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HIGH-PURITY SILICON CRYSTAL GROWTH INVESTIGATIONS

SOLAR ENERGY RESEARCH INSTITUTE

T. F. Ciszek

Investigators

T. F. Ciszek, Principal Investigator
T. Schuyler, Research Technician
J. L. Hurd, Associate Scientist (through 7/85)
M. Fearheiley, Postdoctoral Scientist (from 8/85)
C. Evans, Master Technician (from 3/86)
R. Elder, Summer Student (1985)

Goals

* OPTIMIZE DOPANTS & MINORITY-CARRIER LIFETIME IN FZ MATERIAL
* IMPROVE THE CONTROL OF LIFETIME DEGRADATION MECHANISMS (Impurities, Thermal History, Point Defects, etc.)
* CHARACTERIZE LIFETIME-RELATED CRYSTALLOGRAPHIC DEFECTS

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Topics

* EVAPORATION AND SEGREGATION CONTRIBUTIONS TO IMPURITY PROFILES OF FZ CRYSTALS
* HIGH-PURITY SILICON FLOAT ZONING (FZ)
* MINORITY-CARRIER LIFETIME MEASUREMENT OF HEAVILY DOPED SILICON CRYSTALS
* EFFECT OF SOME CHRYSTAL GROWTH PARAMETERS ON MINORITY-CARRIER LIFETIME
  - feed rod cleaning procedures
  - crystal growth cooling rate
  - p-type dopant species and concentration
* DEFECT INVESTIGATIONS BY X-RAY TOPOGRAPHY
  - dislocation-free FZ silicon
  - silicon ribbons grown by various methods

Comparison of Cz and FZ Growth Methods

Method	CZ	FZ
Production diameter (mm)	150	125
Growth Speed (mm/min)	1 to 2	2 to 4
Crucible?	yes	no
Dislocation-Free?	yes	yes
Oxygen content (atom/cc)	$>1x10^{18}$	$<1x10^{16}$
Carbon content (atom/cc)	$>1x10^{17}$	$<1x10^{16}$
Metalic impurity content	high	low
Consumable material cost	high	low
Bulk lifetime (microsec.)	50	1000
Relative cell efficiencies	1	1 to 1.2
Heat-up/Cool-down time	large	small
Axial resitivity uniformity	poor	good
Typical # of pulls/crystal	one	two
poly feed form	any	crack-free rods
Mechanical strengthening	10^{18} O	10^{16} N
Degree of sophistication	less	more

