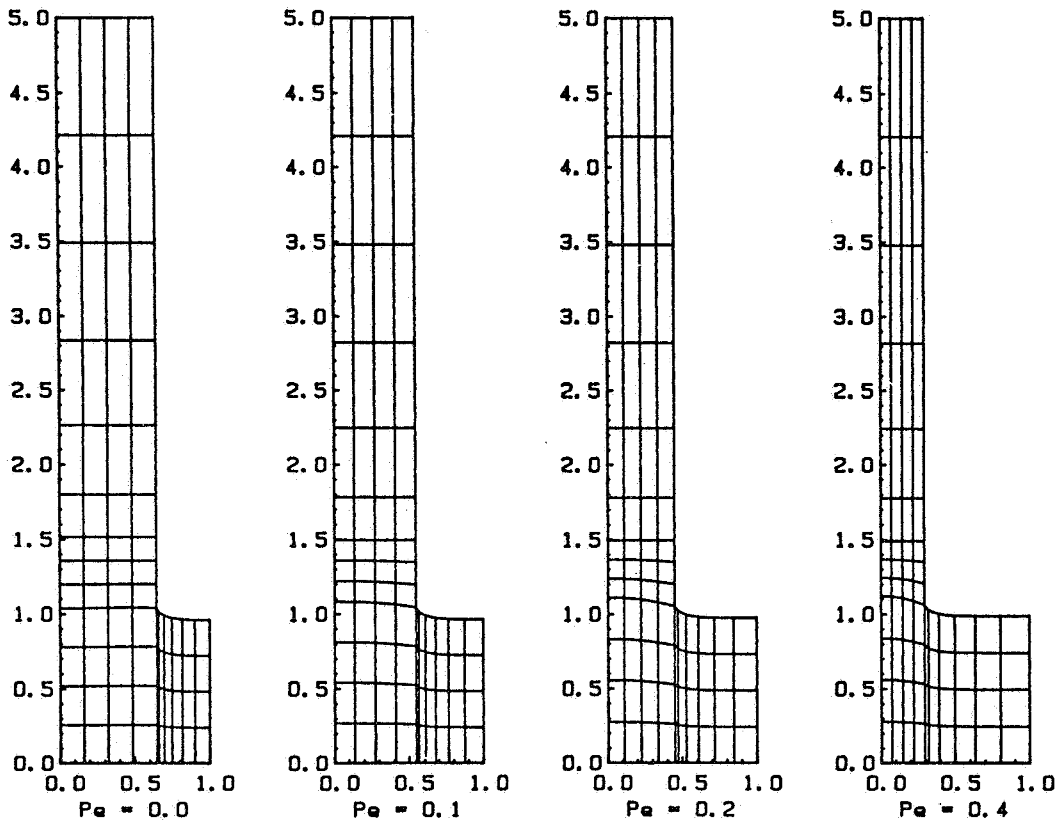
Parameters—Silicon



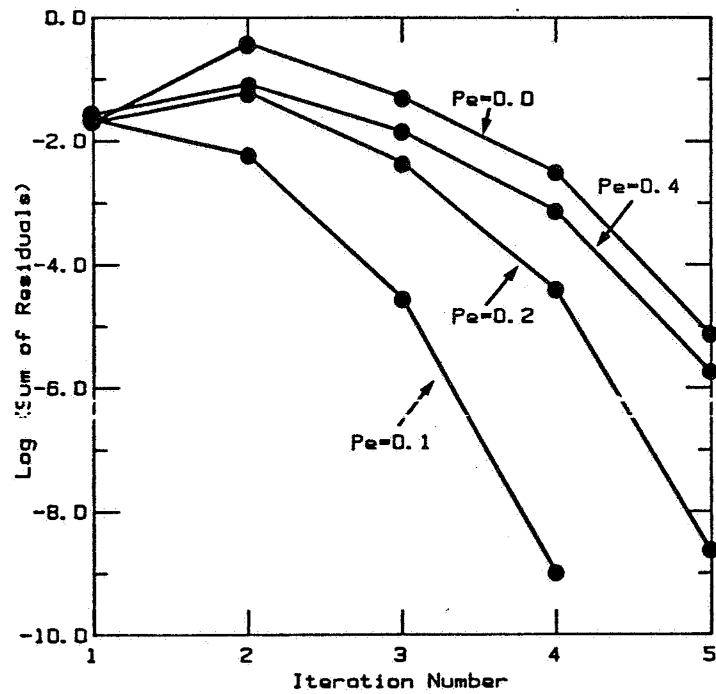
Changes in Pull Rate



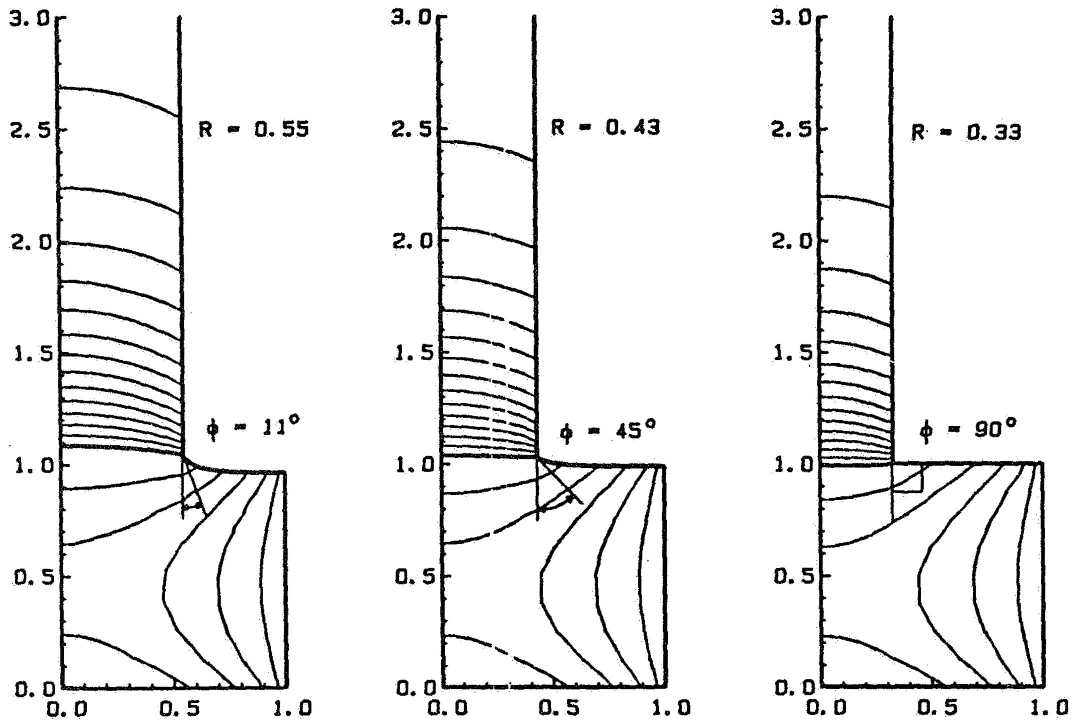
Finite-Element Meshes for Different Pull Rates



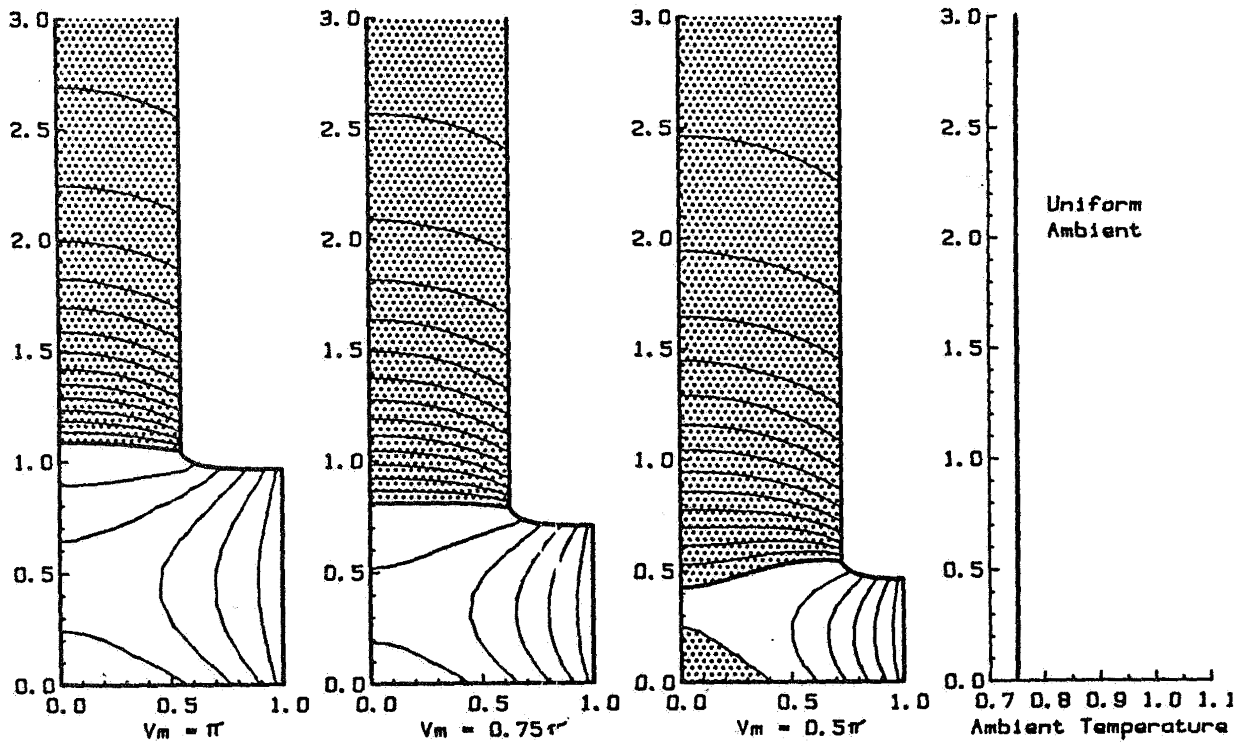
Convergence Behavior



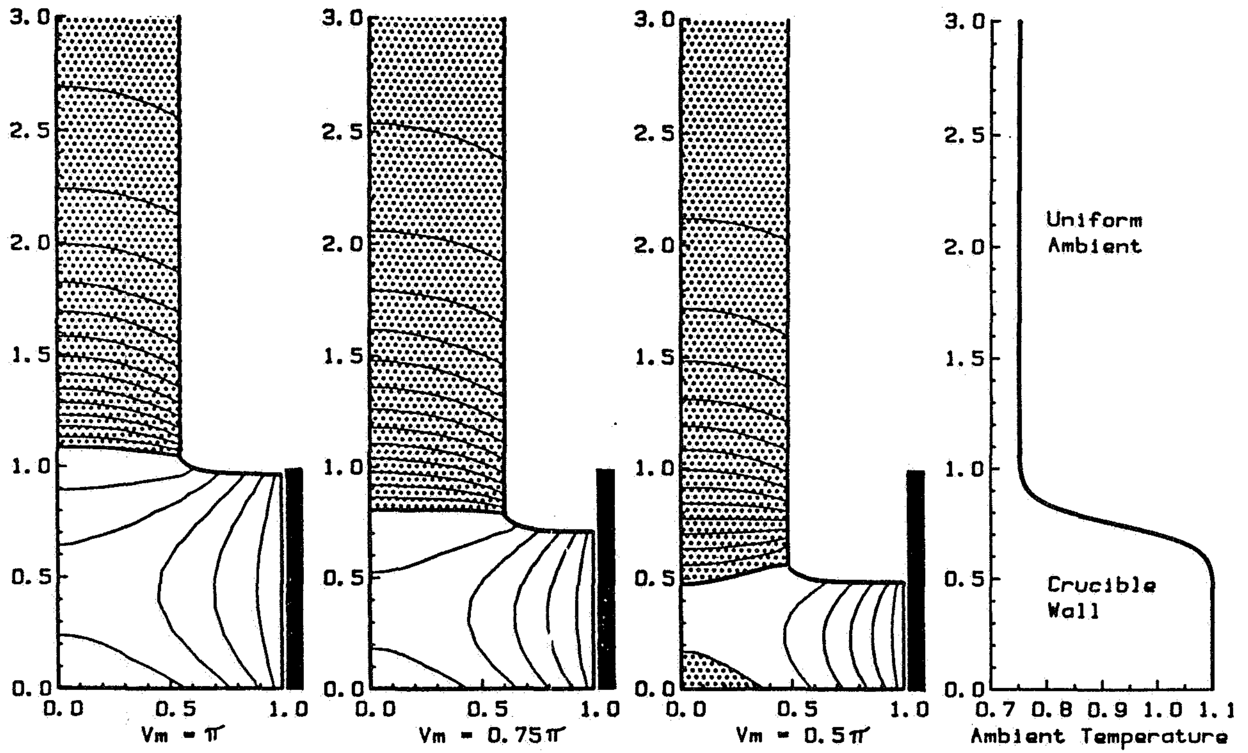
Variations in Equilibrium Angle



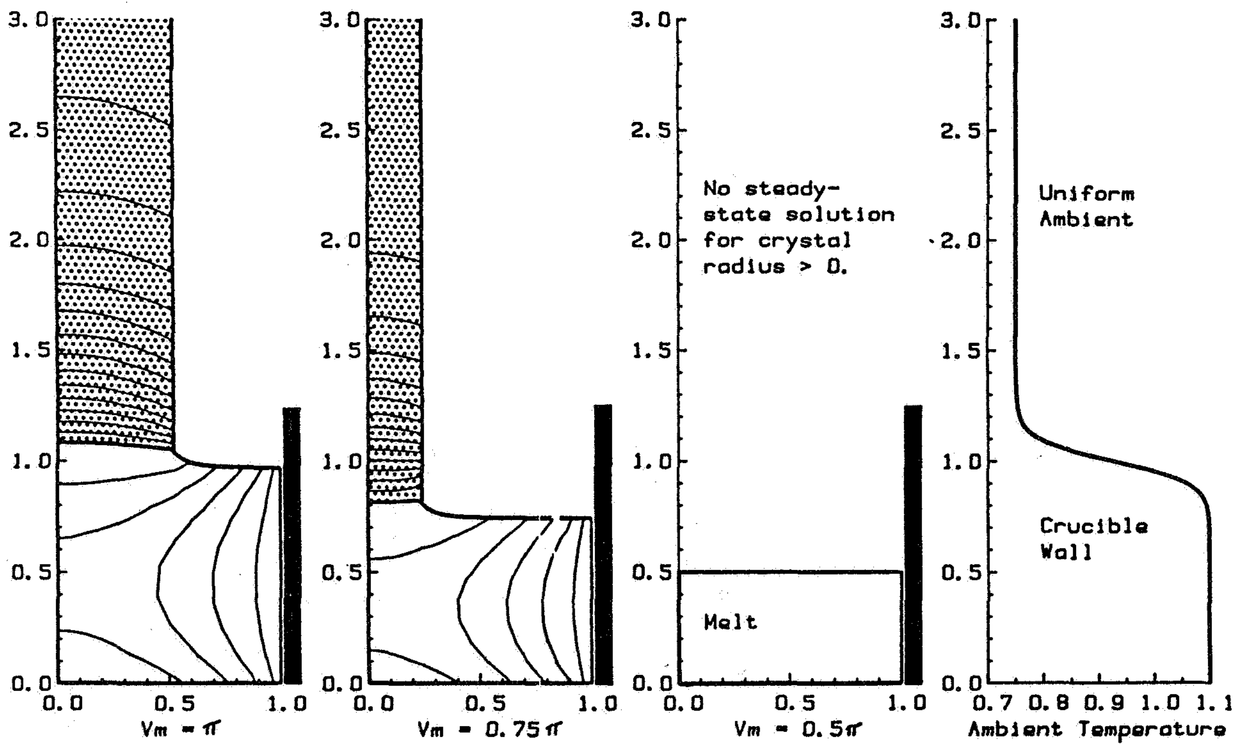
Decreasing Melt Volume—Uniform Ambient



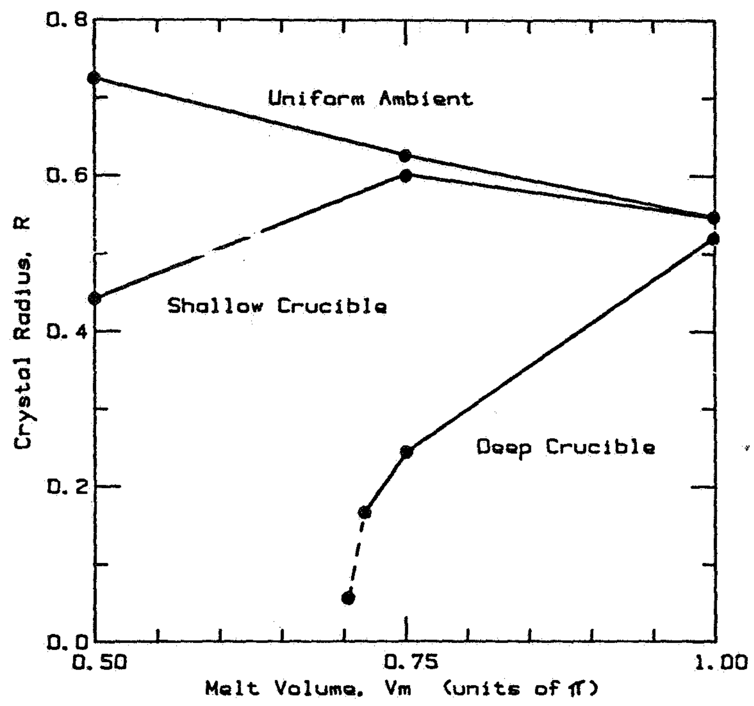
Decreasing Melt Volume—Shallow Crucible



Decreasing Melt Volume—Deep Crucible



Radius as a Function of Melt Volume



DISCUSSION

ELWELL: Is it too complicated to plug convection in the Czochralski system?

BROWN: It depends on your goal. We are working on convection, and we are working on convection in other systems that are quite a bit simpler than this. To come up with a good algorithm for doing convection in a large Czochralski system means you have to handle convection that is in the never-never land between laminar and turbulent flow, which is essentially chaotic. It is too complicated at present to plug that kind of convection model into a calculation like this and hope to get back out some kind of a control strategy. Those are supercomputer-type calculations, unless you are willing to put in a turbulent model, which we are not willing to do right now.

DUDUKOVIC: You use a static value of the contact angle in all of your calculations, which is of course fine because presumably the pulling rates are so low. What do you do about the value of that angle in presence of the Marangoni effect?

BROWN: If you really believe that is a thermal physical property of what is right down at the intersection between melt/solid and gas then you would believe that the bulk fluid mechanics should not have a lot of effect on them. That concept has been shown to have been true not in solidification systems but in normal wetting conditions as long as the contact line is not moving at high rates of speed.

DUDUKOVIC: At the moment that's the best assumption one can make, but isn't there still some doubt about it under dynamic conditions?

BROWN: If it's a microscopic property of the physics of the tri-junction I don't think there is any scaling you can do to show that a bulk flow can affect it. For example, gravity cannot affect it. The same kind of argument you would use to say that the surface tension is independent of gravity is used and, in fact it's one order of magnitude worse.

KIM: In your aluminum segregation study, what was the effective segregation coefficient that you have measured?

BROWN: One.

KIM: What was the solid boundary layer thickness?

BROWN: There is no boundary layer thickness because in the EFG system that is a big problem. The flow field in the die is well developed and there is no effective segregation in the system. Any aluminum that comes up through that die has to go into the crystal. It has no place else to go.

KALEJS: It is quite true for K_{eff} equal to unity that there are a lot of impurities that ended up very close to the meniscus, but this is

true for a lot of the shaped crystal growth systems like web. We have looked at this and found that the change in surface tension with impurity concentration goes opposite to the temperature difference, so you may expect some kind of cancellation due to impurity effects, particularly in K_{eff} equal to unity where a lot of impurities do end up in the meniscus.

SUREK: Regarding Professor Dudukovic's question: the contact angle was determined over many orders of magnitude of growth rate, essentially from zero growth rate to very fast growth rate without much variation, so it seems to be a property of the silicon at a triple junction. My question is if you showed points or regions where there is no existence of a steady-state solution, would that be the limit of stability, in your opinion?

BROWN: The EFG calculations give you the growth-rate limit for steady-state solutions for growing a ribbon with that die at that K_{eff}. We had not found similar limits in the Czochralski system, but I think all one needs to do is play around with the thermal ambient to actually find growth-rate limits in that system also. I don't think people worry about it as much because they concentrate more on high-quality material and less on growth speed.

SUREK: In what system was it that you found no solution?

BROWN: In the Czochralski system. Essentially that's associated with just excessive heat transfer from the ambient directly into the crystal, which essentially just blocks up the heat so that you can't get it out of the melt. We are not sure whether or not that is essentially just the crystal growing to zero diameter or whether or not there really is a limit point there. We haven't refined that enough to find out.

WITT: How do you handle the complication that normally is encountered when you grow dislocation-free silicon? In conventional growth, you end up with the peripheral interface facet, which places the critical portion of the crystal into a supercooled state, and we know that you lose, for one reason or another, the dislocation-free growth configuration. The instantaneous consequence is a significant change in crystal diameter, which means that effectively the growth does not occur in critical portions, particularly at the periphery, which is a critical point way away from the melting point. My second question: a very important element is the rate of crucible consumption or the melt/crucible interaction or the mass transfer related to oxygen and impurities. Are you looking at these factors?

BROWN: We have not been. Obviously, if you take the same segregation model we can dissolve the crucible with it if you want. We have not been doing it. In answer to your first question, interface faceting is a fantastic piece of physics that could be put in here if I knew the orientation and undercooling law for doing it. There's nothing that keeps us from putting in a faceted growth mode at the interface. It would be very interesting to do, and there are some mathematical

reasons why it's very nice to do in the finite-element formulation. You could very easily come up with an interface that has facets along part of it and equilibrium growth on other parts. If someone would stick their neck out and give me the undercooling law I'd love to do it, because I think it would be very interesting. I think that introduces an additional non-linearity, which I think can give you catastrophic behavior, which is what you referred to with the loss of the facet in the growth of the crystal. Do you know of someone that has written down this nucleation law?

WITT: It is still very controversial in details. The theory is worked out.

N86-19735

IMPURITIES IN SILICON SOLAR CELLS

R.H. Hopkins

Westinghouse R&D Center
Pittsburgh, PA 15235

We studied how metallic impurities, both singly and in combinations, impact the performance of silicon solar cells. Czochralski silicon web crystals were grown with controlled additions of secondary impurities. The primary electrical dopants were boron and phosphorus. The metal elements were selected because of their occurrence in silicon raw materials, possible introduction during subsequent device processing, or because there were common construction materials for process equipment or the cells themselves. Some 26 elements were examined including Ag, Au, Al, C, Cr, Co, Cu, Fe, Gd, Mn, Nb, Ni, Pd, Sn, Ta, Ti, V, W, and Zr. Impurity concentrations were in the range of 10^{11} to 10^{18} cm^{-3}.

All silicon ingots were grown under controlled and carefully monitored conditions from high-purity charge and dopant material to minimize unintentional contamination. Following growth, each crystal was characterized by chemical, microstructural, electrical, and solar cell tests to provide a detailed and internally consistent description of the relationships between silicon impurity concentration and solar cell performance.

Analysis of vacuum-cast melt samples provided an accurate determination of the melt impurity concentration at the completion of crystal growth. Melt concentrations coupled with reliable effective segregation coefficients in turn were used to calculate ingot impurity concentrations, which were in excellent agreement with the ingot impurity concentrations measured directly by spark source mass spectroscopy and neutron activation analyses. Deep-level spectroscopy measurements were used to measure impurity concentrations at levels below the detectability of the other techniques and to study thermally-induced changes in impurity activity.

