N87 - 16407

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

This work was supported by the U.S. Department of Energy under contracts DOE/JPL-WO8762-84-1 & DE-AC02-83CH10093: Sept. 1, 1984 - Mar. 31, 1986.

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 CHYSTAL 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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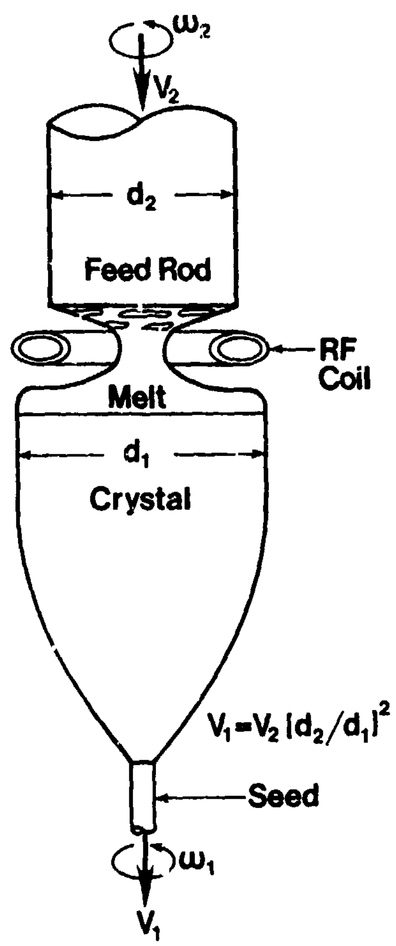
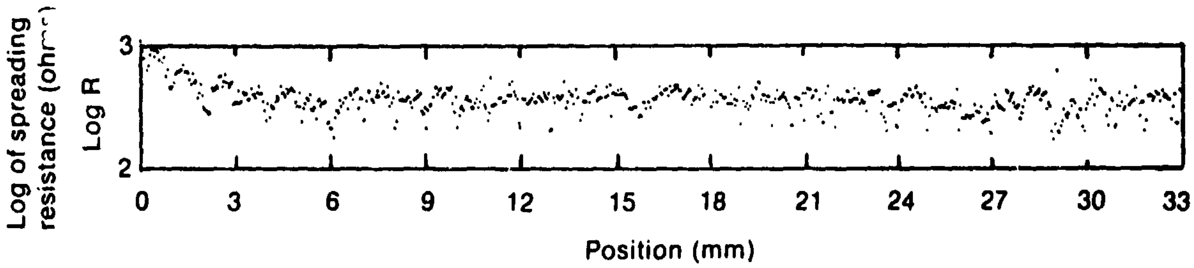
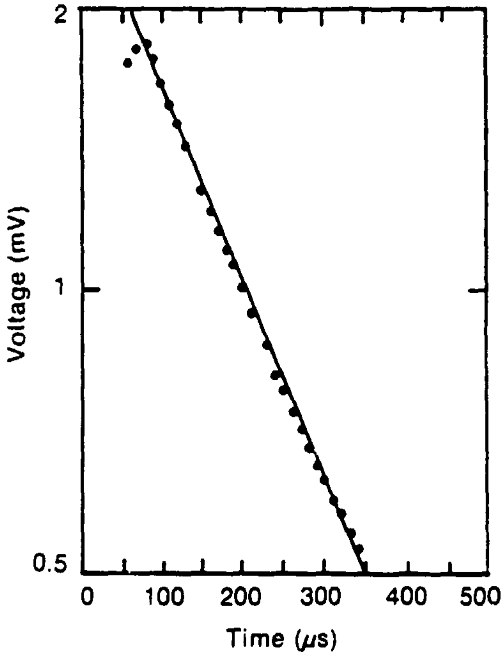