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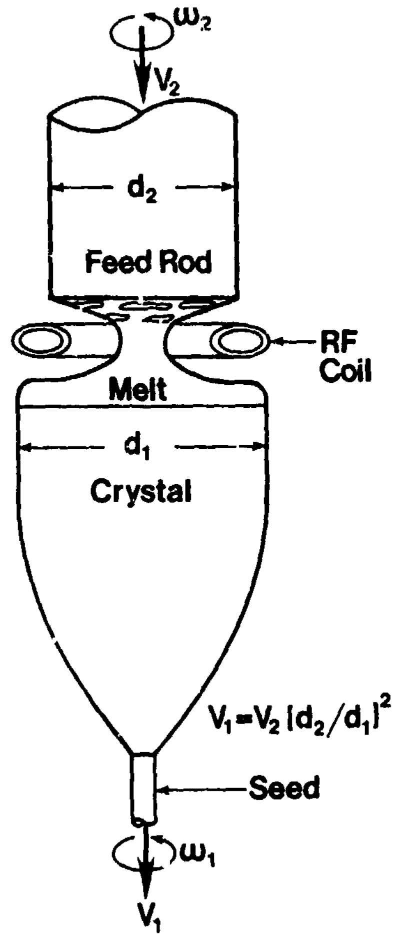
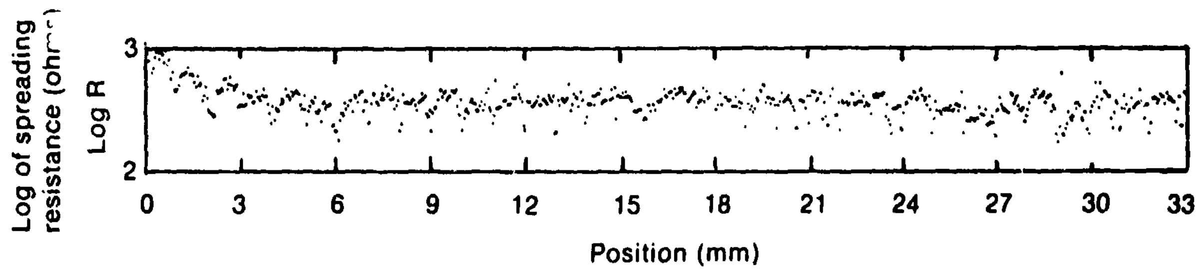
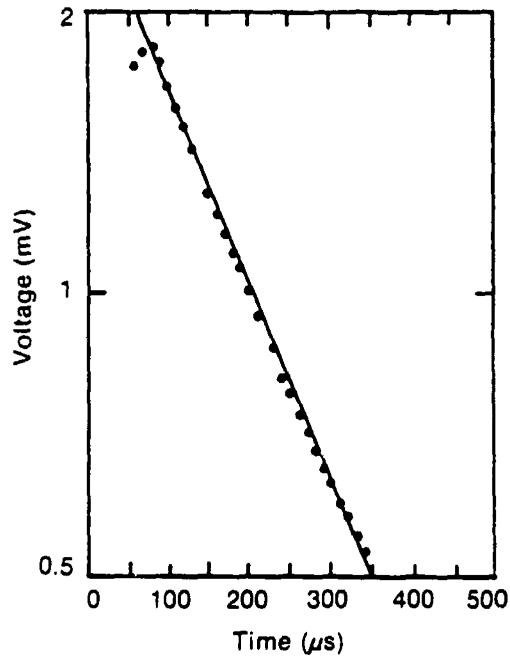
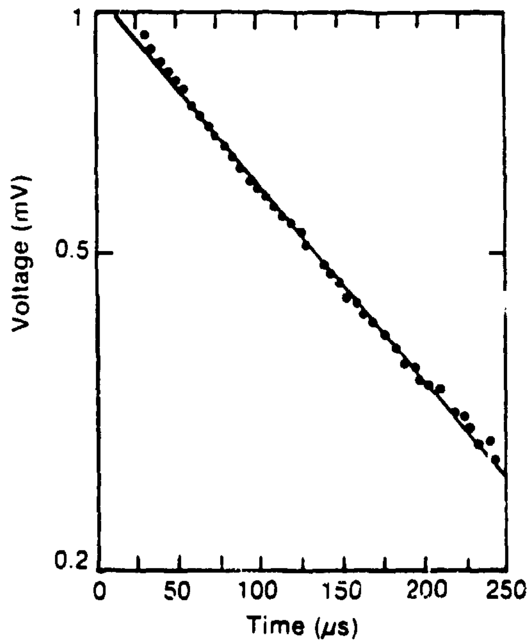