Solar cells made using a conventional diffusion process optimized for repeatability and reliability were used to evaluate the effect of impurities. For the majority of contaminants, impurity-induced performance loss was due to a reduction of the base diffusion length. From these observations, we formulated a semi-empirical model which predicts cell performance as a function of metal impurity concentration. The calculated performance parameters agree well with measured values except for the impurities Cu, Ni, and Fe, which at high concentrations degrade the cell performance substantially by means of junction mechanisms. The model was used successfully to predict the behavior of solar cells bearing as many as 11 different impurities. The concentration of recombination centers identified by deep-level transient spectroscopy not only correlates directly with the concentration of metallurgically added impurity, but also with solar cell performance.

The effects of impurities in n-base and p-base devices differ in degree but can be described by the same modeling analysis. Some of the more deleterious impurities in p-base devices produce significantly less performance reduction in n-base silicon. For example, nearly ten times more Ti is acceptable in n-type silicon to produce the same cell efficiency as in a similarly contaminated p-base device. N-base cells containing V, Mo, and Mn exhibit somewhat smaller efficiency improvements.

When the model-calculated and measured cell performance for multiple impurities are compared, there is limited indication of interaction between impurities. For example, copper improves the efficiency of Ti- and V-doped cells, although the effect is small. Apparently, Cu diffuses to and combines with the second transition metal to reduce its electrical activity. Precipitated impurities have little or no effect on carrier-transport properties in the low-field base region of the solar cell, but do affect cell performance when they occur in or near the high-field junction region. The latter effect is manifested by large shifts in the lower segment of transformed dark I-V curves measured on cells containing the metal-rich precipitates. (The presence of precipitation was confirmed by X-ray topographic analysis of the devices.)

Extension of the impurity performance model to high-efficiency solar cells indicates, in general, that such devices will be more sensitive to impurities than are their more conventional counterparts. This increased impurity sensitivity will be exhibited in widebase cells and medium-base cells with back-surface fields or passivated surfaces, but may be significantly reduced by making cells with narrow (≈ 100 µm) basewidths. For example, we calculate that raising the base diffusion length of our standard efficiency device (275 µm thick) to 450 µm from 150 µm lowers the impurity threshold for performance loss onset from 6×10^{11} Mo atoms per cm^{-3} to 9×10^{10} atoms per cm^{-3}. The <u>absolute</u> efficiency of cells with the 450 µm diffusion length of course remains higher than that of cells with the 150µm diffusion length until the performance becomes dominated by impurity effects. Similar shifts in impurity sensitivity are calculated for passivated cells with back-surface fields using a one dimensional analytic model.

In addition to the direct impact on device performance, impurities also can degrade crystal structure. Crystal structure breakdown (constitutional supercooling) or precipitation effects largely affect junction behavior. Since the concentration thresholds are higher for structural impairment than for lifetime degradation, the latter is a dominant performance loss mechanism in solar cells.

We examined the redistribution of impurities during silicon web growth and found that, like Czochralski silicon growth, the segregation coefficients for metals are small, typically 10^{-7} to 10^{-5}. In addition, the performance loss of web cells due to impurities can be modeled in a fashion identical to that employed for devices made on Czochralski wafers. The predicted and measured cell performance values are in good agreement.

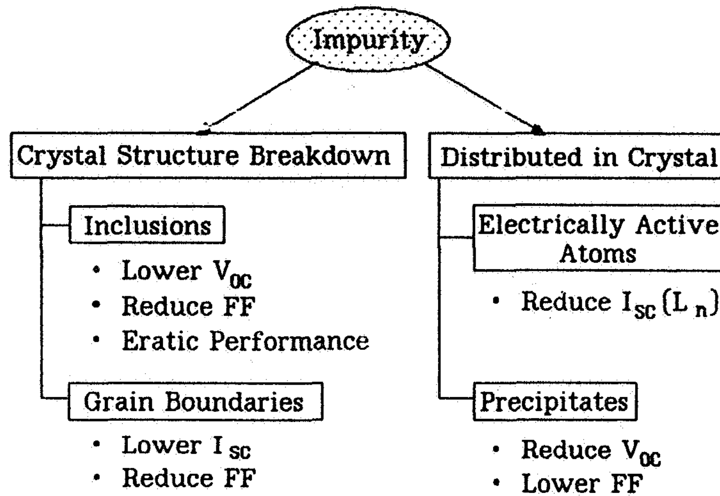
Solar-Cell Impurity Data Base

- 240 crystals
- 26 impurity species
- Over 7,000 solar cells.

Material Characterization

- Impurity Analysis
  - Neutron Activation
  - Spark Source Mass Spectroscopy
  - Infrared Absorption
  - Deep Level Transient Spectroscopy
- Electrical Properties
  - Four-point Resistivity
  - Spreading Resistance
  - Photoconductive Decay
  - Open Circuit Decay
  - Dark I-V Analysis
  - Laser-scanned Photoresponse
- Structural Characterization
  - Etch Pit Density
  - X-ray Topography
  - Optical/Electron Microscopy
- Solar Cell Characterization
  - Lighted I-V
  - Spectral Response

Impurity Degradation Mechanisms in Silicon Solar Cells



Crystal Growth Conditions

Doping:	boron 3–6 Ωcm or phosphorus 1–3 Ωcm	+ metal impurities
Czochralski:	‹111› orientation 3.5 cm diameter 7 cm/hr growth rate 10 rpm cw seed rotation 3 rpm ccw crucible rotation argon atmosphere	
Dendritic Web Ribbon:	‹211› orientation 3 cm width 1 cm/min growth rate argon atmosphere	

Effective Segregation Coefficients in Silicon

ELEMENT	SEGREGATION COEFFICIENT
Ag	1.7×10^{-5}
Al	3×10^{-2}
Au	2.5×10^{-5}
Co	2×10^{-6}
Cr	1.1×10^{-5}
Cu	8.0×10^{-4}
Fe	6.4×10^{-6}
Mn	1.3×10^{-5}
Mo	4.5×10^{-8}
Nb	4.4×10^{-7}
Ni	1.3×10^{-4}
Pd	5×10^{-5}
Sn	3.2×10^{-2}
Ta	2.1×10^{-8}
Ti	2.0×10^{-6}
V	4×10^{-6}
W	1.7×10^{-8}
Zr	1.6×10^{-8}

Solar-Cell Design and Fabrication: Standard Efficiency (SE)

Baseline Cell

- 1.03 cm^2, five finger grid (5.4% coverage)
- Ti – Pd – Ag contacts
- Cell efficiency 14.1 ± 0.7% AM1 (2000 cells)

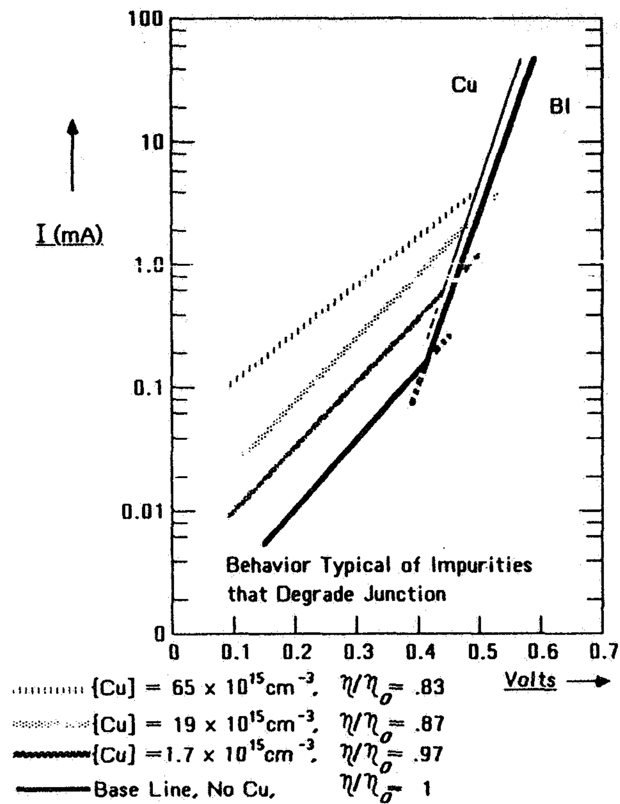
n^+p Cell

$POCl_3$ diffusion
$850^\circ C$, 50 min
0.35 μm junction depth
Contacts sintered @
$400^\circ C$, H_2

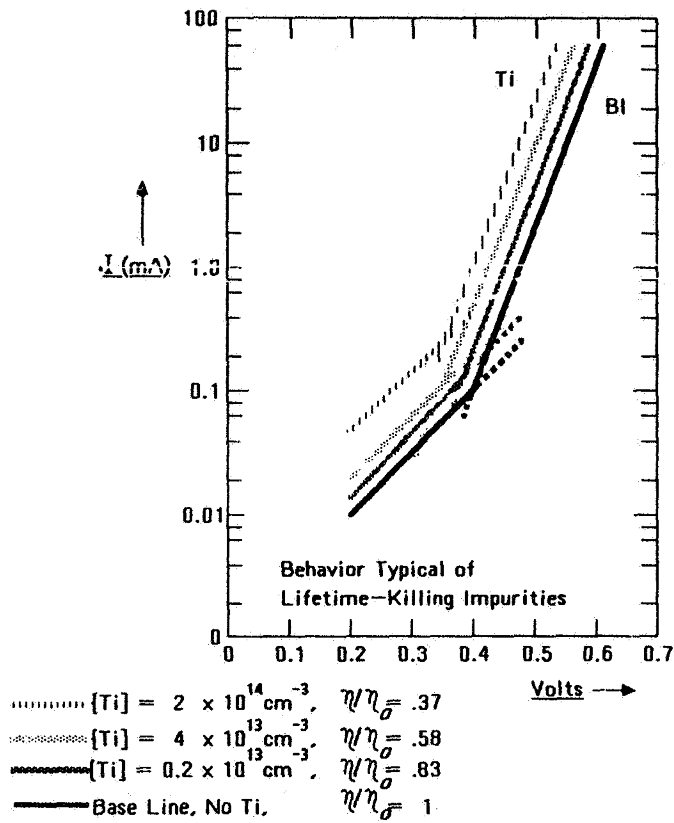
p^+n Cell

BBr_3 diffusion
$875^\circ C$, 30 min
0.35 μm junction depth
Contacts sintered @
$350^\circ C$, H_2

Transformed Dark I-V Curves for Cu-Doped Solar Cells



Transformed Dark I-V Curves for Ti-Doped Solar Cells



Impurity Behavior

- Degrade Junction

  Cu, Ni

- Reduce Diffusion Length

  Nb, Ti, V, Ta, W, Mo, Pd, Au, Zr, Mn, Al, Sn

- Both

  Fe, Co, Ag

Impurity Model Assumptions

1. Device can be modeled as if the cell consisted wholly of a single base region with uniform electrical properties.

2. Impurity effect is exclusively to reduce carrier diffusion length in the effective base region.

3. Impurity–induced diffusion length reduction is due either to carrier recombination at deep centers or mobility loss by ionized impurity scattering.

4. The number of electrically active centers is a species–dependent linear function of the total metallurgical concentration of that impurity.

Impurity Model Equations

$$\left[\frac{I_{n\infty}}{I_n} - 1\right]^2 = C_1\left[1 + \frac{N_x}{N_{ox}}\right] \quad \text{Normalized } I_{sc}$$

N_{ox} : Impurity Thresold Degradation Concentration

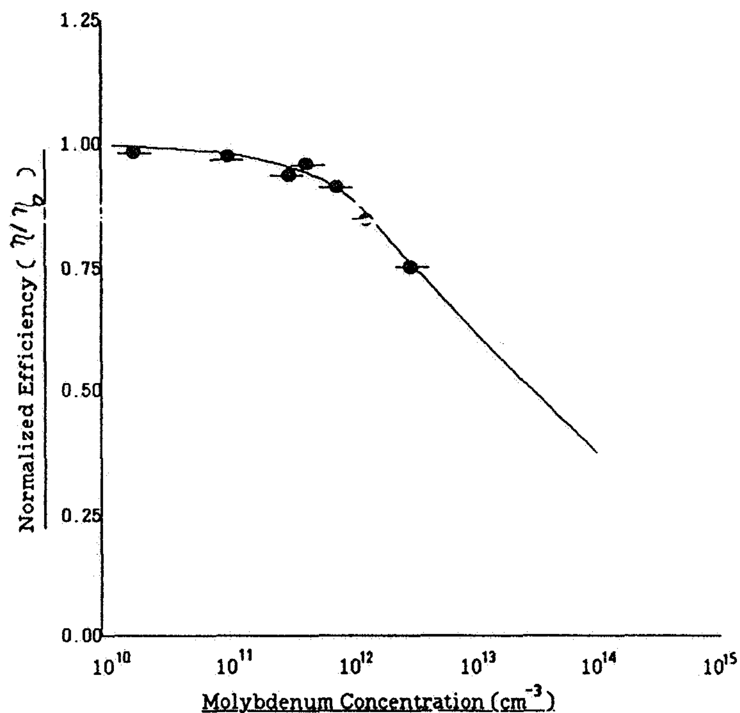
N_x : Total Impurity Concentration in Cell.

$$\frac{\eta}{\eta_o} = \frac{i_p V_p}{i_{po} V_{po}} \quad \text{Normalized efficiency.}$$

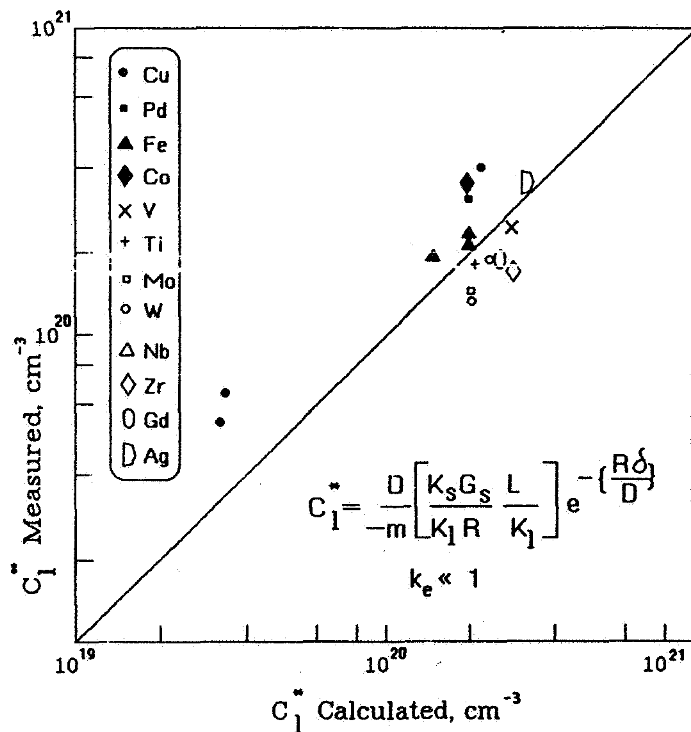
$$\frac{\eta}{\eta_o} = 0.872\ I_n^{1.128} + 0.128\ I_n^{12}$$

[After J.R. Davis, R.H. Hopkins, and A. Rohatgi, IEEE Transactions Elec. Devices, ED–27, 677 (1980)]

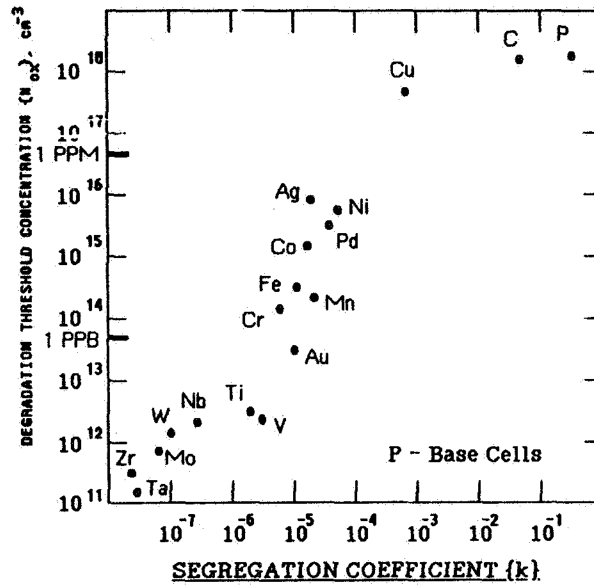
Normalized Silicon Solar-Cell Efficiency versus Content of Molybdenum in the Silicon



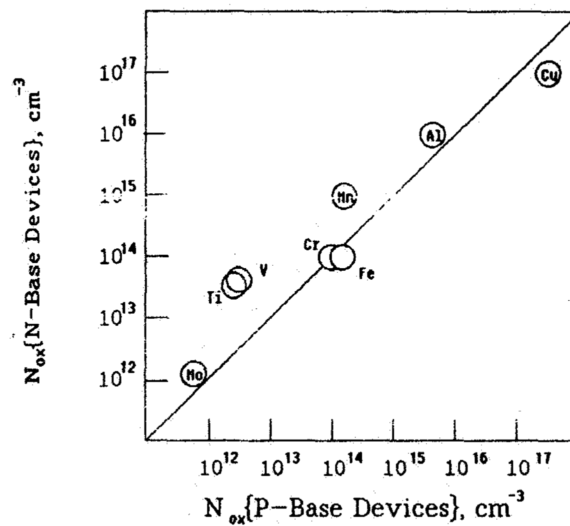
Critical Impurity Concentration for Crystal Structure Breakdown



Relation of Cell Degradation Threshold to Impurity Segregation Coefficient



Degradation Threshold Concentrations, n-Base versus p-Base Devices



Impurity Model Extension to High-Efficiency Cells

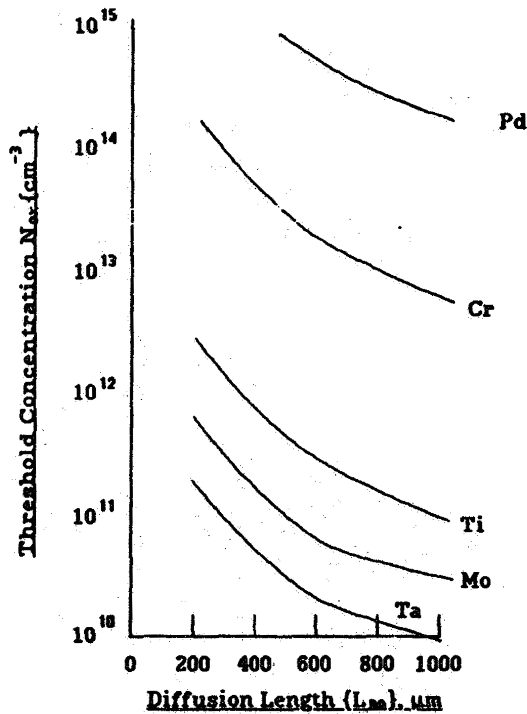
$$N_{ox}(HE) = N_{ox}(SE) \left[\frac{L_{no}(SE)}{L_{no}(HE)}\right]^2 \left[\frac{D_{nb}(HE)}{D_{nb}(SE)}\right]$$

N_{ox}: Impurity Degradation Threshold

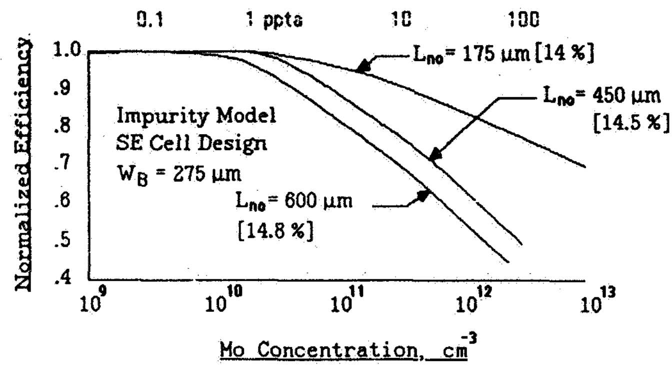
L_{no}: Diffusion Length of Uncontaminated Baseline Cell

D_{nb}: Minority Carrier Diffusion Constant

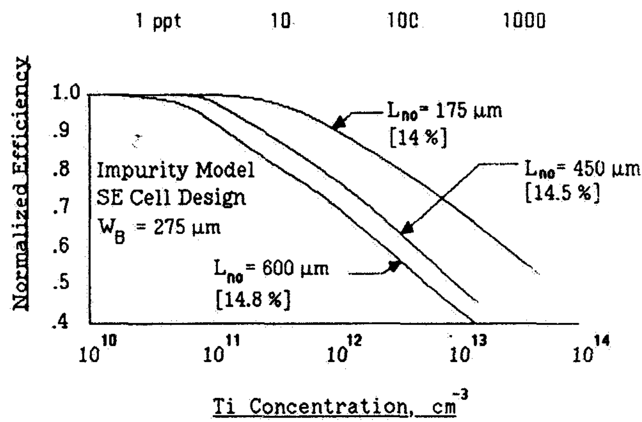
Variation in Degradation Threshold With Diffusion Length of Baseline SE Cell



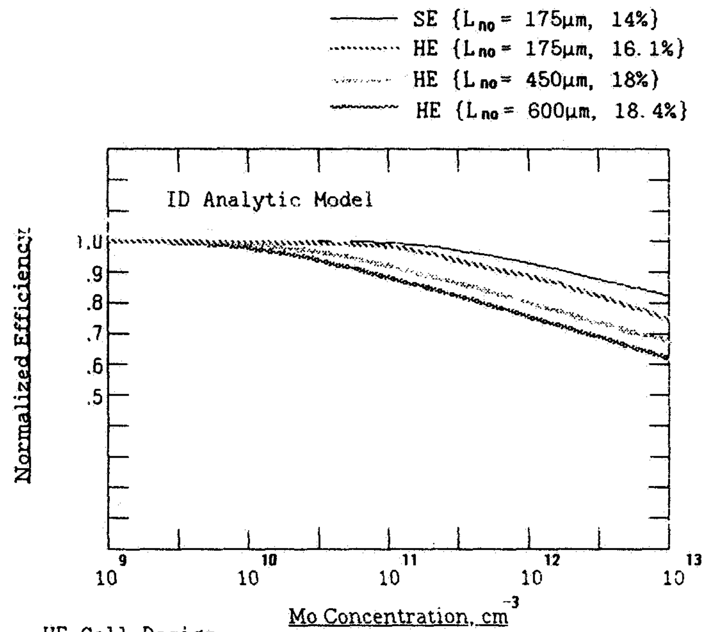
Cell Efficiency Change With Mo Concentration for Various Initial Base Diffusion Lengths



Cell Efficiency Variation With Ti Concentration for Various Initial Base Diffusion Lengths



Variation in Cell Performance With Mo Concentration: HE Cell Design



HE Cell Design

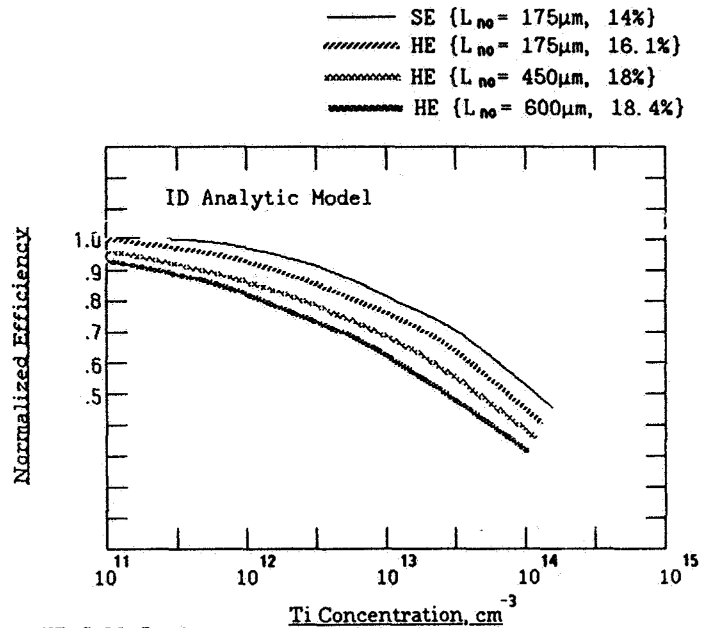
SiO_2 Passivated{$S_{on^+} = S_{op^+}$ = 500 cm/sec}