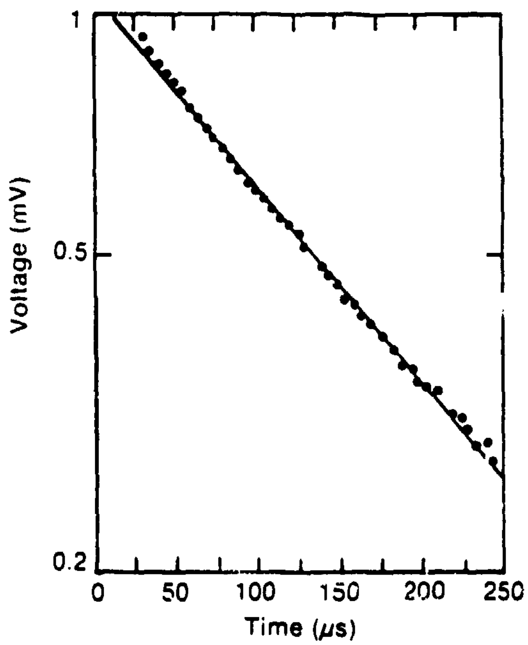
ω_2
V_2
d_2
Feed Rod
RF Coil
Melt
d_1
Crystal
$V_1 = V_2 (d_2/d_1)^2$
Seed
ω_1
V_1



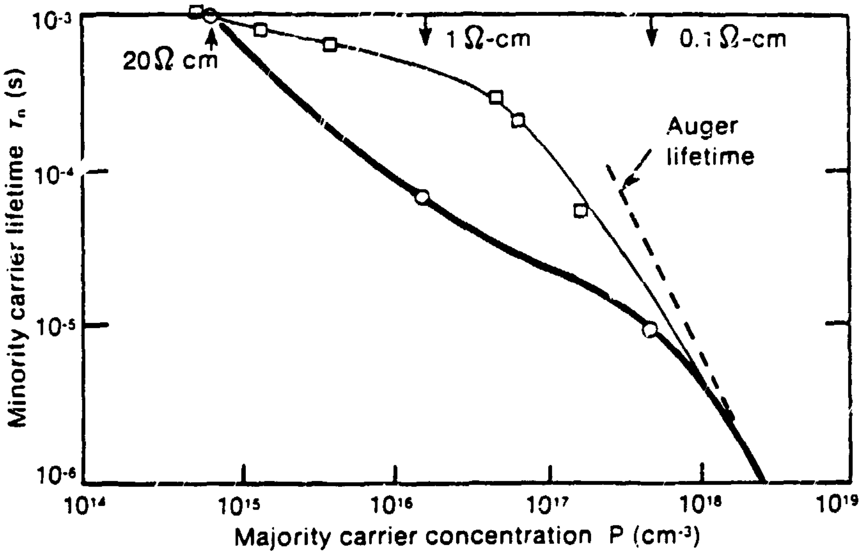
Log of spreading resistance (ohms)
Log R
3
2
0
3
6
9
12
15
18
21
24
27
30
33
Position (mm)



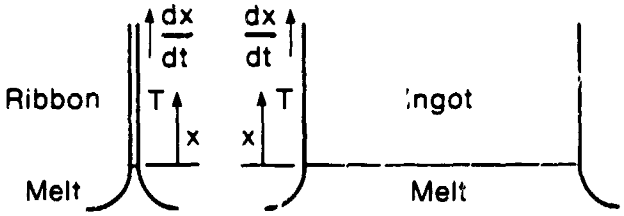
Crystal:	5032001
No. of passes:	4 (3 in vac.)
Orientation:	[100], DF
Resistivity:	0.46 ohm-cm
Traces averaged:	20
Temperature	27° C
Filament lifetime:	205 μs
Bulk lifetime:	303 μs
	(@ V_s/V = 0.002)