ω2
V2
d2
Feed Rod
RF
Coil
Melt
d1
Crystal
V1=V2 (d2/d1)^2
Seed
ω1
V1

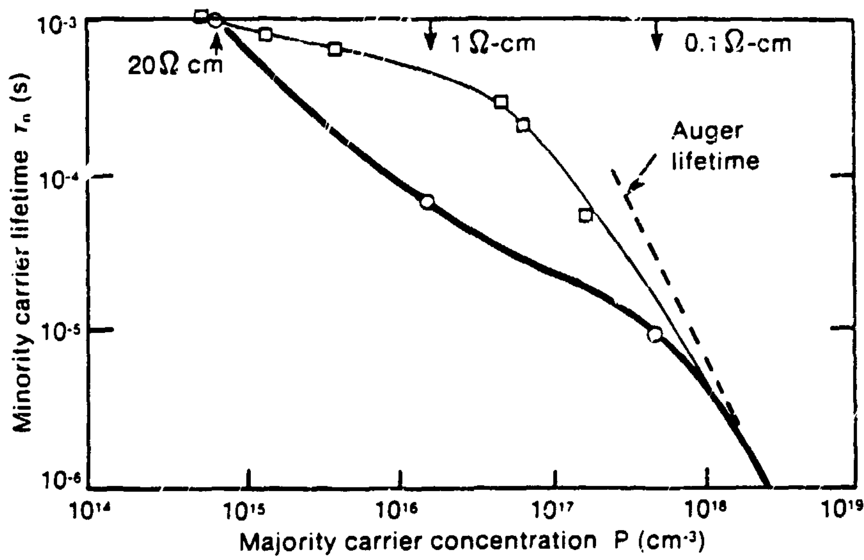

Log of spreading resistance (ohms)
Log R
3
2
0
3
6
9
12
15
18
21
24
27
30
33
Position (mm)



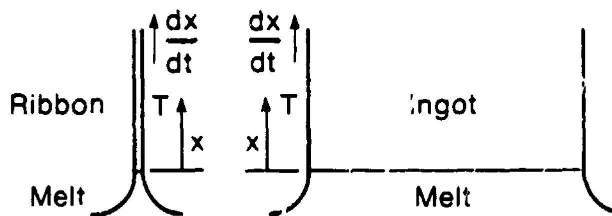
Crystal: 5032001
No. of passes: 4 (3 in vac.)
Orientation: [100], DF
Resistivity: 0.46 ohm-cm
Traces averaged: 20
Temperature 27° C
Filament lifetime: 205 μs
Bulk lifetime: 303 μs
(@ $V_s/V = 0.002$)



Crystal: 5041101
No. of passes: 4 (3 in vac.)
Orientation: [100], DF
Resistivity: 0.36 ohm-cm
Traces averaged: 100
Temperature 26° C
Filament lifetime: 181 μs
Bulk lifetime: 231 μs



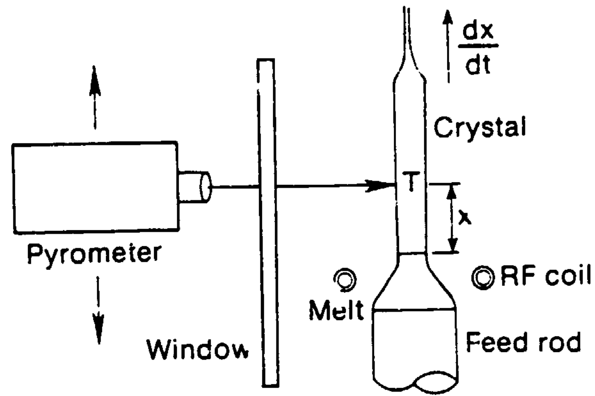
CLEANING PROCEDURE	RESISTIVITY (ohm-cm)	LIFETIME (microsec.)
Cold degreasing	760	7[illegible]0
NaOH etch	2220	600
3:1:2 mixed acid etch	2540	990
"RCA - clean"	4510	1040



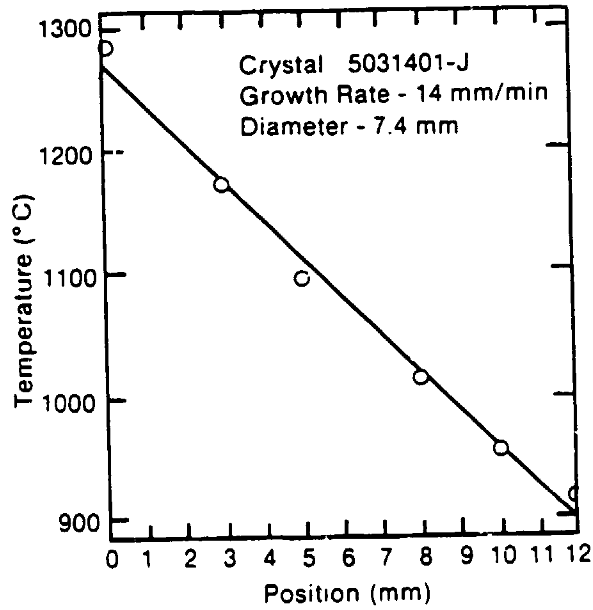
$\frac{dT}{dx} > 250°\,C/cm$ $\qquad$ $\frac{dT}{dx} < 200°\,C/cm$