Back Surface Field

Double Layer AR Coating (1.5)

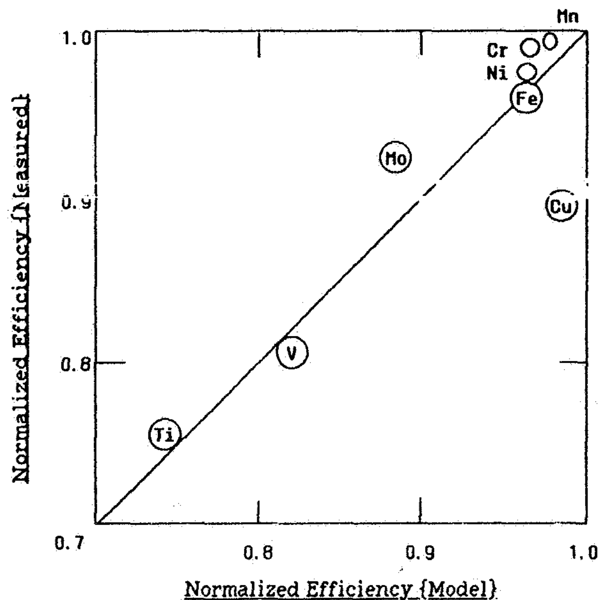
W_B = 275 μm

Variation in Cell Performance With Ti Concentration: HE Cell Design

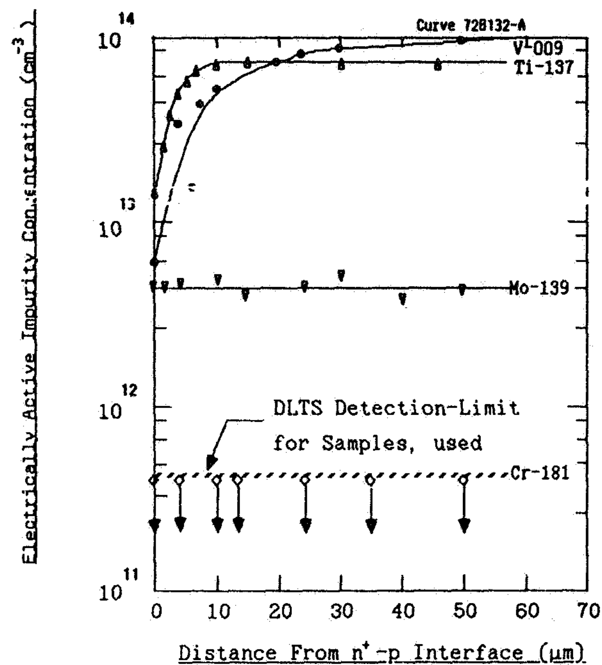


HE Cell Design
Passivated{S_{on} + = S_{op} + = 500 cm/sec}
Back Surface Field
Double Layer AR Coating (1.5)
W_B = 275 μm

Calculated and Measured Performance of Contaminated Web Cells



Electrically Active Impurity Profiles for Several Species After an 825°C, 50-min $POC1_3$ Treatment



Summary

1. Impurities Depreciate Cell Performance
   - Reduce Diffusion Length by Trap Formation
   - Degrade Junctions via Precipitates/Inclusions

2. Impurity Model Describes Well the Behavior of Conventional Cells (SE)with Single and Multiple Contaminants

3. Models Can be Used to Understand Impurity Effects in:
   - High Efficiency Designs
   - Polycrystalline Material
   - Sheet or Ribbon Crystals

4. High Efficiency Devices More Sensitive to Impurities than Conventional Devices

5. Improved Data on Impurity Effects Required to Quantify Model Predictions for High Efficiency

Acknowledgments

- To the late J. R. "Ranny" Davis who provided the intellectual foundation and guiding spirit for our work.

- To my colleagues:
  At Westinghouse: Ajeet Rohatgi, Phil Blais, Maurice Hanes, Paul McMullin, Jit Rai–Choudhury, Bob Campbell, Al Stewart, Dennis Schmidt, Steve Karako, and Carl Seiler.
  At Hemlock Semiconductor Corp.: Jim McCormick and Howard Mollenkopf.
  They turned ideas into solid results.

- To many colleagues at the Jet Propulsion Laboratory, especially Ralph Lutwack and Alan Yamakawa whose enthusiastic support made the work possible.

- To our friends in the photovoltaic community for their positive feedback and constructive criticisms.

- To DOE/NASA/JPL for the financial resources to do the job well.

DISCUSSION

DAVISON: You mentioned that you turned your models on polysilicon. Could you describe some of that work briefly?

HOPKINS: What you have to do is to model the grains as though they are silicon single crystals, and then do some calculations that allow you to take into account the recombination at the grain boundaries. Ajeet Rohatgi at our lab has done a lot of this work.

DYER: Since the sensitivity to impurities is offset by the segregation coefficient, it would seem that you could get a normalized danger factor by multiplying the two together -- that is, the sensitivity and the segregation coefficients. It ought to apply to the ones that reduce diffusion length.

HOPKINS: In the old JPL reports, like our final report, you'll see some calculations of that kind at the back of the report. What we did was to calculate the feedstock concentrations and rate one to the other as a function of the K value of the impurity and as a function of recharging or continuous feeding of impurity-laden silicon into the melt, so that you can build up exactly that kind of estimate or rating scheme for these impurities.

ILES: Do you have any general statements on gettering?

HOPKINS: We looked at backside damage. We looked at HCl gettering. We looked at the effect of phosphorus oxychloride. This is a plot of the electrically active titanium concentration measured by DLTS as a function of depth into a wafer that has undergone a phosphorus oxychloride gettering at different temperatures (1100°C and so on). You find these curves generally fit an out-diffusion model in which you assume that the impurity is diffusing into that phosphorus-rich layer because its site in that layer is a lower energy site. As you go to higher temperature, these curves shift farther and farther into the bulk. What we did after that was to strip off the phosphorus oxychloride-rich layer and make a solar cell on it. You find that you can improve the efficiency of the solar cell by doing something like this. I think for the case of 2×10^{14}, where the solar cell efficiency is down around 8%, you can gain 1% or 2% by doing this kind of thing. It's not clear whether it's a totally practical thing to do. While you buy a couple of percent, the cell efficiency is still so poor that it would never make a high-efficiency device. But yes, you can getter these things. We looked at other kinds of thermal processing as well, and, for those of you who are interested I refer you to the three summary reports on that program where a lot of these data are presented in exquisite and gory detail.

KALEJS: At 1100°C, if you do process it or anneal it under a phosphorus source, do you not get some degradation of the bulk lifetime that gives you a problem in recovering some of the efficiency?

HOPKINS: The problem I have with giving an answer to that is that the bulk lifetime of these devices is already very low because of the titanium present, and bulk lifetime gets better when you getter, but it's not good because you still have a fair amount of titanium left.

KALEJS: You didn't do any low temperature treatment, 500°C, 600°C, afterwards?

HOPKINS: No, we did some very crude experiments but I don't think I would hang much on those results.

SUREK: Would the effective segregation coefficient in web eventually go to unity if you do continuous growth?

HOPKINS: I don't see why it would. We measured those on strips that were a meter or two long, which would still represent a small part of the volume. If you keep pushing the volume down until there is not very much left, the segregation is going to build up. We have never seen anything that suggested to us when we grew multiple strips that we were reaching anything like K equals one. We did molybdenum, titanium, and a number of others where we ran several crystals from the same melt and we never saw any behavior that suggested that.

SUREK: What would you predict would be the effect of impurities in cases like EFG where the K_{eff} is supposedly unity all the way through the process?

HOPKINS: I think the effect of impurities, if you getter with concentrations like this, is going to be to degrade the cell performance. Both by virtue of their presence in the grains themselves and also by virtue of the fact that you have grain boundaries in the material to start with.

KALEJS: In connection with Tom's [Surek] first question, I think the only way that you can get K_{eff} down is to imply that the stirring under the meniscus is equally as strong in your case as it is in Czochralski. That's the only physical way you could produce it.

HOPKINS: There is definitely stirring in the melt. There is no doubt about it. If you look at the paper that Ray [Seidensticker] and I did, we postulated a relatively simple model in which you have a 7 mm-high meniscus which is effectively a cone through which the impurities diffuse. Once they have diffused through that cone they then mix in the melt. Some recent calculations by Julian Szekely on fluid flow in the web system indicate that you do have fluid flow. It does mix.

KALEJS: Does that not bring hot fluid up to the interface and give you problems with stability?

HOPKINS: It depends on how fast the fluid moves.

KALEJS: It has to move fairly fast to reduce K_{eff} down to Czochralski levels.

HOPKINS: We can grow web 10 or more meters, and that doesn't seem to be the biggest problem by any stretch.

JEWETT: You showed results for carbon and oxygen. Were these measured results or an extension of the model?

HOPKINS: We did relatively little with oxygen and I think the values that Ranny Davis plotted were simply concentrations that were known to be in the melt. We did a little bit with carbon and that probably represents some real data. I think we did two or three purposely carbon-doped runs. I wouldn't want to say that we know anything about carbon and oxygen to the degree of confidence that we know things about the metal contaminants. I think one of the interesting studies to be done yet is the interaction between the metal contaminants and the carbon and oxygen, in the context of a solar cell, along the lines of what we have done. I think that is a very fertile area for research.

BROWN: I'd like to go back to this problem of melt convection in web. Since you are seeing the same kind of convective patterns that you'd seen in Czochralski, then I would expect that you would see essentially time-dependent fluctuations in the melt.

HOPKINS: We do have some.

BROWN: Do you see those kinds of striation fluttering in the crystal?

HOPKINS: We use boron as a primary dopant and you see very little effect on the borane concentration.

BROWN: Because K is close to one. Have you looked at any other dopant?

HOPKINS: We looked at phosphorus but I don't think we ever looked for striations. It's not really a concern, because we are not making devices of that kind.

BROWN: I'm not really worried about the striations. I'm worried about the back melting that they imply, because the thermal mass of your system is so small.

HOPKINS: One potential retardant to the back-melting problem is that as far as we can guess the web interface is a faceted one, requires an undercooling to propagate it, and I think it is a relatively stable interface in that sense. I know there is a small amount of back melting but you also have that 7-mm-high meniscus that's a thermal buffer as well. The fluid flow is in the melt itself. I don't know to what extent there is much fluid flow in the meniscus unless it's Marangoni, and we don't have any way of estimating that.

BROWN: I would agree that it's buffered against it but I also would think the fluctuation would propagate through it.

HOPKINS: I'm interested in seeing those data myself. It's something that would be satisfying in a scientific sense but we have never really had the time to do it.

N86-19736

OXYGEN AND CARBON IN SILICON

J. W. Corbett

State University of New York at Albany
Albany, NY 12222

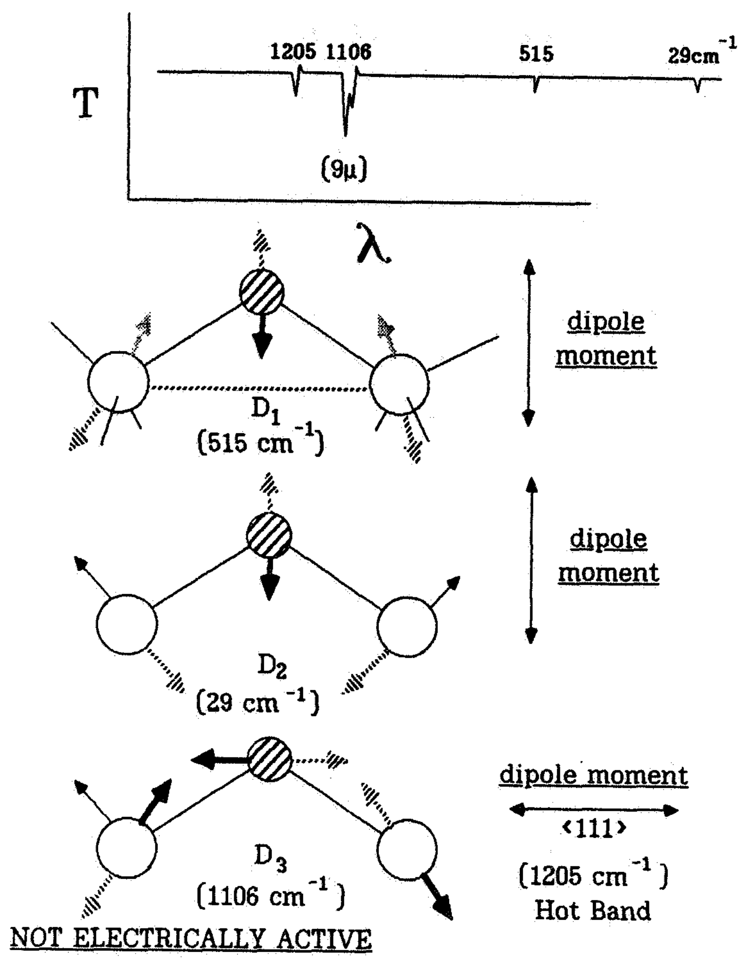
The properties of the early transistors were determined by the minority-carrier lifetime, as is the silicon photovoltaic solar cell. Most of the devices on the modern integrated circuits are majority carrier devices, in part to avoid this lifetime dependence. It is pertinent to note that the micro-electronics industry typically starts with wafers with a minority-carrier lifetime of ca. 1000 micro-seconds, but during device fabrication this lifetime is reduced to below ca. 1 micro-second, in spite of extraordinary cleanliness and precautions. Process-induced defects (PID) are the cause of this lifetime reduction, but PID is a rubric covering many poorly identified defects or unidentified defects. These defects include point defects, defect complexes, line defects, and bulk precipitates. We have some ideas about the nature of recombination at point defects and point defects complexes, but one of the aspects that needs to be understood is the nature of minority carrier recombination at line defects and at precipitates.

Some of the PIDs are known to be related to the fast-diffusers of the iron-series transition elements. One of the common techniques of dealing with these elements is "intrinsic" gettering by the oxygen precipitates. But even in the gettered state, there may be a residual effect on the lifetime.

Oxygen is an almost ubiquitous impurity in silicon and plays an important role in both integrated circuits and solar cells. The knowledge about oxygen in silicon will be reviewed. The isolated oxygen interstitial is electrically inactive, but in its various aggregated forms it has a variety of electrical activities. The impact of these defects on the minority carrier lifetime is unknown. The agglomeration and precipitation of oxygen, including impurity gettering and the complicating role of carbon, will be discussed.

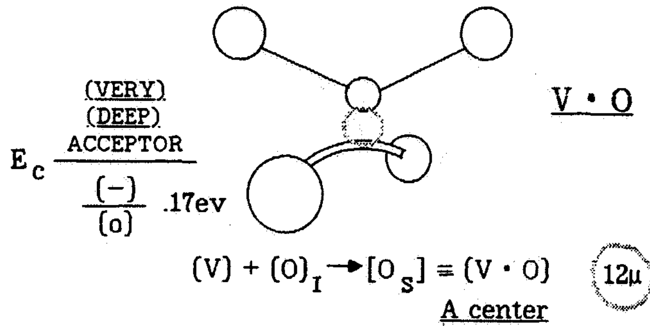
The recent work on the thermal donors is providing a great deal of insight into the structure of the precipitates and has promise of leading to an understanding of the complex processes associated with oxygen in silicon. These results will be discussed.

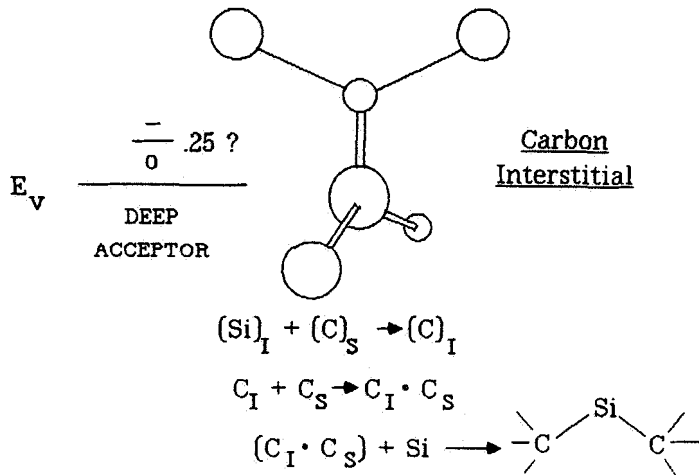
PRECEDING PAGE BLANK NOT FILMED

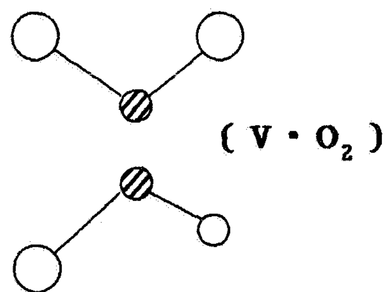


PRECEDING PAGE BLANK NOT FILMED

DEFECT INTERACTIONS







$(V \cdot O_2 + O)$

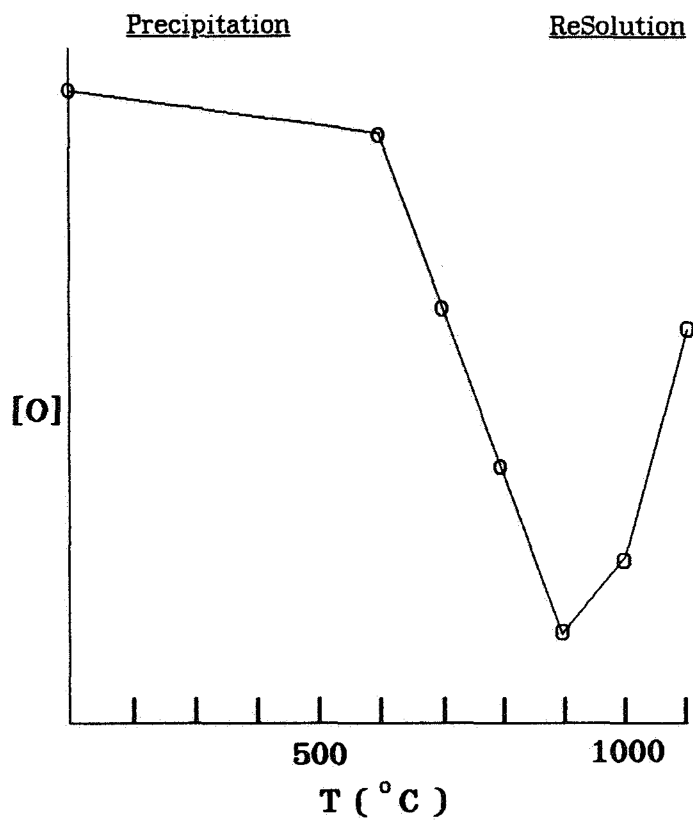
$(V_2 \cdot O)$

$(V_2 \cdot O_2)$

$(V_3 \cdot O)$

$(V_3 \cdot O_2)$

$(V_3 \cdot O_3)$



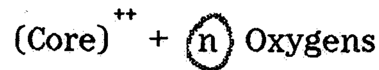
But this precipitation is very COMPLEX

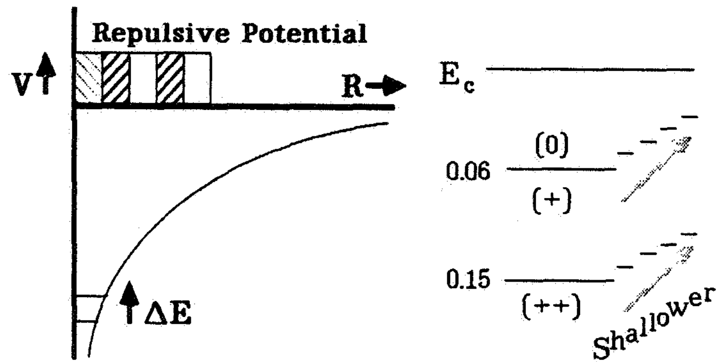
Precipitation at 450° C

THERMAL DONORS
(without carbon)

Hierarchy of DOUBLE DONORS
(at least 9)

Model

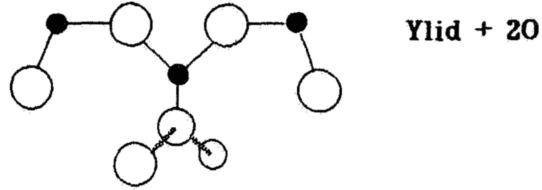




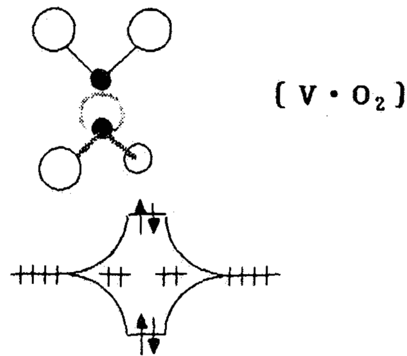
The volume of the
repulsive potential grows w/ "n"

What's the core?

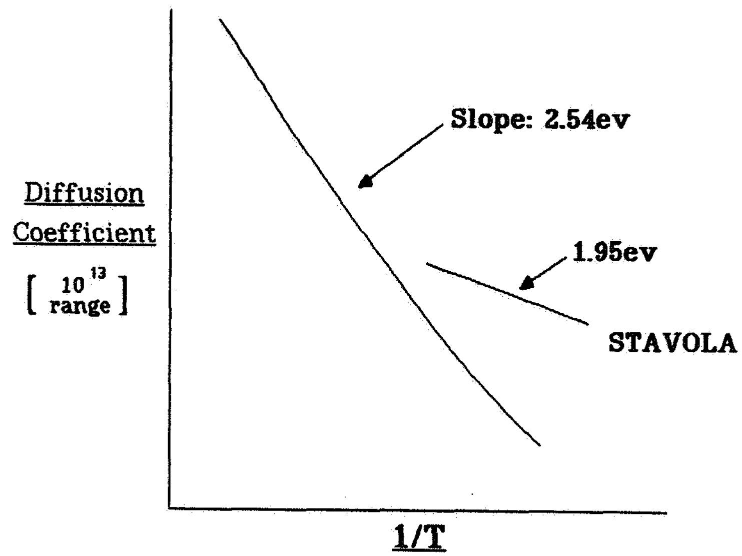
[How can oxygen make a donor?]



Ylid≡ Split <100> [O • Si] Interstitial



If these THERMAL DONORS have
OXYGEN ONLY,
does that mean that the
NUCLEATION IS *HOMOGENEOUS?*



Vacancy Assisted?