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



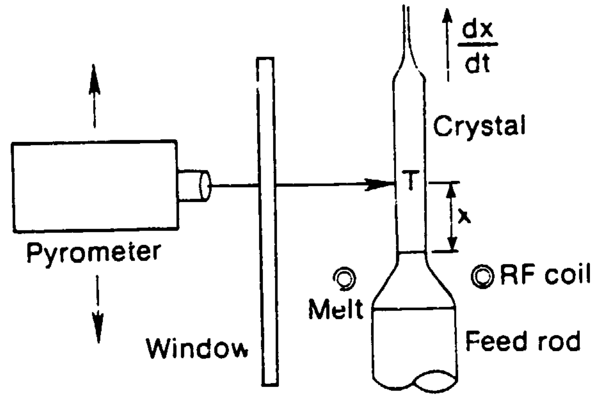
CLEANING PROCEDURE	RESISTIVITY (ohm-cm)	LIFETIME (microsec.)
Cold degreasing	760	7[illegible]0
NaOH etch	2220	600
3:1:2 mixed acid etch	2540	990
"RCA – clean"	4510	1040



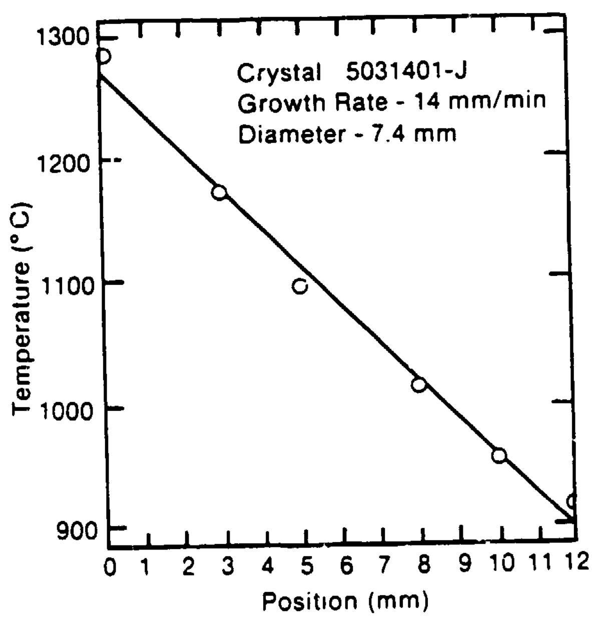
$\frac{dT}{dx} > 250°$ C/cm $\qquad \frac{dT}{dx} < 200°$ C/cm

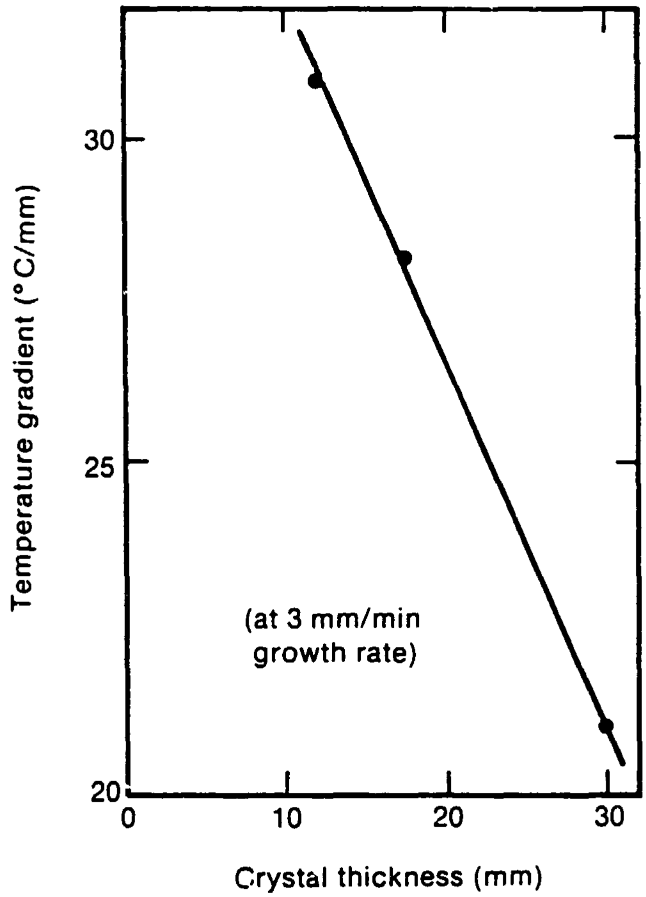
$\frac{dx}{dt} > 2$ cm/min $\qquad \frac{dx}{dt} < 0.5$ cm/min