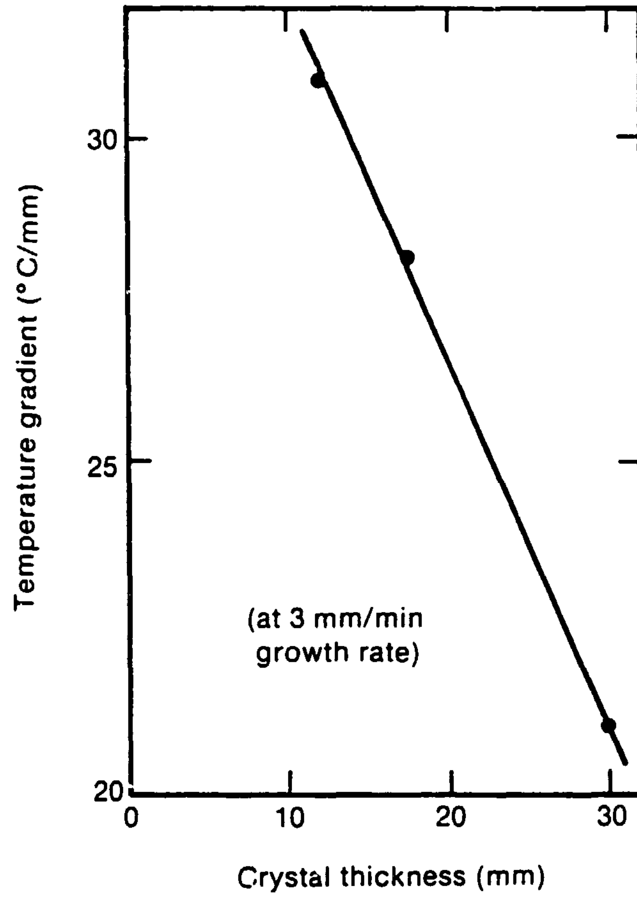
$\frac{dx}{dt} > 2\ cm/min$ $\qquad$ $\frac{dx}{dt} < 0.5\ cm/min$