Lindström

Svensson

(Still "NO" Carbon)

After 450° C Annealing
TEM

<110> Rods	Black Dots
(15%)	(85%)

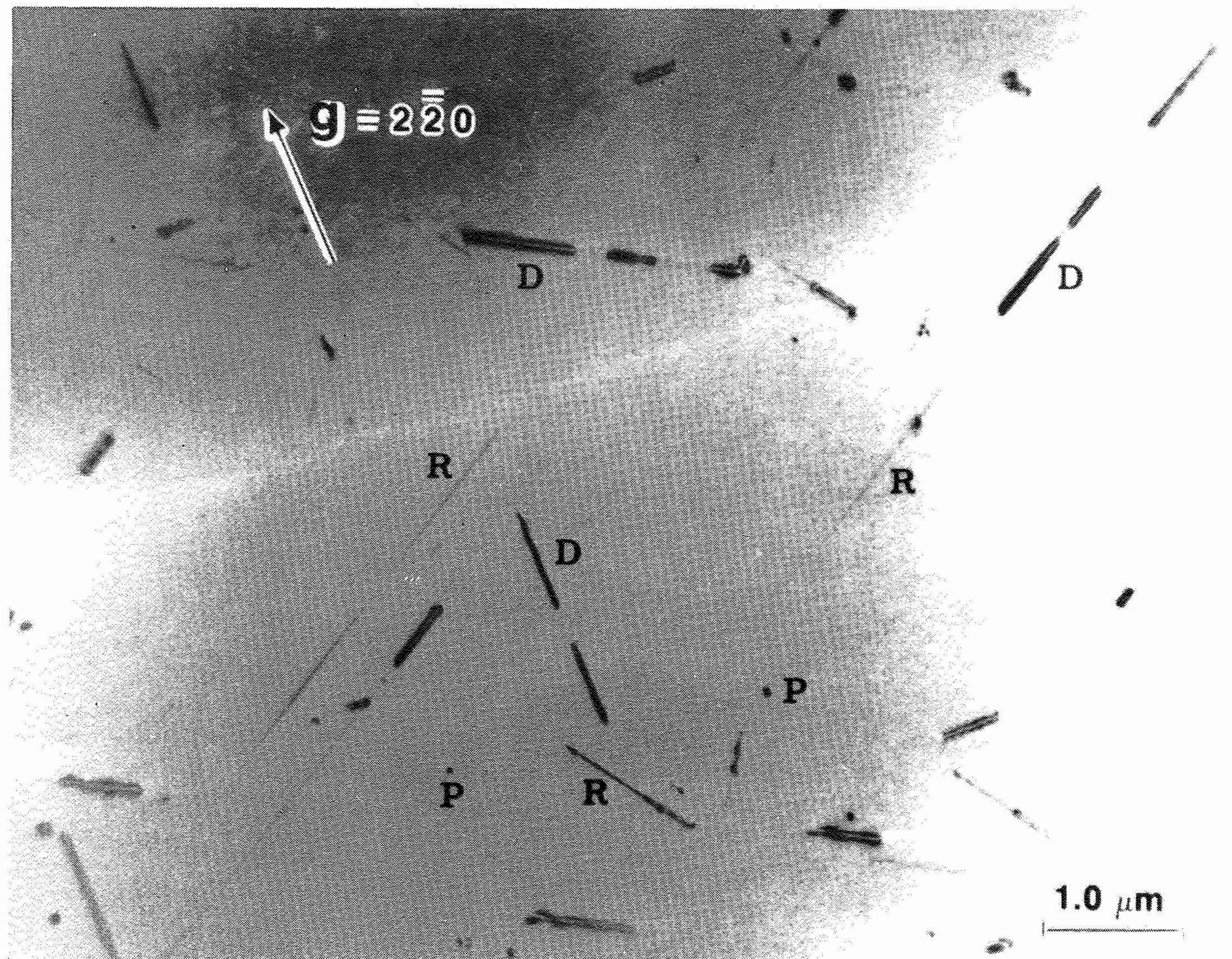
After Annealing at 650° C,

The Thermal Donors

are

GONE

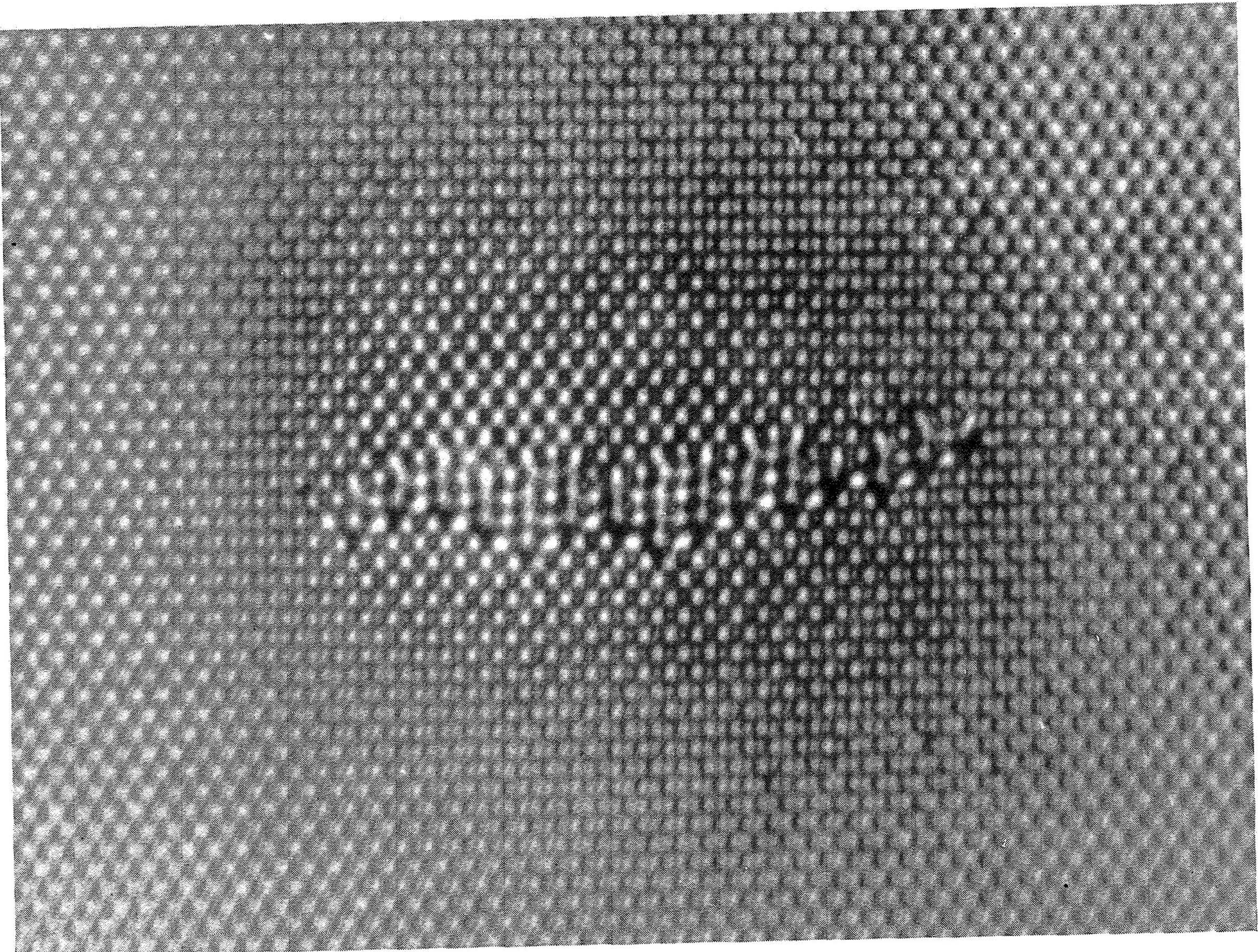
In the TEM?



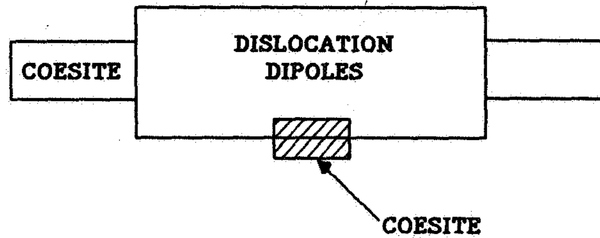
Transmission Electron Microscopy of Heat-Treated Czochralski Silicon Showing "Rods" (Coesite Precipitates), Associated Dislocation Dipoles, and "Black Dots." CN. Yamamoto, P.M. Petroff, and J.R. Patel, J. Appl. Phys. 54 (1983) 231.

ORIGINAL PAGE IS
OF POOR QUALITY

ORIGINAL PAGE IS
OF POOR QUALITY



High-Resolution Transmission-Electron-Microscopy of an Oxygen Precipitate in Silicon, Showing the Coesite Structure of the Precipitate. From a. Bourret, J. Thibault-Desseaux and D. Seidman, "Early Stage of Oxygen Precipitation and Segregation in Silicon." J. Appl. Phys. 55 (1984) 825.



Indications are that during OXYGEN precipitation (and COESITE formation),

SILICON INTERSTITIALS
ARE EMITTED
(hence the dipoles)

And that this process happens even during the 450°C formation of Thermal Donors.
And during oxidation at high temperatures.

On annealing at higher temperatures

"Rods and Dislocation dipoles

DISAPPEAR

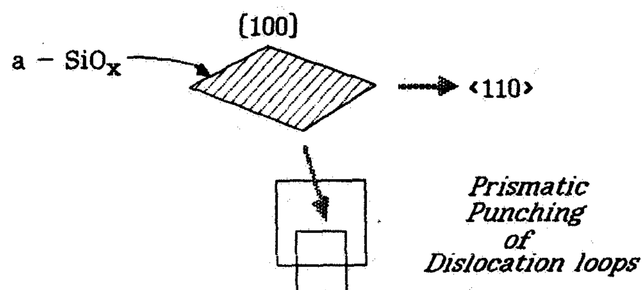
"Black Dots"

grow

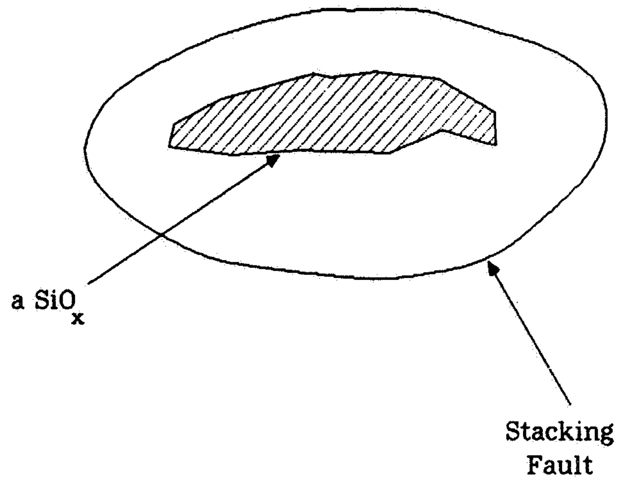
into *AMORPHPUS* SiO_X

PLATELETS

After 1000° C Annealing



Annealing at 1200 °C



Cz – Si
WITH *CARBON*

THE 450 °C THERMAL DONORS
ARE *SUPPRESSED*

BUT

upon 600 °C annealing
NEW DONORS

seem to correlate with
BLACK DOTS

Remaining annealing seems the SAME.

Does that mean that all the Black Dots

(a – SiO_x ppts)

are HETEROGENEOUSLY *(C)*

NUCLEATED?

What else does CARBON do?

From ribbon − Si => (SiC) ppts.
Not (yet) in crystal − Si
(C • III) pairs

Lots of (C • O) Infrared bands.

(V • C • O) = K center p−type damage

$(C)_S + (Si)_{INT} \rightarrow (C)_{INT}$

$(C)_S + (C)_{INT} \rightarrow (C \cdot C)$

$(C \cdot C) + (Si)_{INT} \rightarrow (C \cdot Si \cdot C)$

C in "A and B swirls"

Carbon outdiffuses just like Oxygen.

denuded zone

low O and C

if temperature is right

WHY should the SOLAR

CELL Industry care

about these problems?

Wafer Source	*LIFETIME*
Cz	*≈ 10 µsec*
Fz	*≈ 200 µsec*

Both << 10,000 µsec.

J. O. BORLAND
ECS, Spring 1983

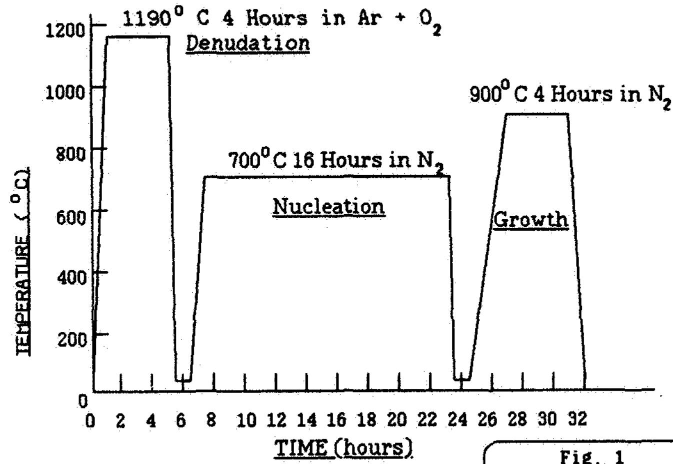


Fig. 1
3-step intrinsic gettering cycle.

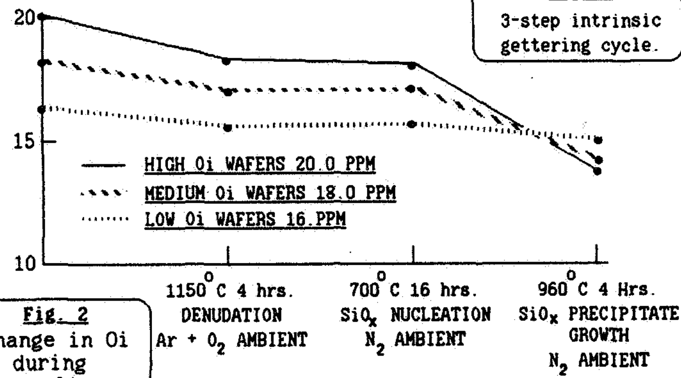


Fig. 2
Change in Oi during annealing.

MOS Cvst lifetime

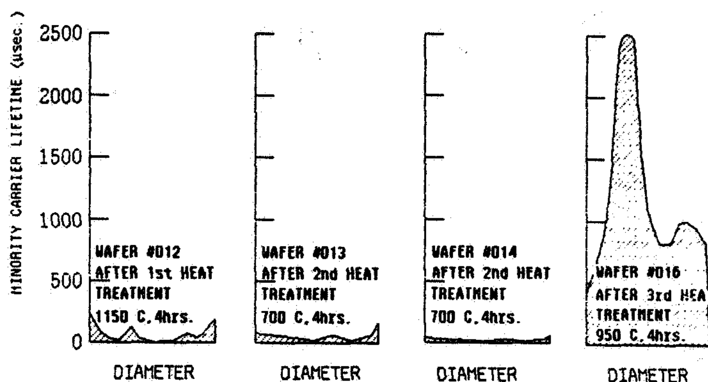


Figure 6.

MOS C-t lifetime comparison of adjacent high Oi wafers.

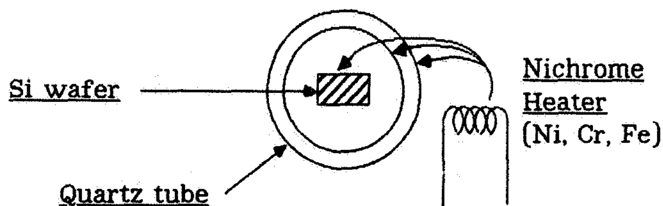
J. O. Borland
ECS, Spring '83

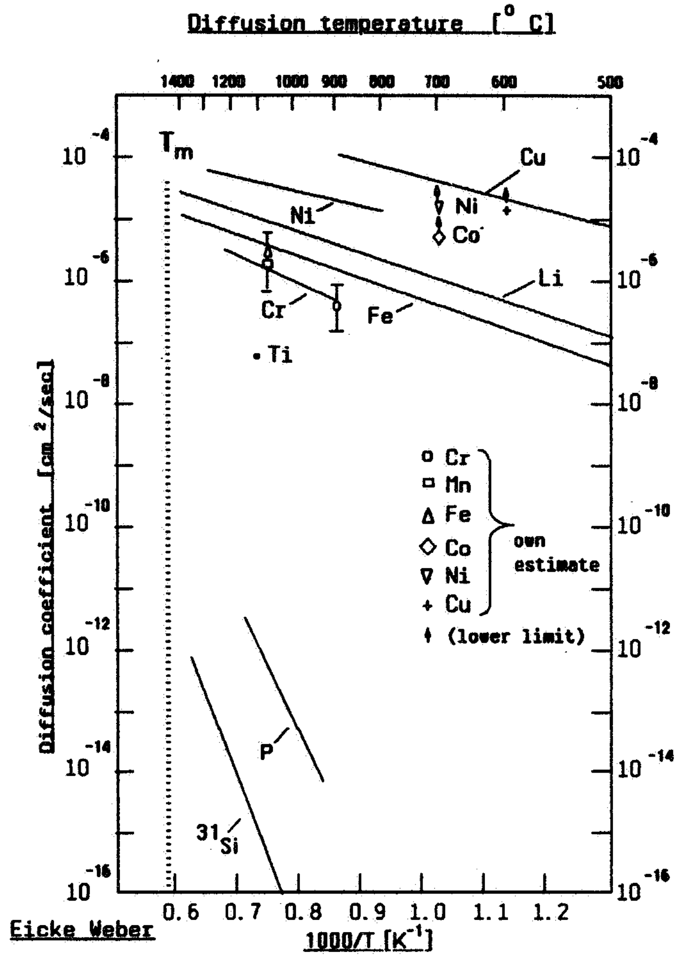
What's the problem?

Grown-in defects
{Recombination centers
Katsuka (luminescence)} } *NOT the big probelm!*

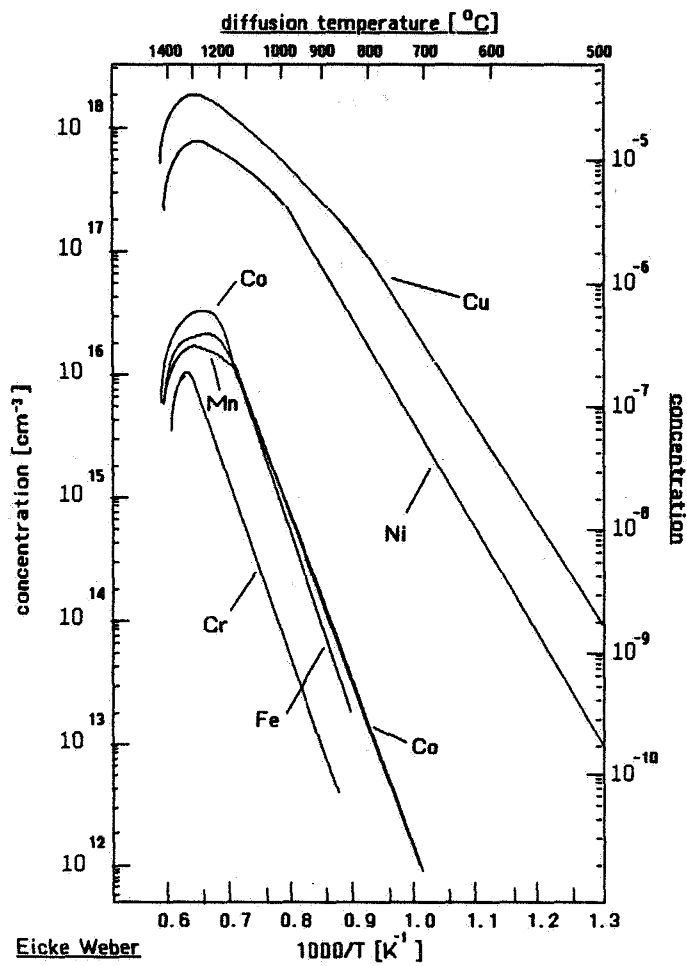
Process-induced defects } *the bigger problem!*

Fast diffusers
Fe, Ni, Cr, Cu, Au, • • •





Diffusion temperature [° C]
1400
1200
1000
900
800
700
600
500
T_m
Cu
Ni
Ni
Co
Li
Cr
Fe
• Ti
Diffusion coefficient [cm ²/sec]
10^{-4}
10^{-6}
10^{-8}
10^{-10}
10^{-12}
10^{-14}
10^{-16}
o Cr
□ Mn
Δ Fe
◇ Co
∇ Ni
+ Cu
own estimate
(lower limit)
P
31 Si
0.6
0.7
0.8
0.9
1.0
1.1
1.2
Eicke Weber
1000/T [K⁻¹]



diffusion temperature [°C]
1400
1200
1000
900
800
700
600
500
concentration [cm⁻³]
concentration
Co
Cu
Mn
Ni
Cr
Fe
Co
0.6
0.7
0.8
0.9
1.0
1.1
1.2
1.3
1000/T [K⁻¹]
Eicke Weber

Quenched in Fe (EPR)

(Fe) – Interstitial at T_d

(Fe • B), (Fe • Al), (Fe • In) pairs

(Fe • C) pair

$(Fe)_4$

Similiar results for Cr, Mn.

Ni, Co, Cu

too fast to catch.

WHAT CAN BE DONE?

GETTERING

Internal gettering at oxygen ppts and associated defects.

Jastrzebski	Cu, Ni, @ SF's
IBM	Cu @ Oxide ppts.
Futagami	"Heavy metals" at SF's.

But we know ALMOST NOTHING about these states.

These are NOT EQUILIBRIUM states.

Remember COESITE is a HIGH PRESSURE phase.

Ourmazd: Ni: in Guinier–Preston phase.
Fe: tetragonal silicide phase.

Back Surface Gettering
Damage
Diffusion

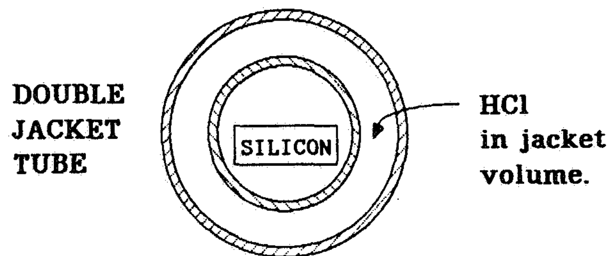
(maybe useful for solar cells)

What ELSE can be done?
[Micro–electronics Industry]

CLEAN ROOM and
Extrordinary Cleanliness

RF Heating } **Keep environment**
Heat Lamp Heating } **COLD.**

Change Processing Tubes from SiO_2
to Silicon (SiC liners).

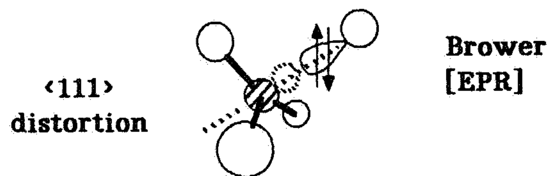


Form Volatile Chlorides.

Interstitial Nitrogen?

An Aside:

Substitutional Nitrogen
is a *DEEP DONOR*



The electrically inactive
nitrogen "must" be a
COMPLEX.
(N·B)?

MRS Symposium:
"Selected Impurities in Silicon:
O, C, H, and N"
2-6 December, 1985 Boston

DISCUSSION

ELWELL: Do you believe that the vacancy-assisted diffusion is what's leading to precipitation of oxygen in silicon for the thermal donors, or do you believe that precipitation is vacancy-assisted? Have you ever studied that by comparing the defects you get by ESR for a slice taken from the top of a Czochralski wafer, where you are subject to a lot of fluctuations, as compared with the early stage of precipitation in a wafer grown in a magnetic field, where you think the interface is much more quiescent during growth?

CORBETT: No, it has not been studied to the extent that I think it should be. We do know a good bit about many of these vacancy interactions, but there is a great controversy raging about what's going on with silicon self-diffusion.

CISZEK: Could you elaborate a little bit on your views of how the carbon and the silicon interstitials are interacting in forming the B-type swirl defect in float-zone silicon?

CORBETT: My own opinion would be the entrapment of liquid in the growth. The liquid is more dense than the solid and it is simply captured and ends up as a material-rich region that throws them into it.

CISZEK: Do you have any comments, Dr. Abe? I would be very interested in perhaps your latest ideas of what may be going on in that interaction of carbon in self-interstitials.

KALEJS: [Question addressed to Dr. Abe] What is your current thinking about how the B-swirl may be formed from carbon and silicon self-interstitials?

ABE: I think these are pre-stages of an A-swirl that are not closely related to the carbon impurity.