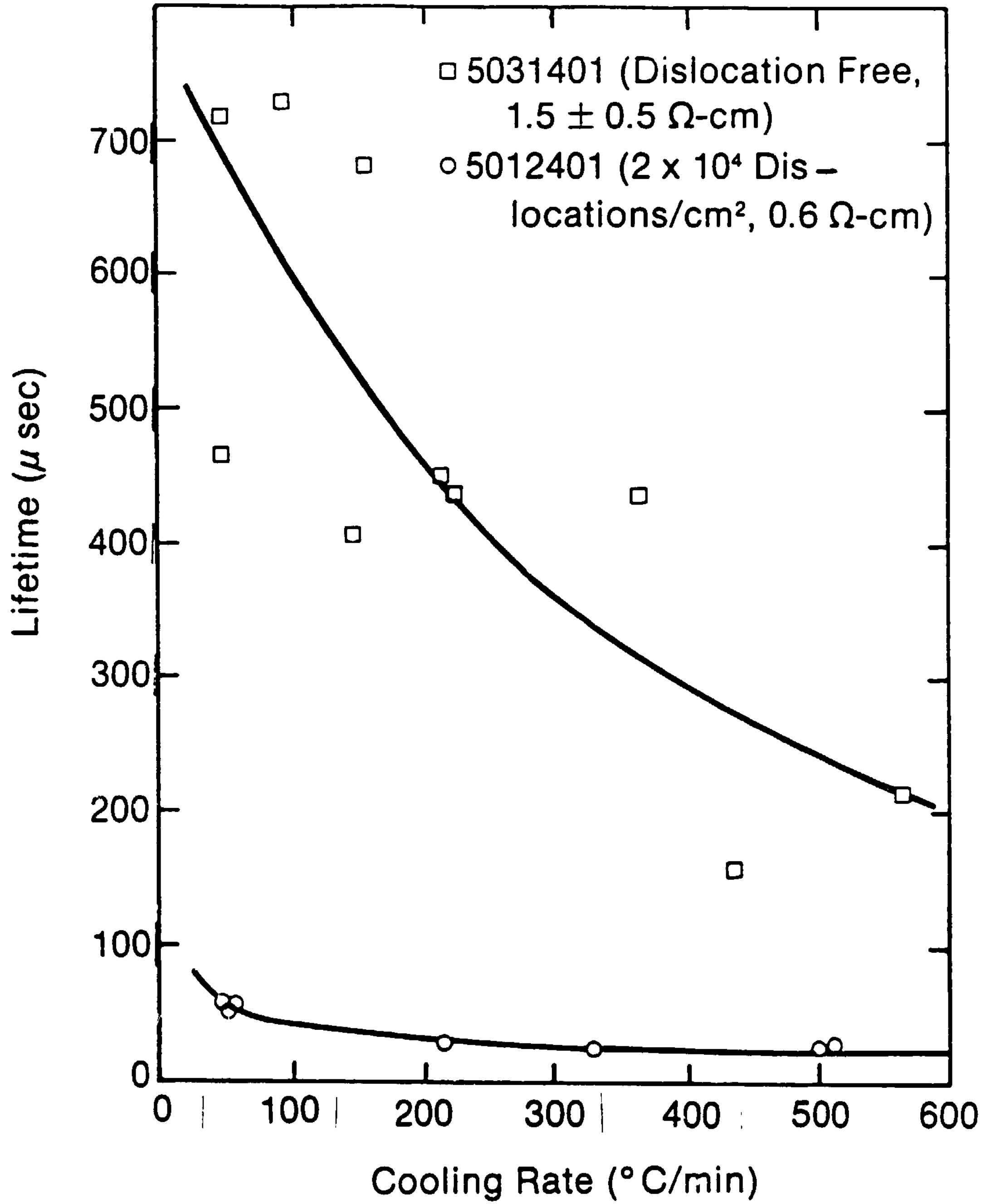
$\frac{dT}{dt} > 500°\,C/min$ $\qquad$ $\frac{dT}{dt} < 100°\,C/min$



$$\frac{dT}{dt} = \frac{dx}{dt}\frac{dT}{dx}$$




Temperature gradient (°C/mm)
30
25
20
0
10
20
30
(at 3 mm/min
growth rate)
Crystal thickness (mm)



□ 5031401 (Dislocation Free, 1.5 ± 0.5 Ω-cm)
○ 5012401 (2 x 10⁴ Dislocations/cm², 0.6 Ω-cm)
Lifetime (μ sec)
0
100
200
300
400
500
600
700
0
100
200
300
400
500
600
Cooling Rate (°C/min)