CORBETT: Can you denude a zone of A and B swirls?

ABE: A and B swirls consist of silicon interstitials. Silicon interstitials diffuse out from the surface so you can perhaps make a denuded zone.

N86-19737

SOLAR CELL AND I.C. ASPECTS OF INGOT-TO-SLICE MECHANICAL PROCESSING

by Lawrence D. Dyer

ABSTRACT

Intensive efforts have been put into the growth of silicon crystals to suit today's solar cell and integrated circuit requirements. Each step of processing the crystal must also receive concentrated attention to preserve the grown-in perfection and to provide a suitable device-ready wafer at reasonable cost.

A comparison will be made between solar cell and I.C. requirements on the mechanical processing of silicon from ingot to wafer. Specific defects will be described that can ruin the slice or can possibly lead to device degradation. These include grinding cracks, saw exit chips, crow's-foot fractures, edge cracks, and handling scratches.

INTRODUCTION

There is abundant literature on the growth and annealing of silicon crystal ingots to provide the proper resistivity, oxygen concentration, and oxygen clustering for electronic devices. In contrast, there is less published on the mechanical processing of the ingot into slices, although this processing affects the cost and survival potential of the wafers and may affect the device quality. The purpose of the present report is to explain how certain defects can arise in ingot-to-slice processing and how they might affect either solar cells or integrated circuits.

DISCUSSION

First, some remarks will be made on the nature of mechanical processing damage and the effect of chemical etching on the resistance of the slice to breakage. Second, solar and I.C. processes will be compared in their exposure and sensitivity to damage. Third, specific defects that occur step-by-step through ingot-to-slice processing will be described and discussed. Fourth, what is needed for improvement in the mechanical processing of both solar cell and I.C. wafers will be assessed.

Nature of Damage and Effect of Chemical Etching

Mechanical damage to crystalline silicon from abrasive processes consists essentially (1,2) of two superimposed types of defects : 1) a thin layer up to 1 micron deep containing dislocations and debris, 2) microcracks up to 2 mils deep, which may have dislocation cracks extending more deeply (3,4).

PRECEDING PAGE BLANK NOT FILMED

Resistance of silicon to chipping or breakage during mechanical processing depends greatly on the size and sharpness of the microcracks that have been introduced. According to the Griffith formula (5,6), fracture stress depends on the inverse square root of the crack size; and, according to the Cottrell formula (7), on the square root of the ratio between tip radius and atomic radius. A calculation shows that chemical etching after an abrasive process can easily increase the resistance to fracture 100-fold.

A common misconception regarding the removal of mechanical damage is that the layer containing the damage must be removed completely. To the contrary, for crystal etching and pre-polish only enough material needs to be removed to relieve abrasion stresses and to make the wafer strong enough for further processing. This can be done with brief chemical etching which removes the dislocated region and converts any cracks to deep grooves.

Comparison of Solar and I.C. Processes

Table I shows the main steps in solar cell and I.C. mechanical processing, as well as some possible crack defects that may occur in those steps. Causes of some of these defects have been identified by the use of fracture tracing techniques (8,9). Solar cell processing has fewer steps, hence less exposure to damage. In addition, solar cell requirements are

TABLE I

STEPS IN INGOT-TO-SLICE PROCESSES vs. POSSIBLE FRACTURE DEFECTS

FOR SOLAR CELLS	FOR INTEGRATED CIRCUITS	FRACTURE DEFECT
CROP	CROP	LARGE CHIPS
	SAMPLE	SAME AS WAFERING DEFECTS
GRIND OR SLAB	GRIND	EXCESS CRACK DEPTH
	ORIENT	
flat (opt.)	FLAT	EXCESS CRACK DEPTH
	ETCH	
WAFER (18 mils)	WAFER (24 mils)	EXIT CHIPS, EDGE FRACTURES DEEP MICROCRACKS, EDGE CHIPS
	LASER MARK	
edge gr. (opt.)	EDGE GRIND	CROW'S-FOOT FRACTURES
	HEAT TREAT	EDGE CHIPPING AND CRACKS
	LAP	CROW'S-FOOT FRACTURES & SCRATCHES
ETCH	ETCH	
	BACKSIDE DAMAGE	
	POLISH	EDGE CRACKS

less severe from a cosmetic standpoint; defects such as the exit chip in sawing are not necessarily a cause for slice rejection. On the other hand, since solar cell wafers are sliced thinner than I.C. wafers, edge fractures and crow's-foot fractures are more predominant.

Specific Defects

Cropping chips.--Figure 1 shows a fracture developed from using too much blade force in a cropping saw. Silicon can be lost immediately at this work station, or the defect may not show up until the slicing stage as shown in Figure 1. This problem can obviously be solved by limiting the force.

Grinding cracks.--Figure 2 shows grinding cracks made by a centerless-type crystal grinder some years ago. The defects were found at epitaxy, where they had caused slip. Figure 3 shows schematic diagram of slip generation from excessively deep cracks formed at the crystal grinding step. Figure 4 shows grinding cracks made by a center-type crystal grinder. Clearly there is a need to limit the severity of the grinding process to minimize such cracks. One means of limiting this is provided on the Siltec crystal grinder (10), i.e. by measuring the current drawn by the drive motor (11).

Exit Chips/Saw Fractures.--Figure 5 shows a saw exit chip on a silicon slice that was made with the I.D. saw. This defect is a cosmetic one for the semiconductor industry, but a slice cannot be sold with an exit chip, partly because of potential of generating increased particle counts in the wafer fabrication facility (12). In the solar wafer the exit chip can, if severe, constitute a "saw fracture"; in fact, it is probably the major limitation on lower slice thickness for solar-cut wafers (13). The causes of exit chips have been outlined previously (14); they fall basically into two categories--bending forces (13) and wedge forces (14). Since there are numerous ways to cause the exit chip, it remains a perennial problem.

Deep Saw Damage ("Sparkle").--Figure 6 shows an area on a (100) sawed slice that reflects light preferentially at the same angle as the exit chip. This appearance is sometimes called "sparkle" and often accompanies the exit chip. The appearance is due to deeper-than-usual microcracks (14) that show up under the microscope as small, scattered facets. This collection of defects probably has one of the same causes as exit chips, but occurs earlier in the cut where the crystal still has enough breadth to resist complete crack propagation.

Saw Edge Fractures.--Figures 7 and 8 show a type of defect related to exit chips and which is cause for immediate rejection. It is a fracture that initiates at the edge and is associated with a depression in the slice caused by saw blade removal. It occurs more frequently in thin slices. Deep saw damage is often evident elsewhere on the slice. It occurs when the I.D. saw blade has lost some of its tension. On (100) slices, the cracks are parallel to saw marks; on (111) slices, they are usually

located at 30 +/- 10 degrees from the exit end. The mechanism postulated for this defect is that the blade becomes too flexible, all or in part, and is deviant before entering the cut. As it enters the cut, it applies a bending stress to the wafer at its edge. In the (111) case, the mounting strip protects the edge to +/- 20 deg. from the exit location. In the (100) case this protection is not enough because of the ease of making the exit chip-like fracture.

Crow's-Foot Fractures.--Figure 9 shows a schematic diagram of the edge grinding process. The wafer is held on a vacuum chuck and slowly rotated. A fast-spinning grind wheel having a groove of the desired shape is brought against the edge as shown in the cross-sections. Cooling medium is directed into the interface.

Figure 10 shows a typical crow's-foot fracture that occurred because of a 1.3-mil burr on a vacuum chuck in the edge-grind operation. Figure 11 shows the mechanism by which such fractures occur; an analysis was given previously (15). Thin slices are more susceptible to this type of fracture.

Another operation in which crow's-foot fractures originate is lapping. Note that the mechanism is different from Fig.11; the edge-grind fracture occurs because of bending stresses, the lap fracture is thought to arise from wedging by abrasive particles (16).

Edge Cracks from Heat Treating.--Sometimes an annealing operation is carried out to stabilize resistivity. Figure 12 shows a crack formed at a slice heat treat operation. These cracks can form either from the impact of transfer into the boats or from boat slots that pinch the slice edges. In the instance of Figure 12, the temperature was high enough for dislocation generation. Such defects can also occur during fabrication of wafers into devices.

Edge Cracks at Polish.--Figures 13-14 show edge cracks that developed during the polish operation. These are characterized by nearly radial development and by polish cloth bevelling. They are envisioned to form in response to the tangential stresses that occur when the slice friction is too high and the slice edge is relatively cool.

Scratches.--Figures 15 and 16 show backside scratches that caused wafer breakages in furnace operations. The fracture origin (9) in each case coincided with the point of tangency of the scratch. This breakage is postulated to occur as follows: Furnace operations cause wafers to undergo transient stresses that bow the wafer one way or the other. If a scratch is located on the convex side of the wafer, it is subject to tensile stress which can exceed the crack propagation stress for the scratch. Such scratches must be avoided in wafer processing not only for the survival of the individual slice, but for avoiding the loss of many other devices from particles generated in the fracture process.

Improvements for Solar Cell and I.C. Mechanical Processing

Better mechanical processing methods and equipment are desired by both solar cell and I.C. industries, but the needs are divergent in some ways. Table II shows trends in slice requirements from both industries. For the electronics industry the trends dictate a broad effort to provide for larger wafer sizes, better flattening, slice identification, better edges, and smoother polishing. This means larger equipment, laser marking, and lap and polish development. For the solar cell industry the overwhelming needs are for lower cost and greater efficiency; if any gain is to be achieved in the ingot-to-slice portion, it is entirely in cost. This puts emphasis on less kerf loss, thinner slices, faster processing, etc., always with the trade-off of more chips and breakage. Increasing wafer size appears to have no benefits for solar cells because of higher I^2R losses, and because the attendant increased metalization to avoid such losses causes sufficient shadowing to negate the benefit.

TABLE II

TRENDS IN SLICE REQUIREMENTS, SOLAR AND I.C.

REQUIREMENT	SOLAR	I.C.
SIZE, INCHES	HOLDING AT 4-5	INCREASING TO 8
FLATNESS	O.K.	FLATTER
BOW	O.K.	LESS BOW
TRACEABILITY	--	DESIRED
LOWER COST	GREAT PRESSURE	SLIGHT PRESSURE
HIGHER QUALITY		
o EDGE	O.K.	REDUCED FRACTURES & PARTICLE GENERATION
o SURFACE	O.K.	GREATER SMOOTHNESS, NO BLEMISHES, FRONT & BACK SIDES
o INTERNAL	IMPURITY CONTROL	INPURITY CONTROL

Considering Tables I and II together, the hopes for improvements in solar cell ingot-to-slice mechanical processing lie mainly in two areas: crop and grind and sawing. In crop and grind it is obvious that limits on sawing force and grinding drag will reduce the defects to a low level, and some benefit may be obtained from a brief crystal etch after grinding. A brief summary of possible advances in sawing for solar cells follows.

Recent advances in substrate sawing for the electronics industry have been reviewed in 1984, namely large capacity saws, slice retrieval, fault systems and productivity increasers (11). Among new features called for by users were in-situ blade tension and drag measurement. For the solar cell industry, all but the first of these advances will be useful. Unfortunately, most present equipment does not include the advances; even the blade tracking systems are mostly retrofits. Any of the new large saws may be used, but the larger blade size usually means that a thicker blade core is necessary to obtain the same stiffness, and the kerf loss is increased. The new saws may, of course, be ordered with the smaller head sizes if desired. It is the author's opinion based on the foregoing discussion that some development of new saws especially for solar cell slicing should be done, aiming more at thinner slices and thinner cuts than larger size. The following is a list of studies or developments in sawing which in the author's opinion would be of specific benefit to solar cell cost.

- improvements in blade core strength so that thinner cores may be used.

- in-situ blade tension measurement.

- a method to maintain fairly constant blade tension without sacrificing blade concentricity.

- a method of assessing the degree of damage to the slice while the slice is freshly off the saw. This would allow the operator to take corrective action before many other slices are ruined.

- a study of why rotary crystal slicing doesn't work and the design of a saw specifically for this. This would permit smaller blades, thinner cores, and less kerf.

- autobalancing. Silicon Technology Corporation has an autobalancing attachment, presently available for 22-inch saw heads, that does an excellent job of rebalancing the saw while running. This feature increases productivity by avoiding shutting down the saw for the imbalance that comes with broken slices, but may be a refinement that permits lower slice thicknesses.

SUMMARY

The nature of mechanical damage/chemical etching are discussed with regard to ingot-to-slice mechanical processing of solar cell and I.C. silicon material. Various examples of fracture defects are described and explained. Solar and I.C. mechanical processes are compared as well as trends in requirements in slice parameters. These considerations combine to suggest that the main area for innovative improvement in the mechanical processing of solar cell slices lies in aiming at lower cost in the wafering step. Various studies or desired features in sawing that would benefit the solar cell effort are suggested.

ACKNOWLEDGMENTS

The author would like to express appreciation to Sam Rea and Jim Rinehart for helpful discussions.

REFERENCES

1. R. Stickler and G.R. Booker, Phil. Mag. 8(1963)859.
2. T.S. Kuan, K.K. Shih, J.A. Van Vechten and W.A.Westdorp, J. Electrochem. Soc., 127(1980)1387.
3. J.W. Allen, Phil. Mag. 2(1957)1476.
4. J.W. Allen, Phil. Mag. 4(1959)1046.
5. A.A. Griffith, Phil. Trans. Roy. Soc. London A , 221(1921)163.
6. A.A. Griffith, First Internat. Congr. Appl. Mech. (Delft) (1924)55.
7. A.H. Cottrell, in "Fracture", ed. by B.L. Auerbach, D.K. Felbeck, G.T. Hahn, and D.A. Thomas, (John Wiley & Sons, New York, 1959)20.
8. L.D. Dyer, Electrochem. Soc. Ext. Abstr. 83-2(1983)553.
9. L.D. Dyer, "Semiconductor Processing, ASTM STP 850, Dinesh Gupta, Ed., American Society for Testing and Materials, 1984.
10. Siltec Corporation, Product Bulletin--Model 540/590 Grinders, Nov. 1982.
11. L.D. Dyer, Industrial Diamond Review, No.2, Feb. 1984, p.74.
12. L.D. Dyer, Electrochem. Soc. Ext. Abstr. 81-1(1981)785.
13. C.P. Chen and M.H. Leipold, Electrochem. Soc. Ext. Abstr. 80-2 (1980)712, and J. Electrochem. Soc. 129(1982)2835.
14. L.D. Dyer, "Proceedings of the Low-Cost Solar Array Wafering Workshop", 8-10 June 1981, Phoenix, Ariz. Publ. No. 5101-187 DOE/JPL-1012-66.
15. L.D. Dyer and J.B. Medders, "VLSI Science and Technology/1984", ed. by K.E. Bean and G. Rozgonyi, (Electrochem. Soc., Pennington, N.J. 1984)48.
16. S. Maruyama and O. Okada, Japan J. Appl. Phys. 3(1964)301.

ORIGINAL PAGE IS
OF POOR QUALITY

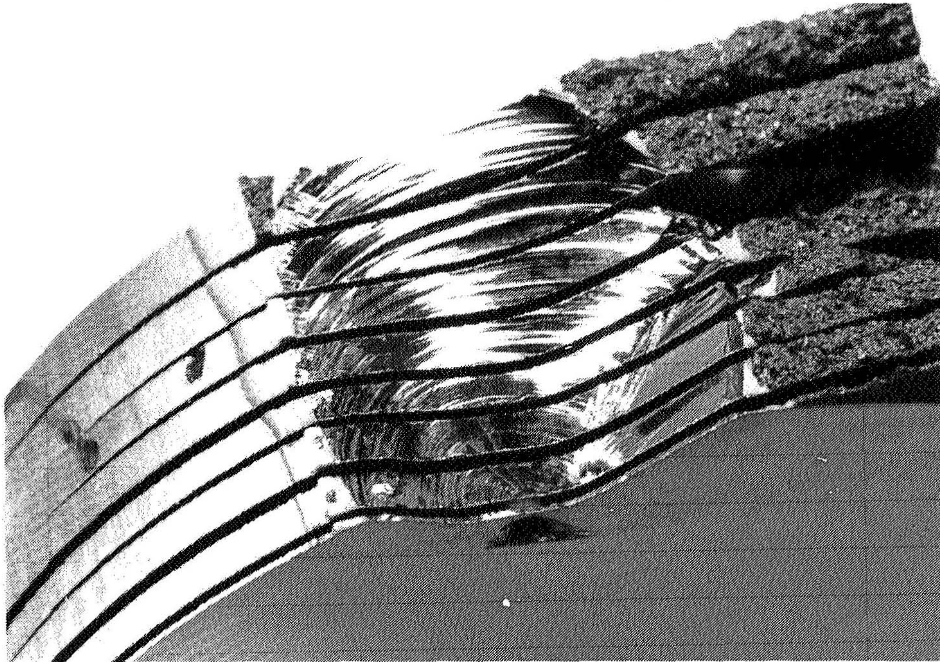


Fig. 1. Cropping chips on 100 mm silicon crystal, detected at wafering step.

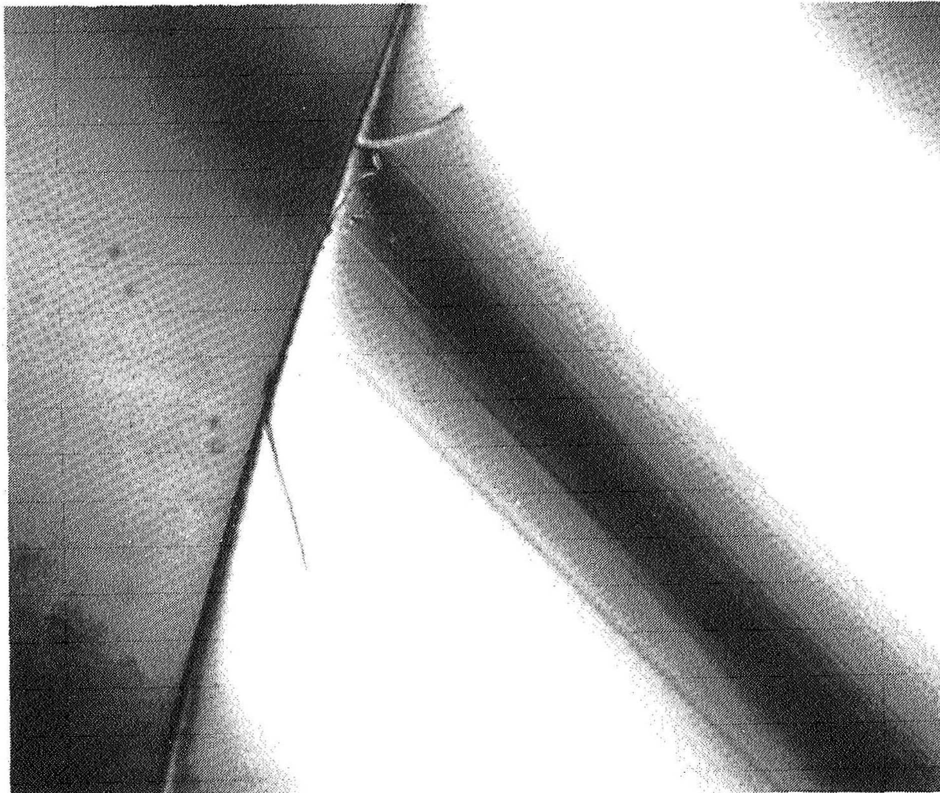
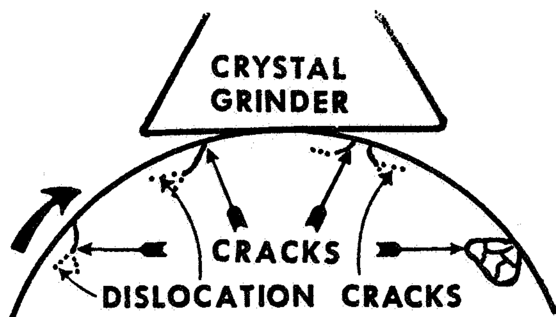
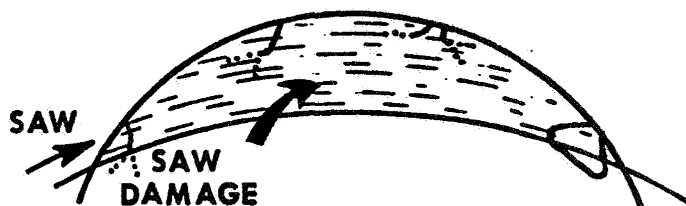


Fig. 2. Cracks produced by centerless crystal grinder and subsequent slip in epitaxial processing.

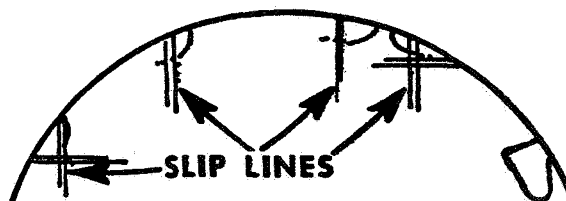
PRECEDING PAGE BLANK NOT FILMED





A. GRINDING OF SILICON INGOT CAUSES CRACKS AND DISLOCATION CRACKS.

B. SLICING PUTS IN SAW DAMAGE AND CHIPS OUT SOME GRINDING CAVITIES.



C. LAPPING, ETCHING AND POLISHING REMOVES SAW DAMAGE BUT NOT ALL OF THE GRINDING DAMAGE.

D. PROCESSING IN FURNACE OR EPI REACTOR GENERATES SLIPLINES.

FIG. 3 SCHEMATIC OF SLIP GENERATION FROM EXCESSIVELY DEEP CRYSTAL GRIND CRACKS.

ORIGINAL PAGE IS
OF POOR QUALITY

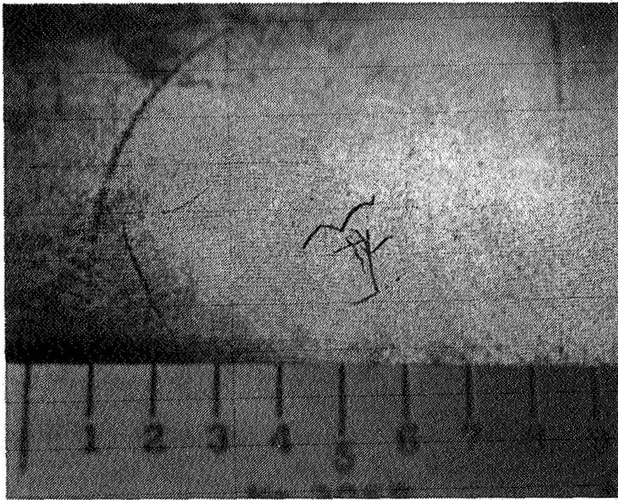


Fig. 4. Cracks produced by center-type crystal grinder.

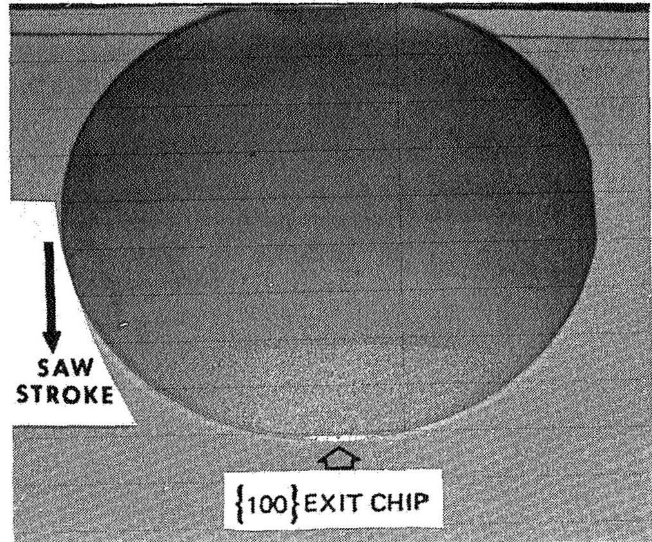


Fig. 5. Saw exit chip.

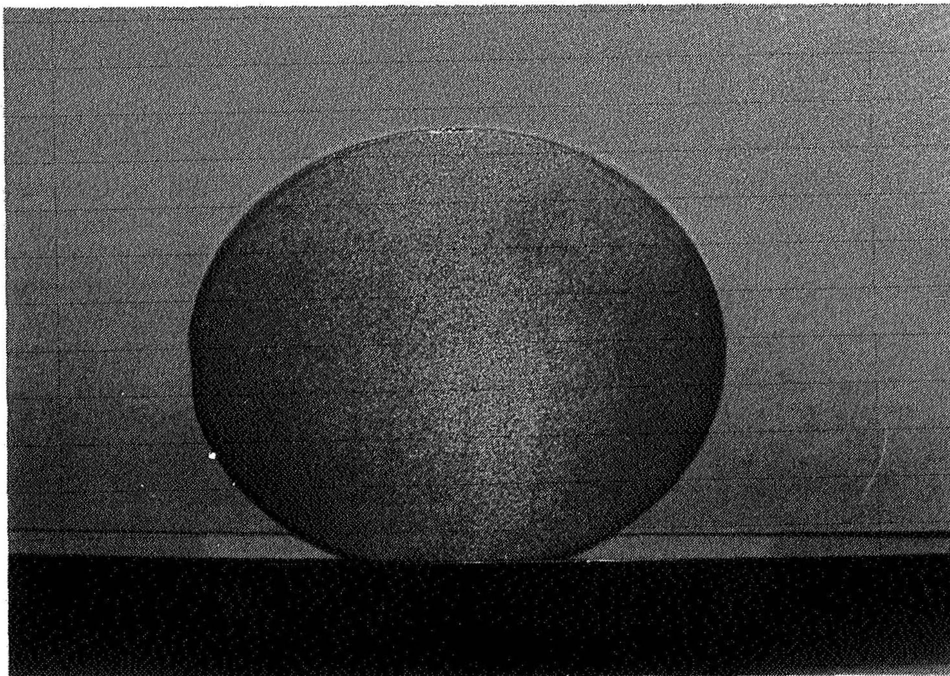


Fig. 6. Deep saw damage ("sparkle") on (100) silicon.

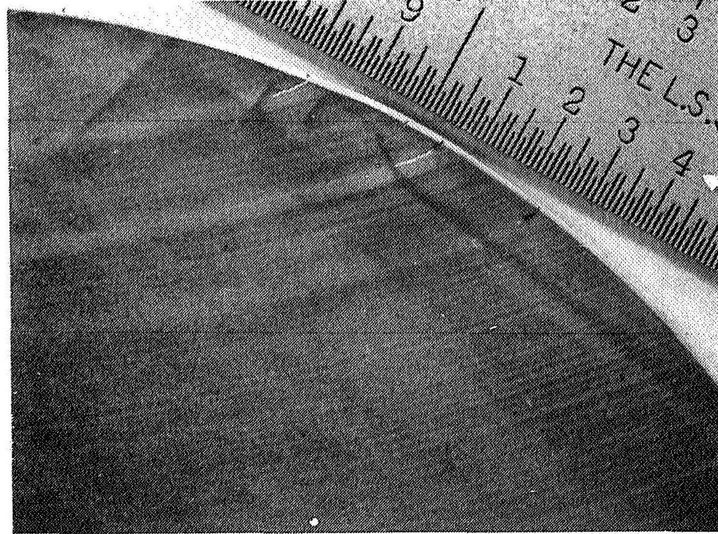


Fig. 7. Saw edge fractures--(111) silicon.

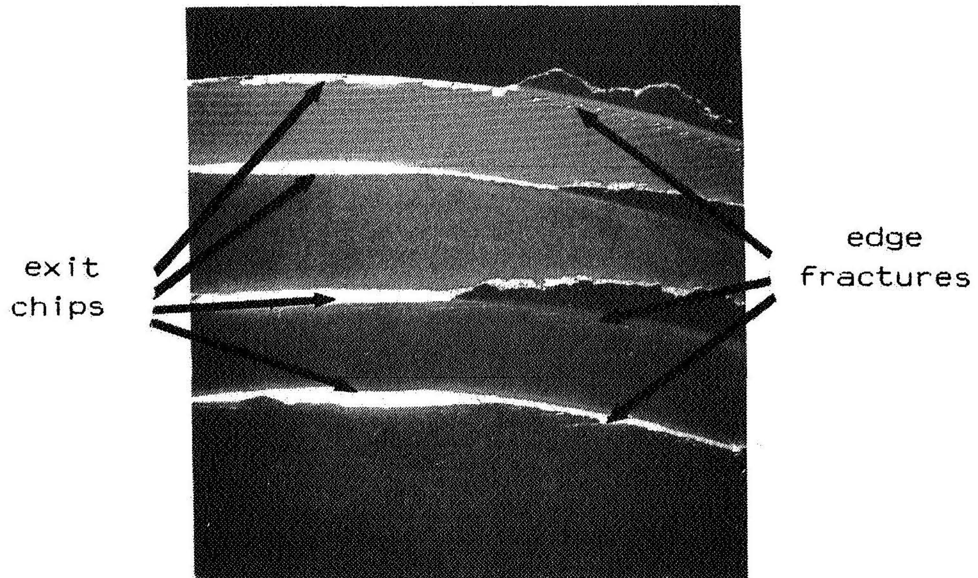
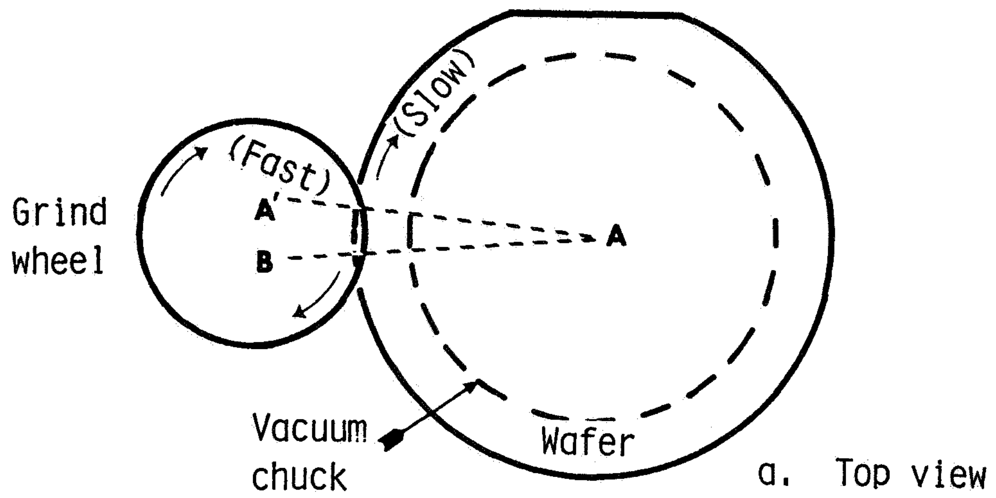
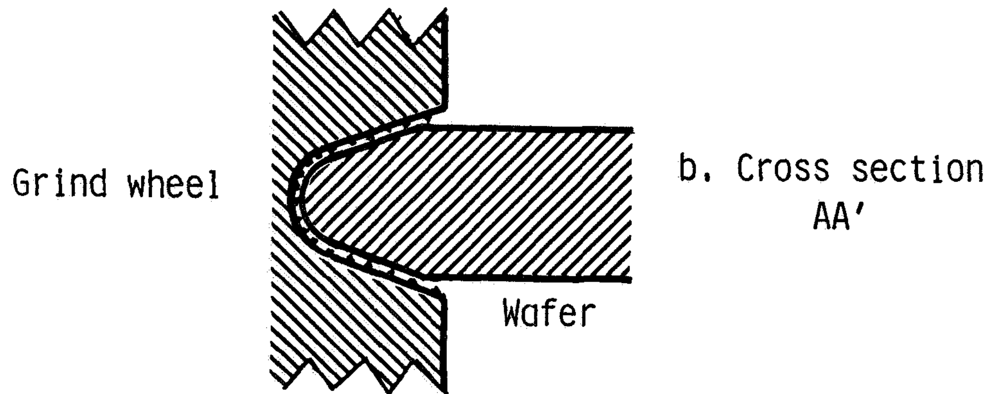


Fig. 8. Saw edge fractures--(100) silicon.





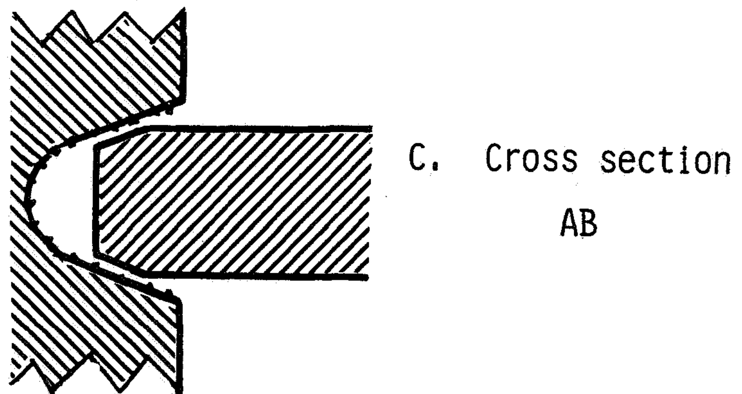


Fig. 9. Schematic Diagram of Edge Grinding Operation

ORIGINAL PAGE IS
OF POOR QUALITY

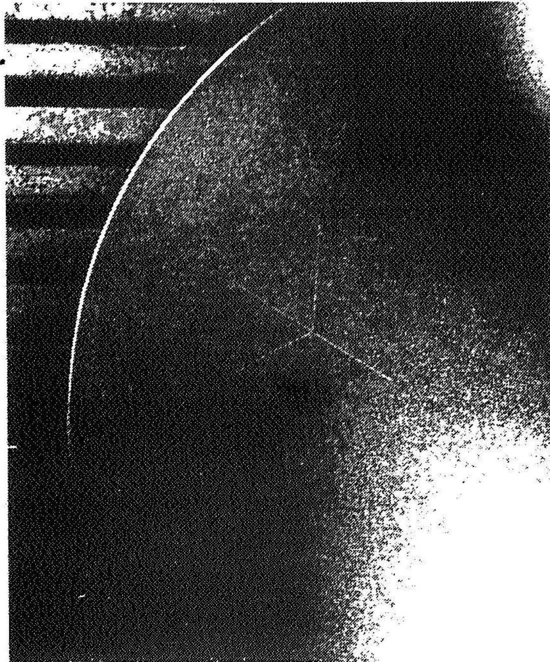


Fig. 10. Crow's-foot fracture from burr on vacuum chuck.

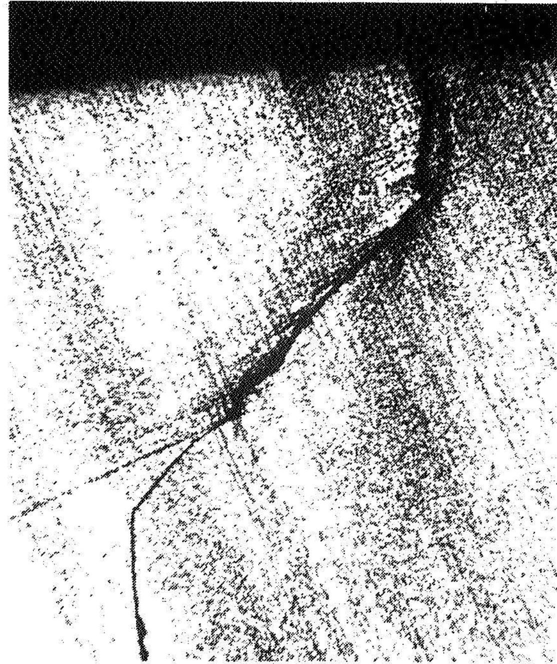


Fig. 12. Edge crack from heat-treating silicon slice in quartz boat.

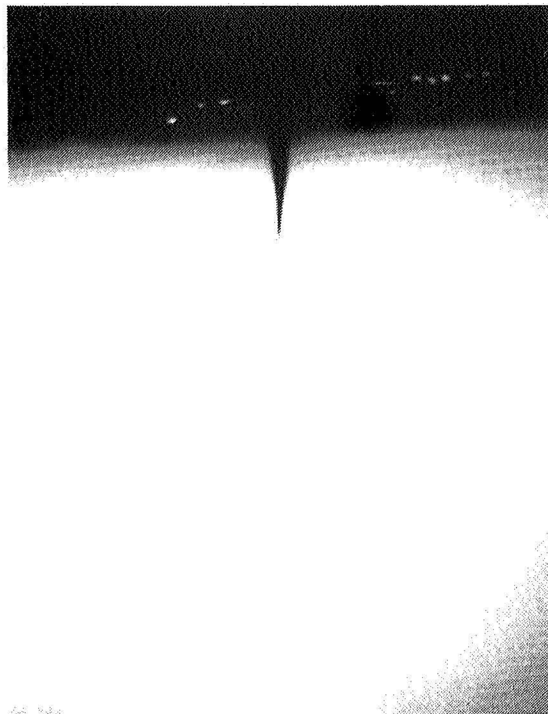
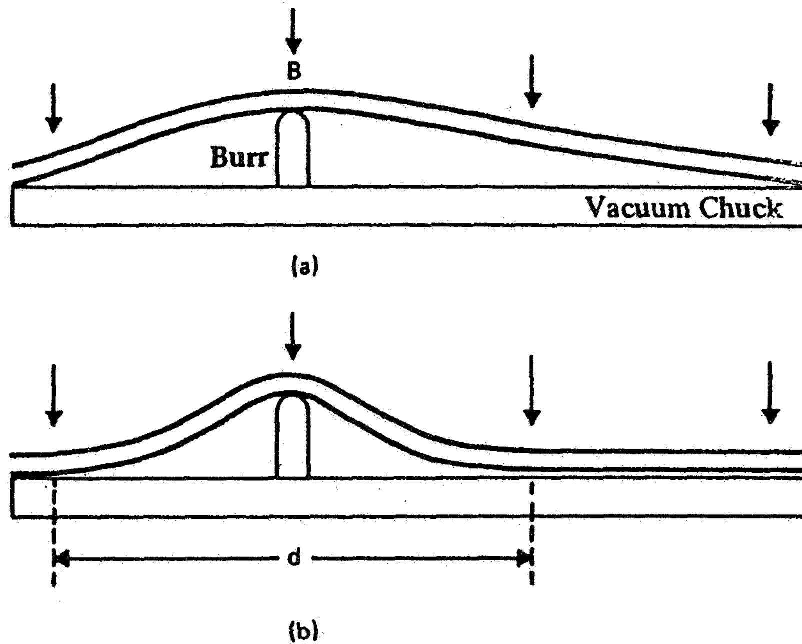


Fig. 13. Edge crack at polish.

Fig. 14. Edge crack at polish.

Fig. 11. MECHANISM OF BURR-INDUCED FRACTURE ON VACUUM CHUCK



(a). Slice is bent over burr: max tensile stress at B. Weak vacuum

(b). Strong vacuum flattens outer regions against plate and increases curvature and stress at 'B.'

(c). (Not shown). Crack starts near "B" but stops as reverse curvature area is reached. (Within "d").

ORIGINAL PAGE IS
OF POOR QUALITY

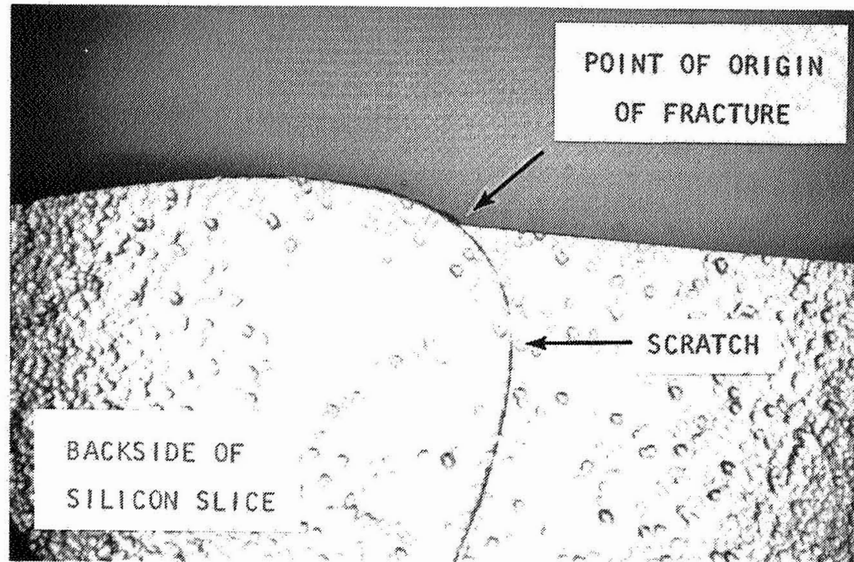


Fig. 15. Scratch leading to furnace breakage. 30X

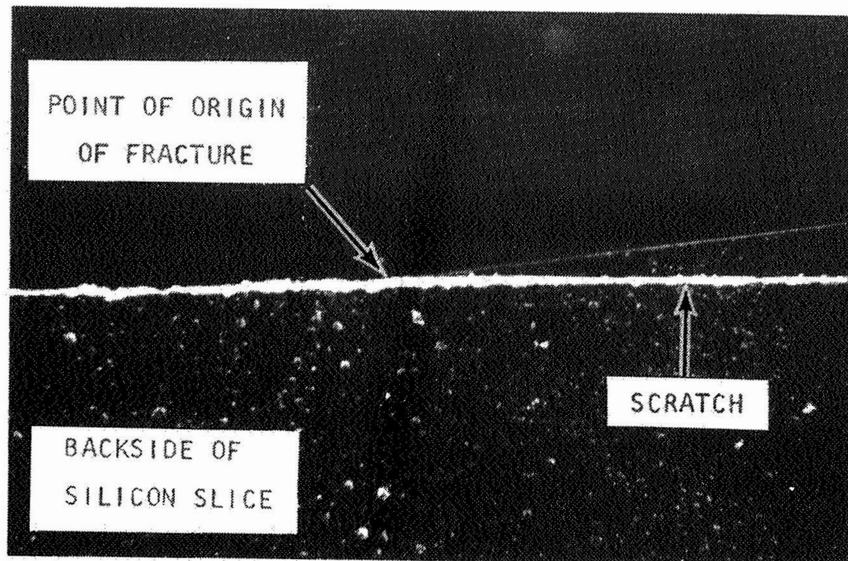


Fig. 16. Scratch leading to furnace breakage. 30X

DISCUSSION

KALEJS: What is the size of the microcracks you are talking about? Can you give us a feeling particularly of the edges versus this sparkle type of microcrack?

DYER: Normally the microcracks would be less than a mil deep. The crow's feet type of microcracks extend from 0.4 to 1.4 µm in size and average about 0.8 µm. When you get into sparkle you get much larger ones (larger than a mil).

CISZEK: It seems to me that the sawing rates that the ID saws are capable of, about 0.15 m^2/h, are hopelessly low to have the kind of throughput needed for the large photovoltaic industry. In your talk you didn't mention multiblade slurry sawing at all, and I'm wondering what your views are on that. Wacker recently demonstrated, on a pilot scale, 0.007 m^2/h per blade, which would mean a 22-blade pack would be about like an ID saw. If we really did have to get higher throughputs for photovoltaics, do you think multiblade slurry slicing is the way to go, or do you think there is some other magic solution out there, or do you think we are stuck with ID slicing?

DYER: I hope there is something better. We had a conference on this subject some years ago and at the time, multiblade sawing was not quite ready to overtake ID sawing. What bothers me about going from a 22-blade saw up to what you need to make a significant improvement is that everybody ignores the trouble it takes to get more than 22 blades on there. They talk about going to 100 or 250 or 500-blade saws, and they never mention the intensive labor to get those things all lined up, spaced properly, and so forth, and then what it would take to keep them from warping as they cut through a 6-in. slice.

LESK: If you look at sliced cast poly, you can see the grain structure very well right after slicing. Is that the sparkle effect you are talking about?

DYER: Any slice that you cut, whether poly or single-crystalline, will have a certain amount of reflection, a certain amount of preferred opening up of the cracks in crystallographic directions. I don't know whether to say that yours is the standard amount, or an enhanced amount from the presence of all the other grains, or some preferred orientation.

SCHWUTTKE: I want to answer Dr. Lesk's question of why we see the grain structure if we slice polysilicon. The fracture is orientation-dependent, and basically every grain reflects its orientation. If you look at the grain surface after fracture, you have the different cleavage planes. If you shine a point light source on it, you see light figures that can be used to orient every single grain. It is an un-isotropic hardness that is present in silicon, which is orientation-dependent, so we get different cleavage phenomena on every single orientation, and therefore after sawing you see every single grain.

RAO: You talked about mil-deep cracks that are there after the slicing operation. If you take a slice like that and go through some sort of an acid-etching procedure, you are obviously going to blunt the tip of the crack so that crack propagation is now going to be reduced if not totally eliminated. In a case like that, one can still get fairly decent yields instead of throwing the slice out. Is that going to alleviate some of the problem?

DYER: Yes, any etching will help solar cell processing. For integrated-circuit processing you are going to go through a lapping step first, and if you have done the etching step first, it actually hinders you because the lapping step is another controlled fracture process. You have to initiate the cracks all over again, so it doesn't buy you much there. Any time you etch it, it strengthens it.

WOLF: With the viewpoint that you need very perfect material right up to the surface, it seems that one wants to etch everything away that has any microcracks. Then there seems to be additional bothersome evidence that the etching itself causes damage. How do we get good material right up to the surface?

DYER: If you are going to make integrated circuits you have to polish one side, and therefore you can't end up with any blemishes at all. In fact, you use the polishing to remove the entire previously damaged area. In the in-between steps it's not necessary to take off a couple of mils on each side, as some people have said, because you are going to do that later in polishing. Dr. Schwuttke has shown that the polishing step is a more efficient step of more or less catching up with the damage. To end up with a nice surface to be able to put junctions on, and metallizations, you want to etch a little more deeply for the solar cell than you do for the integrated-circuit process. All that is necessary for the integrated-circuit process is that you enlarge the microcracks so that they are no longer cracks, but just deep grooves, until you get to the polishing stage in which you want to remove the material. We still end up with solar cells with a caustic-etched surface. There are great ups and downs, and you can still make a solar cell very well out of that without having to go to the extreme of polishing it.

WOLF: In solar-cell manufacturing, one replaces the polishing step by an etching step to try to get rid of all the penetrating damage.

DYER: What happens is that the grooves that you would be putting in an integrated-circuit etch have just widened out to be fairly wide cavities.

SCHWUTTKE: The crack tip is very sensitive to the chemical potential it sees when you do chemical etching. This is why the crack propagation or the crack removal depends very much on the etchant being used. It has been shown that safer chemical etching is actually propagating every crack. It's almost impossible by chemical etching to remove the crack tip, so this is why the modern semiconductor technique has introduced mechanical-chemical etching. Syton polishing is the most

reliable in removing cracks. You cannot remove cracks by using chemical etching because you propagate the cracks.

DYER: It may be that all chemical etching propagates cracks that are in there. Dr. Schwuttke found that for acid etches but we don't seem to find that for the caustic etches. I agree that polishing is a good way to get off that final amount of damage.

KEYACK: A couple of years ago, a lot of work was done on additives to the coolant in cutting. Can you comment on any recent work to minimize the cracks?

DYER: I'm not aware of any definitive study on the types of coolants that you add to saws. The things that have been studied were not a broad spectrum of saw coolants. The goal is not to eliminate cracks entirely, but to actually make it so that cracks form very easily, lots of them and short.