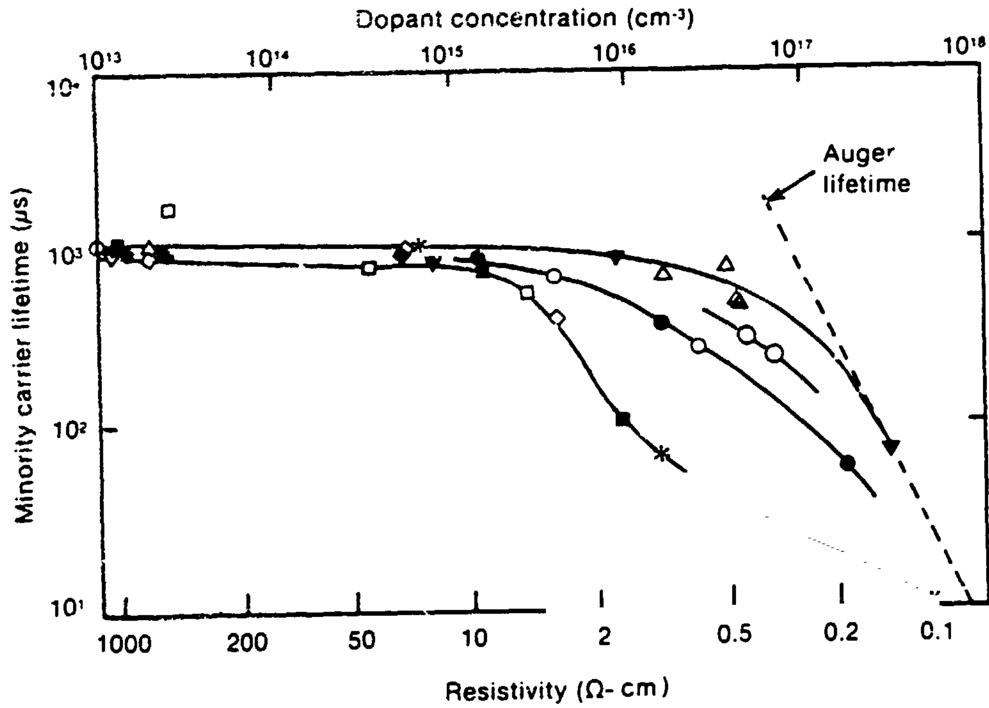
Lifetime (μ sec)

800
700
600
500
400
300
200
100
0

○ 6042301 (Dislocation Free, 2.4 ± 0.9 Ω-cm)