N86-19738

DEFECTS AND DEVICE PERFORMANCE

G. Storti, R. Armstrong, S. Johnson, H.C. Lin
W. Regnault, and K.C. Yoo

Washington, DC

The necessity for a low-cost crystalline silicon sheet material for photovoltaics has generated a number of alternative crystal growth techniques that would replace Czochralski (Cz) and float-zone (FZ) technologies. A major thrust with these alternative techniques has been to increase the efficiency of FZ and Cz silicon. At present, efficiencies of devices fabricated from low resistivity FZ silicon are approaching 20%, and it is highly likely that this value will be superseded in the near future. FZ silicon has an advantage in obtaining this goal since sufficiently long-minority carrier lifetimes are possible at low resistivities ($\approx$ 0.1 ohm-cm.). However, FZ silicon is expensive, and is unlikely ever to be used for photovoltaics. Cz silicon has many of the desirable qualities of FZ except that minority-carrier lifetimes at lower resistivities are significantly less than those of FZ silicon. However, it appears that an efficiency of 20% can be exceeded even for Cz silicon, but more of the burden will fall on the fabrication of the device, i.e., to compensate for higher-resistivity material that has a longer-minority carrier lifetime, thinner silicon and effective back-surface fields will be necessary to attain higher efficiencies. Even with Cz silicon, it is unlikely that cost goals can be met because of the poor-material yield that results from sawing and other aspects of the crystal growth. It is as a consequence of the cost that other sheet technologies have been investigated. However, at this stage, almost all of the technologies result in materials that have characteristics that significantly limit efficiency. Not only are efficiencies limited by the minority carrier lifetimes but also by space charge recombination currents associated with both impurities (gross and point) and structural defects (sub-grain boundaries, dislocations, etc.). The considerable effort that has been expended on these alternate materials has shown that high efficiencies (>16%) can be obtained and that there is not necessarily any fundamental limitation in further improving at least some of these materials. Casting technologies will show some improvement in the cost per watt figures over Cz silicon, because nearly comparable efficiencies can be obtained at lower production costs. However, this technology has the same problem as Cz silicon in that silicon utilization is poor. Some ribbon materials also have the potential for very high efficiencies at reasonable cost, but further work is required in order to resolve structure and impurity problems, as well as problems of dimensional uniformity, stress, throughput, etc.

In summary, 20% efficient solar cells can likely be fabricated from both FZ and Cz silicon, but costs are likely to be ultimately unacceptable. Alternate silicon technologies are not likely to achieve this goal, but cost per watt figures may be eventually better than either of the single crystal technologies and may rival any thin-film technology.

 PRECEDING PAGE BLANK NOT FILMED

Objectives

- o EVALUATE IMPACT OF CRYSTAL DEFECTS ON DEVICES
- o PRESENT EXAMPLES FROM EXPERIENCES WITH CAST SILICON AND GENERALIZE TO OTHER SILICON TECHNOLOGIES

Evaluation Criteria

- o QUALITY - EFFICIENCY
- o YIELD - CONSISTENT QUALITY, DIMENSIONAL CONTROL, ETC.
- o RELIABILITY
- o COST

Diode Equation

$$I = \frac{V - IR_S}{R_{SH}} + I_{SCO}\left[e^{e(V-IR_S)/nkT} - 1\right] + I_{QNO}\left[e^{e(V-IR_S)/kT} - 1\right] - I_L$$

I - MEASURED CURRENT
V - MEASURED VOLTAGE
R_S - SERIES RESISTANCE
R_{SH} - SHUNT RESISTANCE
I_{SCO} - SPACE CHARGE RECOMBINATION CURRENT
I_{QNO} - QUASI-NEUTRAL RECOMBINATION CURRENT
n - DIODE QUALITY FACTOR
kT - THERMAL ENERGY
I_L - LIGHT GENERATED CURRENT

PRECEDING PAGE BLANK NOT FILMED

Material Impact, Float-Zone Silicon

$$I = I_{QNO}\left[e^{eV/kT} - 1\right] - I_L$$

WHERE $I_{QNO} = I_{EO} + I_{BO}$
EMITTER BASE

$$I_{BO} = \frac{en_i^2}{N_A}\frac{D_n}{L_n}\tanh\frac{d}{L_n} \qquad \text{WHERE } L_n = \sqrt{D_n \tau_n}$$

∴ WE SEE THAT THE MATERIAL CHARACTERISTICS OF IMPORTANCE ARE:

1. THE BASE DOPING, N_A
2. THE MINORITY CARRIER DIFFUSION LENGTH, L_n

➡ HIGHEST EFFICIENCIES ARE OBTAINED FROM HIGHEST N_A AND L_n FOR LOW INJECTION CASE

LIMITS ON EFFICIENCY SET BY AUGER RECOMBINATION (L_n IN FZ SILICON APPROACH AUGER LIMITS)

EVALUATION:

- ✓ QUALITY
- ✓ YIELD
- ✓ RELIABILITY
- X COST

Material Impact, Czochralski Silicon

$$I = I_{QNO}\left[e^{eV/kT} - 1\right] - I_L$$

$$I_{BO} = \frac{en_i^2}{N_A}\frac{D_n}{L_n}\tanh\frac{d}{L_n}$$

AS WITH FZ SILICON, MATERIAL CHARACTERISTICS OF IMPORTANCE ARE:

1. THE BASE DOPING, N_A
2. THE MINORITY CARRIER DIFFUSION LENGTH, L_n

➡ HIGHEST EFFICIENCIES ARE OBTAINED FROM HIGHEST N_A AND L_n FOR LOW INJECTION CASE, HIGHEST L_n FOR HIGH INJECTION CASE.

IN CZ SILICON ~, $L_n << L_n^{AUGER}$, PARTICULARLY AT LOW RESISTIVITY.

➡ HOWEVER, HIGH EFFICIENCY CELLS CAN BE FABRICATED FROM CZ SILICON

.

EVALUATION:

- ✓ QUALITY
- ✓ YIELD
- ✓ RELIABILITY
- (?) COST

Alternative Silicon Technologies

o COST ISSUE HAS DRIVEN EFFORTS TO FIND AN ALTERNATE SILICON TECHNOLOGY

1 - CASTING
2 - SELF-SUPPORTING RIBBON
3 - RIBBON ON A SUBSTRATE

Efficiency/Yield-Limiting Materials Characteristics

- DISLOCATIONS IN GRAIN BOUNDARIES
- DISLOCATION SUB-GRAIN BOUNDARIES
- INTRA-GRAIN ISOLATED DISLOCATIONS
- GROSS IMPURITIES - INCLUSIONS, PRECIPITATES
- ISOLATED IMPURITIES
- DIMENSIONAL EVENNESS, PROCESSABILITY

Cast Polycrystalline Silicon Examples

1. ELECTRICALLY ACTIVE GRAIN BOUNDARIES - SMALL GRAINS

<u>IMPACT</u>: INCREASE IN SPACE CHARGE RECOMBINATION CURRENTS

DECREASE IN EFFECTIVE MINORITY CARRIER LIFETIME

INCREASE IN DARK CURRENT BECAUSE OF GREATER JUNCTION AREA

<u>CONSEQUENCE</u>: I_{SC}, V_{OC}, FF DECREASED

<u>SOLUTION</u>: CONTROL TEMPERATURE OF CONTAINER AND SOLIDIFICATION RATE

<u>RESULT</u>: POLYCRYSTALLINE WAFERS WITH GRAIN DIAMETERS $\geq$ 5 mm

<u>ALTERNATE SOLUTION</u>: GRAIN BOUNDARY PASSIVATION

Electrically Actived Sub-Grain Boundaries/Isolated Dislocations

IMPACT: INCREASE IN SPACE CHARGE RECOMBINATION CURRENTS

DECREASE IN EFFECTIVE MINORITY CARRIER LIFETIME

INCREASE IN DARK CURRENT BECAUSE OF GREATER JUNCTION AREA

CONSEQUENCE: I_{SC}, V_{OC}, FF REDUCED

SOLUTION: CONTROL OF HORIZONTAL TEMPERATURE PROFILES DURING SOLIDIFICATION AND COOL DOWN

RESULT: REDUCED SUB-GRAIN BOUNDARY DENSITY AND ISOLATED DISLOCATIONS ($< 5 \times 10^3$ CM^{-2})

Gross Impurities—Inclusions in Grain Boundaries

IMPACT: SHUNTS

LOW MINORITY CARRIER LIFETIME

CONSEQUENCE: VERY LOW I_{SC}, V_{OC}, FF

SOLUTION: REDUCTION OF CARBON IN MELT, CONTROLLED SOLIDIFICATION RATES

RESULT: GREATER YIELD OF "HIGH" QUALITY MATERIAL, FASTER SOLIDIFICATION RATES

Table 1. Polysilicon Solar Cell Illuminated I-V Characteristics (100 mW/cm^2, 25°C)

CELL AREA (cm^2)	NO. CELLS	STATISTIC	J_{SC} (mA/cm^2)	V_{OC} (mV)	F.F.	EFFICIENCY (%)
100	50	MEAN	30.6	574	0.761	13.4
		σ	0.66	5.9	0.011	0.31
100	1		31.3	584	0.771	14.1
4.03	1		34.6	601	0.779	16.2

Table 2. Short-Circuit Current Losses for Small and Large Area Polysilicon Cells in the Region 400 to 1100 nm

	16.2% (4.03cm^2)		14.1% (100cm^2)	
LOSS MECHANISM	FRACTION AVAILABLE AFTER LOSS	J_{SC}(mA/cm^2) AVAILABLE AFTER LOSS	FRACTION AVAILABLE AFTER LOSS	J_{SC}(mA/cm^2) AVAILABLE AFTER LOSS
THEORETICAL MAXIMUM	1.0	43.2	1.0	43.2
INTERNAL QUANTUM EFFICIENCY LOSS	0.87	37.6	0.85	36.7
ANTIREFLECTION COATING LOSS	0.97	36.5	0.97	35.6
GRID SHADOWING LOSS	0.95	34.6	0.88	31.3
NET	0.80	34.6	0.73	31.3

Table 3. Dark I-V Characteristics (25°C) for Small and Large Area Polysilicon Solar Cells

PARAMETER	16.2% ($4.03 cm^2$)	14.1% ($100 cm^2$)
SHUNT CONDUCTANCE G ($m℧/cm^2$)	0.18	0.90
SERIES RESISTANCE R_S (Ω-cm^2)	0.38	0.32
SPACE-CHARGE DIODE QUALITY FACTOR, N	3.5	2.0
SPACE-CHARGE CURRENT J_{SCO} (mA/cm^2)	4.6×10^{-3}	6.3×10^{-4}
QUASI-NEUTRAL CURRENT J_{QNO} (mA/cm^2)	2.3×10^{-9}	3.6×10^{-9}
EQUIVALENT VOLTAGE V_E (mV)	522	496
BASE RESISTIVITY (Ω-cm)	1.0	1.7

ORIGINAL PAGE IS
OF POOR QUALITY

Losses Associated With Dark I-V Characteristics in Table 3 for Small Area (Table 4A) and Large Area (Table 4B) Polysilicon Solar Cells

INCLUDED DARK I-V COMPONENTS	I-V CHARACTERISTICS CALCULATED FROM INCLUDED DARK I-V COMPONENTS			
	V_{OC} (mV)	F.F.	η (%)	$\Delta\eta$ (%)
QUASI-NEUTRAL RECOMBINATION	602	0.829	17.2	-
QUASI-NEUTRAL & SPACE-CHARGE RECOMBINATION	599	0.796	16.4	0.8
QUASI-NEUTRAL, SPACE-CHARGE & SHUNT CONDUCTANCE	599	0.793	16.4	0
QUASI-NEUTRAL, SPACE-CHARGE, SHUNT CONDUCTANCE & SERIES RESISTANCE	599	0.775	16.1	0.3
MEASURED CHARACTERISTICS	601	0.779	16.2	-

TABLE 4A

INCLUDED DARK I-V COMPONENTS	I-V CHARACTERISTICS CALCULATED FROM INCLUDED DARK I-V COMPONENTS			
	V_{OC} (mV)	F.F.	η (%)	$\Delta\eta$ (%)
QUASI-NEUTRAL RECOMBINATION	588	0.826	15.2	-
QUASI-NEUTRAL & SPACE-CHARGE RECOMBINATION	584	0.803	14.7	0.5
QUASI-NEUTRAL, SPACE-CHARGE & SHUNT CONDUCTANCE	583	0.791	14.4	0.3
QUASI-NEUTRAL, SPACE-CHARGE, SHUNT CONDUCTANCE & SERIES RESISTANCE	583	0.777	14.2	0.2
MEASURED CHARACTERISTICS	584	0.779	14.1	-

TABLE 4B

Conclusions and Comments

1. PRESENT DAY FZ AND CZ ARE OF SUFFICIENT QUALITY TO OBTAIN EFFICIENCIES IN EXCESS OF 20%. FZ IS THE PREFERRED MATERIAL BECAUSE HIGHER L_n's CAN BE OBTAINED FOR A GIVEN N_A.

2. FZ AND CZ SILICON ARE VERY USEFUL TO THE DEVICE RESEARCHER FOR DETERMINING THE IMPORTANCE OF THE VARIOUS LOSS MECHANISMS AND FOR DEVISING THE PROCESSING TECHNOLOGIES TO REDUCE THE LOSSES.

3. ECONOMIC CELL PROCESSING TECHNOLOGIES WILL ALSO NEED TO BE DEVISED THAT TAKE ADVANTAGE OF THE EXPERIENCE GAINED IN THE LABORATORY.

4. ULTIMATELY, IT IS UNLIKELY THAT EITHER CZ OR FZ SILICON IS ECONOMIC FOR PHOTOVOLTAICS. THIS IS ALSO TRUE FOR ANY TECHNOLOGY THAT REQUIRES WAFERING.

5. THE IMPORTANT ISSUE FOR THE ALTERNATE SILICON TECHNOLOGIES IS WHETHER SUFFICIENTLY HIGH L_n's FOR A GIVEN N_A AND d ARE ACHIEVABLE, AND, IF ACHIEVABLE, WHETHER IT CAN BE DONE QUICKLY AND ECONOMICALLY.

WHAT ARE THE NECESSARY GOALS?

6. FOR CASTING TECHNOLOGIES, IT HAS BEEN POSSIBLE TO REDUCE LOSSES DUE TO STRUCTURAL DEFECTS AND GROSS IMPURITY CONTAMINATION WITH THE RESULT THAT L_n's NEAR 200 μM FOR $\rho \simeq 1\ \Omega$-CM HAVE BEEN ACHIEVED. FURTHER IMPROVEMENTS APPEAR TO BE POSSIBLE, AND EXPERIENCES WITH CZ AND FZ MATERIAL MAY BE USEFUL.

Questions

1. WHAT ARE THE LIFETIME KILLERS IN AS-GROWN CZ AND FZ SILICON?

2. HOW REPRODUCIBLY CAN THE AS-GROWN LIFETIME BE OBTAINED?

DISCUSSION

RAO: You talked about shadowing losses because of grid-line broadening. Why are you getting the grid-line broadening?

STORTI: In those particular cells, we were trying to use a relatively inexpensive processing technique, similar to what Green has used. We used titanium as the base metal on the silicon with a palladium layer and then we use electroplated silver. What happened was that there was too much silver deposited.

RAO: You talked about isolated dislocation densities of $\leq 5 \times 10^3/cm^2$ and about a diffusion length of 200 μm in the material. If you back-calculate, assuming 5×10^3, the spacing between dislocations is of the order of 150 μm and you have a 200 μm diffusion length material. In that case, these dislocations actively act as sinks for the carriers. How do you reconcile these two numbers?

STORTI: Up until about a year ago the dislocations that we would see in the material for the most part were electrically active. We are beginning to see that there are dislocations that are not electrically active. As a consequence of that, we no longer can use that particular simple relationship. Other people have also found that once they get below a certain level, quite a few of the dislocations that are in the material are not electrically active, at least at room temperature.

WOLF: I'm not certain that today's Cz and FZ can get us to 20% or over 20% efficiency and certainly not anywhere near 25%. The problem really gets down to the lifetime of the material. Anything on device design and processing that you can do has essentially been done.

STORTI: No, I don't think people have tried, for example, to go to narrower bases and at the same time have it such that you will have good back-surface fields, or in other words, a condition where essentially your recombination at the back surface is low. You indicated in one of your papers that 50 μm might be the best thickness to actually use. There is very little work that has been done on those particular levels.

WOLF: On the other hand, for the thicknesses they used, they have not been able to get the diffusion length.

STORTI: This is a polycrystalline cell that had about 601 millivolts open circuit voltage, with a thickness of about 120 μm. We specifically chose that particular thickness because of the possibility of having an effective back-surface field. My contention is that if some of these other people who are working on these problems also went to thinner layers, they have a chance of not having to worry quite so much about the diffusion length of the material.

WOLF: Why not go the high-perfection route of growing Cz material that is single-crystal, rather than casting, which has no capital equipment or throughput economic advantage?

STORTI: It is possible to get a higher volume rate of solidification in a casting process than you can get in the case of Czochralski. In other words, you have the possibility of going out in the X and Y dimensions that you do not have in the case of Czochralski and float-zone silicon. We had cast 120-kg slabs, not by going up in this dimension (vertically), but by going out in that dimension (horizontally). There is some economic advantage associated with that. I will agree there is some question as to how much of an additional advantage you do get.

CISZEK: I would just like to reply to Martin Wolf's comment about the casting process that he saw at Osaka. That must be very different from what Wacker is doing. Wacker's viewpoint, and what I myself think is the real beauty of the casting process, is that throughput is not limited by the solidification rate, and I believe it. In Wacker's operation the pouring is done in an expensive apparatus, but then through a lock that poured material, with appropriate insulation around it and on top of it, is taken out, essentially, on a conveyor belt and another one is brought in. So the cooling takes place in a very low-capital-investment kind of situation and the only limitation is on how fast you can melt and pour the silicon, not how fast you can solidify it. I think that is a strong point of casting. It has other limitations, of course.

KALEJS: It's interesting that the polycrystalline material has achieved 16% efficiency. You showed a lot of problematic grain boundaries where phosphorus diffuses down. Presumably the better cell did not have too many of these. Do you have any feeling for how to avoid them, or why it is that certain boundaries are like that?

STORTI: It has been our feeling that there are dislocations in some of these grain boundaries. There is some circumstantial evidence that if you control the temperature gradients in the X and Y directions, then you will tend to end up with boundaries, even second-order twinning boundaries that are coherent boundaries, rather than boundaries that contain dislocations, so there is a possibility that you can reduce these. I'm not too sure that you have to worry that much about it. The penetration is about 1 µm and you have grain sizes that are on the order of half a cm to several cm.

KALEJS: Did you look at the defects in the high-efficiency cell?

STORTI: We took X-ray topographs at several angles, to get some idea of what the densities were. The dislocation densities were on the order of $5 \times 10^2/cm^2$.

KALEJS: A lot of dislocations perhaps could have migrated into the boundaries during the growth.

STORTI: That particular cell had maybe three or four grain boundaries. It was quite low density.

SESSION V

M. WOLF, CHAIRMAN

PRECEDING PAGE BLANK NOT FILMED

INTRODUCTION

A panel discussion opened the final session of the meeting. The chairman of the panel was Professor Martin Wolf (University of Pennsylvania), and the other members were Professor Robert Brown (Massachusetts Institute of Technology), Professor James Corbett (State University of New York at Albany), Dr. Krishna Koliwad (Jet Propulsion Laboratory), and Dr. Guenter Schwuttke (Arizona State University). The panel discussion was followed by a general discussion in which the panel and the Workshop participants were given the opportunity to express their opinions on what future research activities are necessary to achieve high-efficiency silicon solar-cell material. The following is a transcription of these interactive discussions, edited for clarity and continuity.

PRECEDING PAGE BLANK NOT FILMED

PANEL AND GENERAL DISCUSSION

WOLF: As chairman of this general discussion session, I would like to propose several questions that I hope as a group we can discuss and get a consensus on. Probably the No. 1 question is, can we make 20% efficient silicon solar cells from the material that is available today? If the answer is no, then would we know how to make material that's good enough for 20% efficient solar cells? Another question is, do we understand enough about the generation of recombination centers to make material that is significantly better than what we make today, and what is the relationship of this defect center generation to the growth conditions of the ingots or the crystals? This conference raised the question of whether to use Cz versus FZ. There is a big debate whether FZ can ever be made as cheap as Cz. We heard a presentation by the Shinetsu people that this should be very, very possible, while other people believe it isn't. Another question is, can Cz material ever be made as good as or of higher perfection than FZ material?

KOLIWAD: For the sake of those in the audience who are not exposed to the DOE program, I want to state what the driving forces are for our work on high-quality, high-efficiency material. The primary DOE goal is that by 1988 there should be a technology base to make 15% modules at $\$90.00/m^2$, which translates to something like 15¢/kWh. In light of this goal, there are two questions one should ask: what level the cell efficiencies have to be, and what will it cost. The conclusions from a Research Forum on device research held last summer indicated that the cell efficiency goals require values in the neighborhood of 19% or 20%. It was also concluded at the meeting that among other requirements, the substrate stood out as the main factor that determines the ability to reach 20% efficiency. The quality requirements of the substrate, simply stated, are that you have to have large areas of silicon sheet with lifetimes in the neighborhood of 500 µs or higher, and most important, be very uniform. It has been shown in the laboratory that float-zone material has the quality required to make a high-efficiency cell. The silicon substrate requirements for high-efficiency cells, in my view, far exceed those for conventional ICs, like the CMOS VLSIs. This is because a solar cell is a bulk device where uniformities count in terms of yield. In the case of VLSIs, you have some reclamation possibilities. The uniformity issue is very, very critical and the purity requirement is very stringent. Dick Hopkins and his colleagues at Westinghouse have shown that the trace level of metallic impurities we are talking about are in the parts per trillion. The answer to Martin Wolf's question about whether or not we have any material today that can make 20% efficient cells is that there is one that can at least reach 19%, and that is the float-zone material. The question now is, should we look at the feasibility of float-zone as a possible candidate to make 15% modules, at $\$90.00/m^2$, or should we look at the Czochralski technique and see if we can make it more like float-zone? In this conference Dr. Abe showed that float-zone is a

PRECEDING PAGE BLANK NOT FILMED

good production process and it can be at least competitive with, or even better than, the Czochralski process. Also the magnetic Cz work indicates that there are potential steps that one can take to reduce the oxygen level as well as to improve the uniformity. Neither of these things is being addressed in the DOE program. What is being done in the program is addressing the ribbon issues. Ted Ciszek commented that the ideal ribbon technique has not been invented yet, so there is a need to continue ribbon work that addresses how we can improve the quality to the level where we can start getting higher efficiency. Besides float-zoning, and Czochralski investigations, the other aspects of the work should continue toward understanding the basic limitations that can make improvements in the state of the art.

CORBETT: The perspective I have is that competition is a good thing, but so is cooperation. I would argue that we are still science-limited. As a scientist I am well aware that an engineer can often come up with a working solution and we scientists still don't know what's going on. The point I would make here is that we are in the situation where you slightly change the process conditions and chaos can break out, and I think there is still a certain amount of science that's needed there. By 1988, with a finite amount of money, you are not going to solve all those problems. I don't think that we have been as effective as we could be in exploiting all of our expertise. If we can have a lot of communication across the industrial lines, we can move this technology ahead by exploiting the information that's there. If you have a big enough research effort that is backing up your development and backing up your technology, you can be on top of what is going on, and that's why I say the "IBM" of that particular industry is the one that I would bet on. The difficulty is that I am not sure there is such a company. I suggest we somehow have to collectively, as a nation, find ways to marshall all the resources we have, particularly by 1988, to get it done.