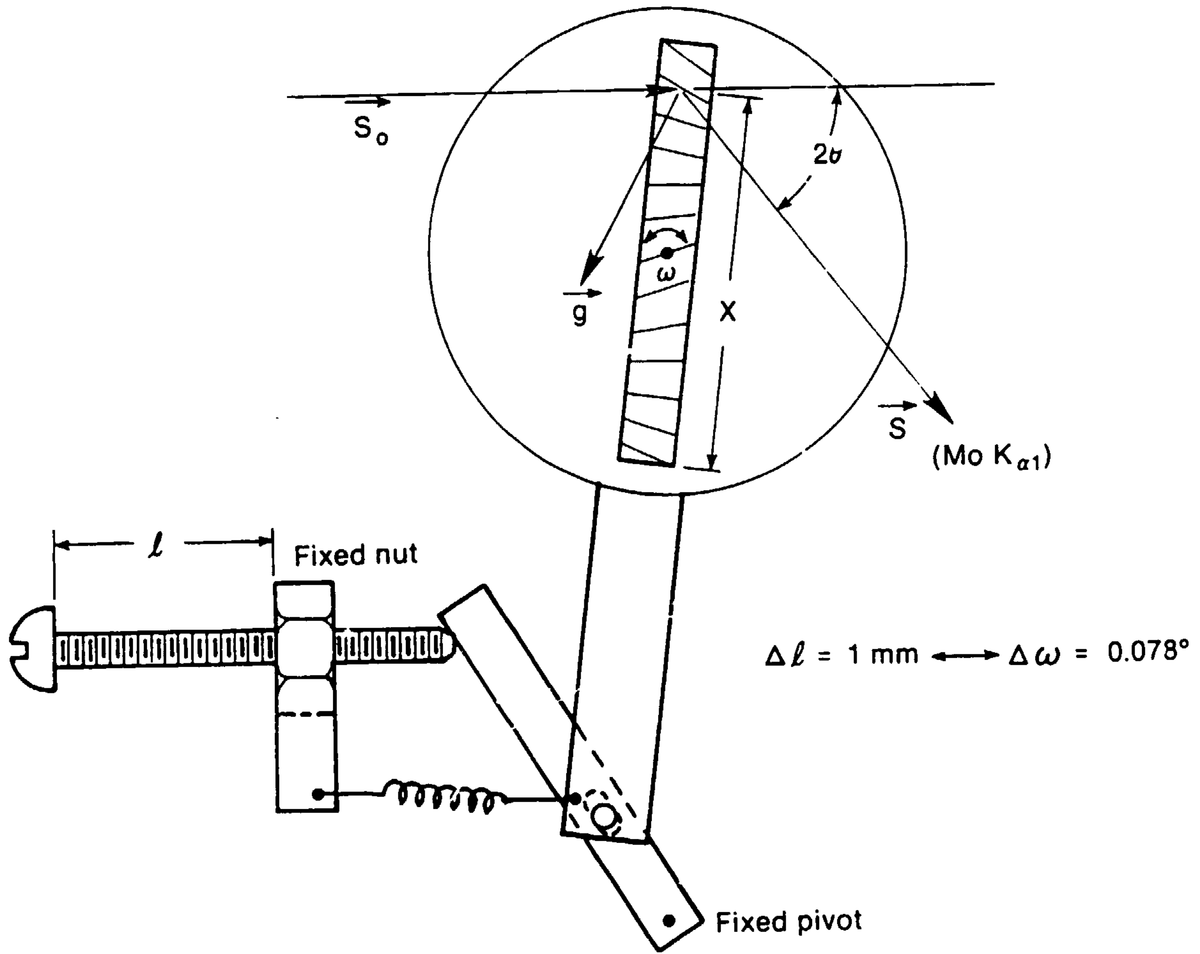
0 100 200 300 400 500 600

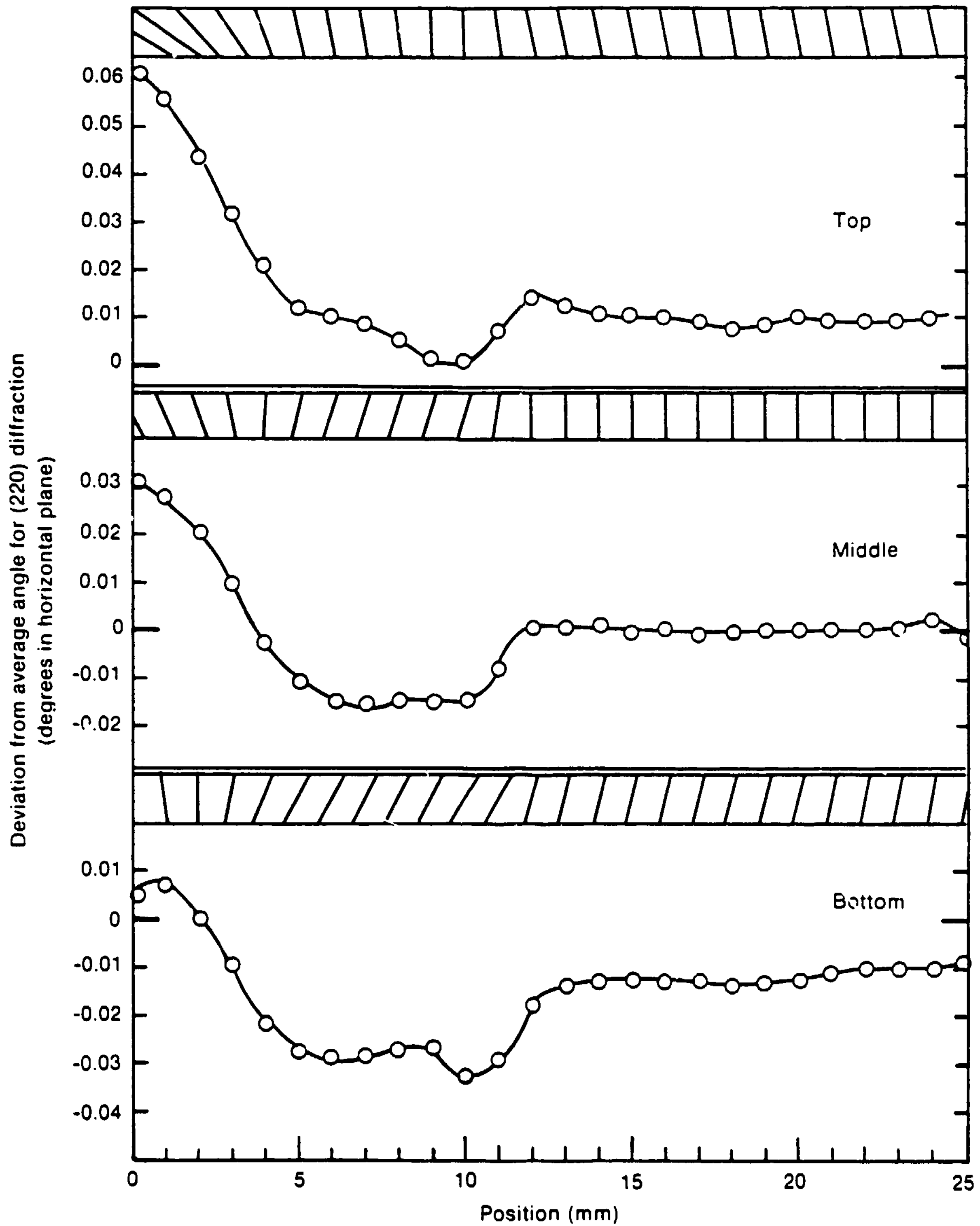
Cooling Rate (°C/min)



- ■ Al, 20 mm dia. poly Si vendor A
- □ Al, 20 mm dia. poly Si vendor B
- ▼ B, 20 mm dia. poly Si vendor A
- △ B, 20 mm dia. poly Si vendor B
- ● Ga, 20 mm dia. poly Si vendor A
- ○ Ga, 20 mm dia. poly Si vendor B
- C Ga, 34 mm dia. poly Si vendor B
- ◆ In, 20 mm dia. poly Si vendor A
- ◇ In, 20 mm dia. poly Si vendor B
- * Experts group best values

RESISTIVITY (ohm–cm)	LIFETIME (microsec.)
1	700
0.5	490
0.2	120
0.1	40


S₀
2θ
ω
g
X
S
(Mo Kα1)
ℓ
Fixed nut
Δℓ = 1 mm ⟷ Δω = 0.078°
Fixed pivot


Top
Middle
Bottom
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
-0.02
-0.03
-0.04
Deviation from average angle for (220) diffraction (degrees in horizontal plane)
0
5
10
15
20
25
Position (mm)

Summary and Conclusions

* EVAPORATION CONTRIBUTES SUBSTANTIALLY TO IMPURITY REDUCTION WHEN FZ OR COLD-CRUCIBLE GROWTH IS CONDUCTED IN A VACUUM.
* BORON AND GALLIUM MAY BE MORE FAVORABLE DOPANTS THAN INDIUM OR ALUMINUM FOR OBTAINING HIGH MINORITY-CARRIER LIFETIMES.
* MINORITY-CARRIER LIFETIMES GREATER THAN 100 microseconds ARE FEASIBLE AT A 2×10^{17} cm^{-3} DOPING LEVEL.
* MINORITY-CARRIER LIFETIME DECREASES WITH INCREASING CRYSTAL COOLING RATE AND ALSO WITH THE PRESENCE OF DISLOCATIONS.
* THE METHOD USED TO CLEAN SILICON FEED RODS AFFECTS LIFETIME.
* MICRODEFECT DENSITIES IN DISLOCATION-FREE FZ CRYSTALS APPEAR TO BE LOWER WITH Ga DOPING THAN WITH B DOPING.
* A VARIETY OF SI RIBBONS WERE EXAMINED BY X-RAY TOPOGRAPHY; A METHOD FOR QUANTIFYING LATTICE PLANE BENDING WAS DEVELOPED.