BROWN: What I think we are seeing in this industry is a degree of maturity that comes when a lot of the entrepreneurial things are done and you get down to the hard business of doing engineering science to meet goals. That is the emphasis that I think a program like this has to take. If you believe that engineering science is where you have to put your money, you are going to have to put your money in some kind of a concentrated way. There is a lot that fundamental science can offer. The big thing is understanding the relationship between defects in growth conditions, on a material-science, atomistic level, and also on the level of understanding dopant incorporation. This means that we have to get a lot better at understanding convection in the melt in all of these different processes, so that we can really understand this new developing art form of applying magnetic fields and things like this, to get some systemization into how we do it. I think that these are places that the DOE program can have an impact. Because of the cost restrictions that the goals put on the material, we really have to do process analysis optimization and understand process stability. The business of controlling the process stability over a long term, the feasibility

of automatic melt replenishment in whatever kind of system you are talking about, all of these things are going to play very vital roles in meeting the material cost restrictions that are set by the program. How you do that and keep in balance the actual material sciences is an issue that we should talk about.

SCHWUTTKE: Let me start out by asking two questions and qualify each question later. Question one: Can we get a higher than 20% solar cell? My answer is no, if we continue to do research as we did in the past. Second question, is the right material available? I say this question right now has no priority. We rather should ask do we have the right research attitude in place to get to that point. Let me qualify these two items. The semiconductor technology by nature is an interdisciplinary technology. It is finally being recognized that crystal growth is also an interdisciplinary technology. Unfortunately, in the United States, the semiconductor engineering focus has always been in favor of circuit and device design, and because of this came a neglect of crystal-growth technology. Essentially, today we are still pulling Czochralski crystals as described originally by Mr. Czochralski himself. The only improvement we have introduced is that we dip a silicon seed into the melt instead of a steel wire. Crystal-growth technology must be based on dynamic interaction between the device designer, process engineer, and the crystal-growing team. One guy is not sufficient anymore to overcome the materials problem. Our problem is also the missing link between the silicon ingot wafer producer and the silicon wafer user. There is no feedback. We must establish this particular linkage so that whatever material you produce, you make sure that you get data back that will lead to further improvement of your material. In the past, the entire sequence of producing the material, characterizing it, and making the device was done by a single guy or by a few guys. Today our industry is totally different. First of all, we have a very sophisticated technology, and this requires many different specialists to carry out the different steps separated many times by many miles. We need a dynamic characterization system in place. This is where there is an information exchange among the people who produce the material, the people who characterize the material, and the people who make the device. This workshop was very beneficial. It is one of the few workshops where we have different disciplines' people talking to each other and learning from each other.

KOLIWAD: Gunter [Schwuttke], what should the program or DOE do?

SCHWUTTKE: With a limited amount of money, there are two things that I would suggest the program focus on. One is to continue to make the art of crystal growth a science. I believe the workshops have developed a lot of good input in such a direction. The second one is to track and make sure that we maintain a good information exchange among everybody who is working under the program, and that we interchange samples.

SUREK: I agree with everybody that dynamic interaction is important, but I want to play a bit of the devil's advocate. There are three types of people in this audience: PV people who make their own material, and they are probably involved in this dynamic characterization process to optimize their own materials and make as good solar cells as they can. Then there are people here who rely on some material producers to provide them with materials and they are in the business of photovoltaics. Then there are people here whose livelihood is dictated by the semiconductor industry; they couldn't care less about photovoltaics. Are they motivated, by anything that they have heard, to do something for the photovoltaic people who use these materials? Do they see a window for float-zone or improved Cz or whatever materials that they want to do anything with? If they are not going to want to take this communication that has existed here over the past two days and do something with it, then there is very little DOE or anybody can do about it. Maybe DOE ought to try another way of forcing this interaction by setting up their own float-zone manufacturing or Cz manufacturing capabilities to provide the PV industry with whatever advances are needed, because it's doubtful that the existing semiconductor industry is motivated by what they perceive as the PV need.

CORBETT: I think you are absolutely right. I don't see a simple solution, particularly in a finite budget. I think the Japanese model of bringing lots of people together to work on a focused project costs more than you are going to be able to pay, but that's a way of doing it.

ELWELL: If we could make high-efficiency cells right now we cannot afford them as a long-term solution, because the cost of sawing is too great. It seems, therefore, we need a lot more effort in sawing, unless the economics aren't as pessimistic as assumed.

LESK: How much does it cost to saw wafers?

JEWETT: Our sawing add-on cost is 25¢ to 30¢ per wafer.

STORTI: The selling price that Wacker is offering in large volumes for their particular material is less than $2.00 a wafer. That gives you some upper limit. They are 10 x 10-cm wafers.

DYER: I don't see advantages in cutting by an ID technique. I don't see that we can decrease the core thickness greatly. It may be possible to reduce the slice thickness and possibly the kerf by 20% to 30% but, not by a factor of 10. If a 22-multiblade saw equals one ID saw, then it would make sense to extend that further to see if 250 blades would equal 10 saws and count in the difficulty of putting that 250-blade pack together and checking the results of the crystals that it cuts, day after day, month after month, as ID saws are used. They are used seven days a week, 24 hours a day.

STORTI: There is a tremendous uncertainty as to what in fact is going to be the technology in this '89 - '90 time frame. The number of saws required as you go up in production volume represent a very large capital equipment cost that may be totally useless after a certain period of time. It is only one aspect of the uncertainties that are involved, because some other completely different technology may come into being. You have to ask what is your window of opportunity to do various things. It may be a real problem in the case of trying to improve either Czochralski or float-zone or any ribbon or casting technologies because of the amount of time that will be needed to get something effectively into production and operation.

KOLIWAD: The window of opportunity may be more of a scare that is going to hinder the progress of other technologies, like ribbon technologies, for example. The scare is people saying let's not invest anything, let's wait. That scare is real, though the reasons for the scare are not real.

KLOSTERMAN: Whatever we do [at ARCO Solar] has to produce sales in an environment that is somewhat greater than our factory costs, and that's what's going to keep us in the photovoltaic business. Our emphasis is on reducing costs and increasing the efficiency of the cell. We have no basic R&D in progress on Czochralski. Our research and development programs have been related to amorphous thin-film work, and we do have a product that we put on the market this month. Frankly, we feel that that will have a strong influence on our future involvement in photovoltaics.

WOLF: You now have a crystalline-silicon and an amorphous-silicon production line going. How do you foresee the future developing? Will you continue to have two products to address two different markets, or do you think that one type of product will gradually overtake the other?

KLOSTERMAN: My personal feeling is that for some years to come we will continue at our 5-1/2 MW rate in the factory with Czochralski. I suspect that if we are successful, we will see an increase in our production activity in amorphous, which I would classify as a prototype production right now. I suspect that we will continue on with Czochralski for four to five years, maybe longer. I don't anticipate any significant capital outlays to expand it beyond what we are currently capable of doing.

SUREK: As to what the prognosis is, all I can tell you is where we are right now in amorphous; we have a very active program and the results look promising. ARCO has brought some amorphous modules to SERI for outdoor measurements. We measured a square-foot module that was total area efficiency 7.9%, measured over a full-day period under various installation conditions. The active-area efficiency, if you

take the frame and the various integrally interconnected regions into account, would be around 9%. We also measured a four-square-foot module from ARCO that was 5% total area efficiency in an outdoor measurement.

WOLF: In Japan, the No. 1 question was, what will the market be for photovoltaic devices, and tied to that was the question, will it be crystalline material or will it be amorphous material? These questions are related to the question of what efficiency does the market need. If the future market needs the high efficiency, then people essentially look at crystalline silicon. There was no visible confidence that the efficiency of amorphous modules could be brought readily into a competitive range with that of crystalline silicon modules. The Japanese were very confident about their consumer electronics market, which is the largest part of their photovoltaics market. The question was, where does the next larger market lie? There was a talk about the intermediate market of stand-alone systems, and getting past this to a large power-generation market. A repeated question was, how do we get from the present market to the large future market in a way that justifies all the efforts and all the industrial investment? A man from industry stated that if there is no market you have to create one. A good example of this is their solar-powered street lights, which are 25-watt lights powered by a photovoltaic array of about three square feet that uses lead-cell batteries as the primary storage device.

DYER: Will it be possible to give float-zone a shot in the arm so that it is back as a viable technology again? If you want to grow Czochralski material in the solar-cell industry, you can go to a puller vendor who sells also to the electronics industry and get as big a puller as you want. But you can't get a float-zone puller that is designed like you want. What is going to stimulate the float-zone puller up to a level where it's self-sustaining?

LANE: The equipment manufacturer, to survive, has to keep making his equipment better and better and responding to a market that in fact exists. I did a study of float-zone versus Czochralski several years ago, as an attempt at deciding whether we were going to survive or not. When very-large-scale integration began to show its face a few years ago, everybody was saying float-zone is going to be the material that is going to be used for large-scale integration because it has all these fantastic properties. But when we surveyed the marketplace, it turned out that although people did not understand it, it was the Czochralski material that worked best for some reason. I guess what we were seeing was oxygen gettering at the time and didn't know it. But getting back to float-zone, as an equipment manufacturer, we are not in a position to even look at float-zone unless we can see some sort of market there. If there is a market that starts then the equipment will improve and we will improve it, but it has to start from someplace. It has to be more than somebody saying that a solar cell made from float-zone material works better. I guess the solar-cell people have to say they want to buy some equipment.

CISZEK: I've heard several times during these last two days that we have to make Czochralski as good as float-zone, and to me that just doesn't wash, because you have a couple of inherent advantages with float-zoning technology that you will never have with Czochralski. One is that the growth rate is always going to be at least two times as fast, probably more like three or four times as fast. You are never going to have crucible costs, which are a major cost in the Czochralski technique. People are scared of float-zone because they really don't know the techniques to use to approach it, because their familiarity base is with Czochralski growth. I don't think it should be the kind of thing that people are so afraid of -- that they think they have to do Czochralski and make Czochralski look like float-zone. If you see a quality of float-zone that looks useful for high-efficiency cells and you couple that with the fact that the growth rates and the crucible costs are going to be so much better, then you ought to develop the float-zone technique to make it work for the PV industry.

KIM: Regarding making Czochralski silicon just like float-zone, I would disagree. Right now in MCz the oxygen content is about 1 ppma and has fewer metallic impurities than conventional Czochralski material. What I am saying is, MCz is approaching the float-zone quality. Secondly, the float-zone process has a couple of problems. Float-zoning is not as easy as Czochralski growth because it requires a high degree of operator skill. Another problem is the availability of the polycrystalline feed rods, especially the 5-inch-diameter ones. Some rods crack during the operation and create problems.

ABE: In my presentation on potential productivity, I mentioned that we need nice polycrystals. In Japan many of our customers are very interested in amorphous solar cells and not as interested in polycrystalline silicon, so I hope my ideas are realized in the United States. I have a comment that I would like to make. Last week at the MRS meeting in Boston, I attended a symposium on gettering and diffusion effects. Many investigators are very interested in gettering effects, denuded zones, intrinsic gettering, etc., but the device engineers in our country have already finished such studies. From a scientific viewpoint intrinsic gettering is very interesting but the more important thing in device processing is how to keep their process clean. Practicality is the more important thing. In my opinion the scientific approach to understanding the gettering effect is very important, but from a practical point of view it is not as important.

TAYLOR: I have several observations that I would like to make. The goals that have been set by the Federal program are largely directed at the utility industry. That's not to say there isn't a business opportunity out there in calculators and remote power systems, but as far as the Federal program goes it's really a utility-oriented program as is the program at EPRI. The goal of 15% module efficiency at $\$100/m^2$ is not an absolute number and it is not a universal number throughout the United States. There are utilities

whose allowable costs are higher and lower. Observation two is that I think we are very close to getting 20% cells. I think that is going to be by clever device design, not out of the materials-science area. I think it will be achieved probably within the next year. That's not to say that good materials work isn't necessary, because this was already referred to -- that the material on which 20% devices can be made is few and far between. Next general observation: our opinion, not based on a lot of fact but from what we hear in the industry, is that if bulk silicon technology is going to make it for photovoltaics it will have to be in ribbon technology. Anything you have to slice isn't going to make it. What that means is probably what Ted Ciszek referred to, and that is that the technology that can meet those cost and performance, material quality and throughput-rate requirements has not been invented yet. Concentrator technology looks like it stands a chance and could afford to pay the prices required on a per-wafer basis by virtue of the concentration. Next general observation is that there is very little that the photovoltaics industry can do to influence what's going on in the semiconductor industry at this point. A recent report said that 1.4 billion square inches of Cz were grown last year and sold worldwide. The prices are dictated by the semiconductor industry and not the other way around. Next observation is that there is no IBM in this industry. This industry is not large enough. It is not a multibillion dollar industry, and there isn't anything that even ARCO and Solarex, who are the two biggies right now, can do to approach the kind of technology and research of an IBM. The final observation is that for those of us on the sponsored research side, it's really our obligation to do what we can to help this communication problem. It's our responsibility to pick the best people at the best places and force them to work together.

SCHWUTTKE: This industry will be always different from the semiconductor industry. We are not rich enough to afford to start a new technology like float-zoning, but that does not mean we should not pursue a study of float-zone technology. Float-zone technology should be developed in this country and it doesn't have to be a major multimillion dollar program from the beginning. Regarding Czochralski silicon, I obviously would not try to compete head-on with the Czochralski semiconductor industry, but there is no reason that we should switch into different materials properties. If the semiconductor industry at the present time is not interested in low oxygen, there is no reason why the photovoltaic community cannot at least explore what lower-oxygen, homogeneous Czochralski material can do in terms of device performance. All these things should be coupled with good characterization. I think that the sponsor is in a position to put the teams together and make sure that we get what I requested when I started out: good communication and a closed-loop feedback. I think that is the road to progress.

APPENDIX A

LIST OF SPEAKERS

In the following list of speakers, page numbers indicate locations of presentations and questions or comments. Page numbers in parentheses indicate first pages of presentations, those not in parentheses indicate pages where comments or questions are to be found.

Abe, T. (55), 79, 80, 257, 303
Armstrong, R. (279)
Brown, R. (195), 212, 213, 233, 298
Ciszek, T. (17), 26, 27, 28, 79, 257, 275, 291, 303
Corbett, T. 15, 26, 79, (235), 257, 298, 300
Davison, J. 231
Derbey, J. (195)
Dudukovic, M. (147), 172, 212
Dyer, L. 141, 191, 231, (259), 275, 276, 277, 300, 302
Elwell, D. 96, 142, 190, 212, 257, 300
Hopkins, R. (215), 231, 232, 233
Iles, P. 231
Jastrzebski, L. 15, (123), 141, 142, 143
Jewett, D. 233, 300
Johnson, S. (279)
Kalejs, J. 26, 190, 212, 231, 232, 257, 275, 291
Keyack, D. 277
Kim, K. 27, 79, 80, 96, (97), 190, 212, 303
Kimura, H. 79, (109)
Klosterman, B. 301
Koliwad, K. 297, 299, 301
Lane, R. 15, 302
Lesk, A. 15, 27, 54, 95, 107, 275, 300
Lin, H. (279)
Matlock, J. (29), 54, 190
Morrison, A. 54, 95, 141, 172
Neitzel, P. 121, (175), 190, 191, 192
Ramachandran, P. (147)
Rao, H. 15, 28, 141, 276, 290
Regnault, W. (279)
Robertson, G. (109), 121
Schwuttke, G. 15, 95, 96, 141, 143, 172, 275, 276, 299, 304
Storti, G. 15, 27, 54, (279), 290, 291, 300, 301
Surek, T. 213, 232, 300, 301
Taylor, W. 303
Witt, A. (83), 95, 96, 107, 141, 143, 172, 191, 213, 214
Wolf, M. (3), 15, 142, 276, 290, 291, 297, 301, 302
Yoo, K. (279)

APPENDIX B

LIST OF PARTICIPANTS

ABE, Takao
SHIN-ETSU HANDOTAI CO.
2-13-1, Isobe
Annaka-Shi, Gumma 379-01
JAPAN

BAILEY, Craig
J.C. SCHUMACHER CO.
P.O. Box 1158
Oceanside, CA 92054
(619) 433-1663

BENDER, David
ARCO SOLAR, INC.
P.O. Box 2105
Chatsworth, CA 91313
(818) 700-7578

BRIGLIO, Anthony
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 238-343
Pasadena, CA 91109
(818) 354-4883

BROWN, Robert
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Dept. of Chemical Engineering
77 Massachusetts Ave., 66-544
Cambridge, MA 02139
(617) 253-5726

CHEN, Paul
J.C. SCHUMACHER CO.
P.O. Box 1158
Oceanside, CA 92054
(619) 433-1663

CHRISTENSEN, Elmer
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 238-343
Pasadena, CA 91109
(818) 354-7800

CISZEK, Ted
SOLAR ENERGY RESEARCH INSTITUTE
1617 Cole Blvd.
Golden, CO 80401
(303) 231-1769

CORBETT, James
STATE UNIVERSITY OF NEW YORK
Physics Department-SUNY/Albany
Albany, NY 12222
(518) 457-8315

DAVISON, John
J.C. SCHUMACHER CO.
P.O. Box 1158
Oceanside, CA 92054
(619) 433-1663

DIGGES, Thomas G.
VIRGINIA SEMICONDUCTOR, INC.
1510 Powhatan St.
Fredericksburg, VA 22401
(703) 373-2900

DUDUKOVIC, Milorad (Mike)
WASHINGTON UNIVERSITY
Campus Box 1198, Dept. Chem. Eng.
St. Louis, MO 63130
(314) 889-6021

DUMAS, Katherine
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 238-343
Pasadena, CA 91109
(818) 354-6546

DYER, Lawrence
TEXAS INSTRUMENTS, INC.
P.O. Box 84, M.S. 882
Sherman, TX 75090
(214) 892-5351

ELWELL, Dennis
J.C. SCHUMACHER CO.
P.O. Box 1158
Oceanside, CA 92054
(619) 433-1663

FERBER, Robert
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 506-432
Pasadena, CA 91109
(818) 577-9205

FIEGL, George
SILTEC CORP.
423 National Ave.
Mountain View, CA 94043
(415) 968-9359, X41

FORD, Donald W.
GRAPHITE MACHINING
1712 S. Santa Fe
Santa Ana, CA 92705
(714) 835-5275

FREDERICK, Roger
MONSANTO ELECTRONIC MATERIALS CO.
P.O. Box 8
St. Peters, MO 63376
(314) 272-6281

GEARIN, Kevin
STACKPOLE CORP.
P.O. Box 941
Hermosa Beach, CA 90254
(213) 318-6508

HOPKINS, Richard
WESTINGHOUSE R&D CENTER
1310 Beulah Rd.
Pittsburgh, PA 15146
(412) 256-1341

HURD, Jeff
SOLAR ENERGY RESEARCH INSTITUTE
1617 Cole Blvd.
Golden, CO 80401
(303) 321-1779

ILES, Peter
APPLIED SOLAR ENERGY CORP.
15251 E. Don Julian Rd.
City of Industry, CA 91746
(818) 968-6581 X306

JANKOWSKI, Daniel F.
ARIZONA STATE UNIVERSITY
Mechanical and Aerospace Engineering
Tempe, AZ 85287
(602) 965-3809

JASTRZEBSKI, Lubek
RCA LABORATORIES
P.O. Box 432
Princeton, NJ 08540
(609) 734-2655

JEWETT, David
ENERGY MATERIALS CORP.
Sterling Rd., P.O. Box 1143
So. Lancaster, MA 01561
(617) 365-7383

KACHARE, Akaram
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 238-343
Pasadena, CA 91109
(818) 354-4583

KALEJS, Juris P.
MOBIL SOLAR ENERGY CORP.
16 Hickory Dr.
Waltham, MA 02254
(617) 890-0909

KEYACK, Dan J.
ARCO SOLAR, INC.
4530 Adohr Lane
Camarillo, CA 93010
(805) 484-7981

KIM, George
IBM EAST FISHKILL
Dept. 267, Bldg. 300-40E
Hopewell Junction, NY 12533
(914) 894-3020

KIMURA, Hiroshi
HUGHES RESEARCH LABORATORY
3011 Malibu Canyon Rd.
Malibu, CA 90265
(213) 317-5138

KLISCHAT, Gunter
LEYBOLD-HERAEUS
120 Post Rd.
Enfield, CT 06067
(203) 741-2267

KLOSTERMAN, Bill
ARCO SOLAR, INC.
4530 Adohr Lane
Camarillo, CA 93010
(805) 484-7981

KOLIWAD, Kris
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 122-123
Pasadena, CA 91109
(818) 354-5197

LANE, Richard
KAYEX CORP.
1000 Millstead
Rochester, NY 14624
(716) 235-2524

LESK, Arnold I.
SOLAVOLT INTERNATIONAL
P.O. Box 2934
Phoenix, AZ 85061
(602) 231-6458

LORD, Stephen
J.C. SCHUMACHER CO.
P.O. Box 1158
Oceanside, CA 92054
(619) 433-1663

LUTWACK, Ralph
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 238-343
Pasadena, CA 91109
(818) 354-7648

MARKSBURY, Tom D.
UNION CARBIDE CORP.
24241 Via Luisa
Mission Viejo, CA 92791
(714) 770-6907

MATLOCK, John
SES AMERICA
4111 - 112 Avenue
Vancouver, WA 98662
(106) 254-3030

MORRISON, Andrew
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 238-343
Pasadena, CA 91109
(818) 354-7200

NEITZEL, G. Paul
ARIZONA STATE UNIVERSITY
Dept. of Mechanical & Aerospace Eng'ng.
Tempe, AZ 85287
(602) 965-6810

PHILLIPS, Mary
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 502-422
Pasadena, CA 91109
(818) 577-9096

RAO, Hari C.V.
MOBIL SOLAR ENERGY CORP.
4 Suburban Park Dr.
Billerica, MA 01821
(617) 893-8826

REA, Samuel
TEXAS INSTRUMENTS, INC.
P.O. Box 84, M.S. 883
Sherman, TX 75090
(214) 892-5329

ROBERTSON, Glenn
HUGHES RESEARCH LABORATORY
3011 Malibu Canyon Rd.
Malibu, CA 90265
(213) 317-5138

SARMA, Kalluri R.
SOLAVOLT INTERNATIONAL
P.O. Box 2934
Phoenix, AZ 85062
(601) 231-6457

SCHUMACHER, Joseph
J.C. SCHUMACHER CO.
P.O. Box 1158
Oceanside, CA 92054
(619) 433-1663

SCHWUTTKE, Guenter
ARIZONA STATE UNIVERSITY
College of Eng. & Appl. Sciences
Tempe, AZ 85287
(602) 965-2672

STERRY, Janet
POLYCARBON INC.
28176 Ave. Stanford
Valencia, CA 91355
(805) 257-0500

STORTI, George
4740 Connecticut Ave. NW
Unit 707
Washington, DC 20008
(202) 537-1621

SUREK, Thomas
SOLAR ENERGY RESEARCH INSTITUTE
1617 Cole Blvd.
Golden, CO 80401
(303) 231-1371

TAYLOR, Roger W.
ELECTRIC POWER RESEARCH INSTITUTE
P.O. Box 10412
Palo Alto, CA 94303
(415) 855-2162

TUSTIN, David
JET PROPULSION LABORATORY
4800 Oak Grove Dr., M.S. 502-422
Pasadena, CA 91109
(818) 577-9597

WITT, August
MASSACHUSETTS INSTITUTE OF TECHNOLOGY
Dept. of Metallurgy & Material Science
Room 13-413
Cambridge, MA 02139

WOLF, Martin
UNIVERSITY OF PENNSYLVANIA
Dept. of Electrical Engineering
308 Moore, D-2
Philadelphia, PA 19104
(215) 898-4872

WRIGHT, Lloyd
J.C. SCHUMACHER CO.
P.O. Box 1158
Oceanside, CA 92054
(618) 433-1663