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

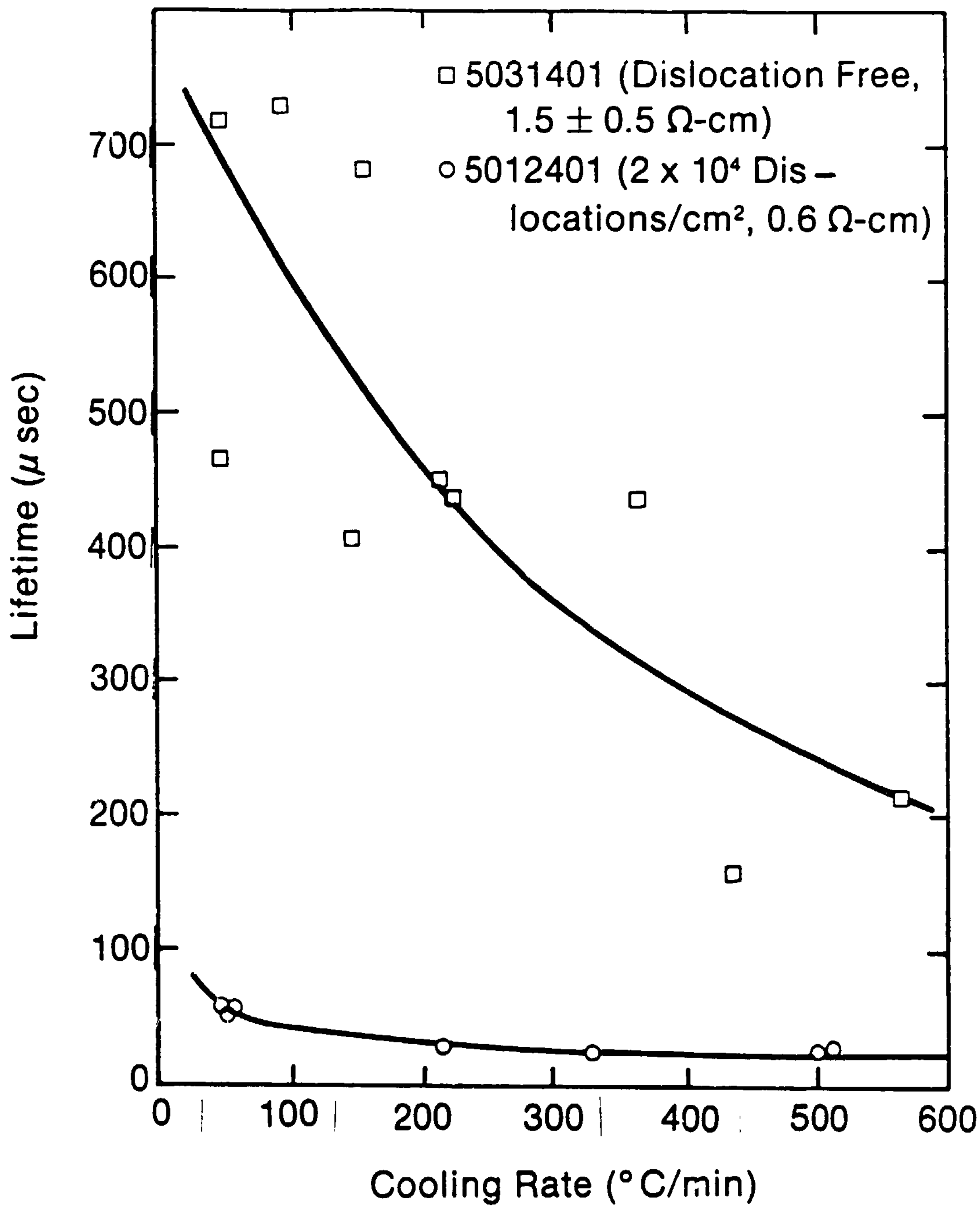


$$\frac{dT}{dt} = \frac{dx}{dt}\,\frac{dT}{dx}$$

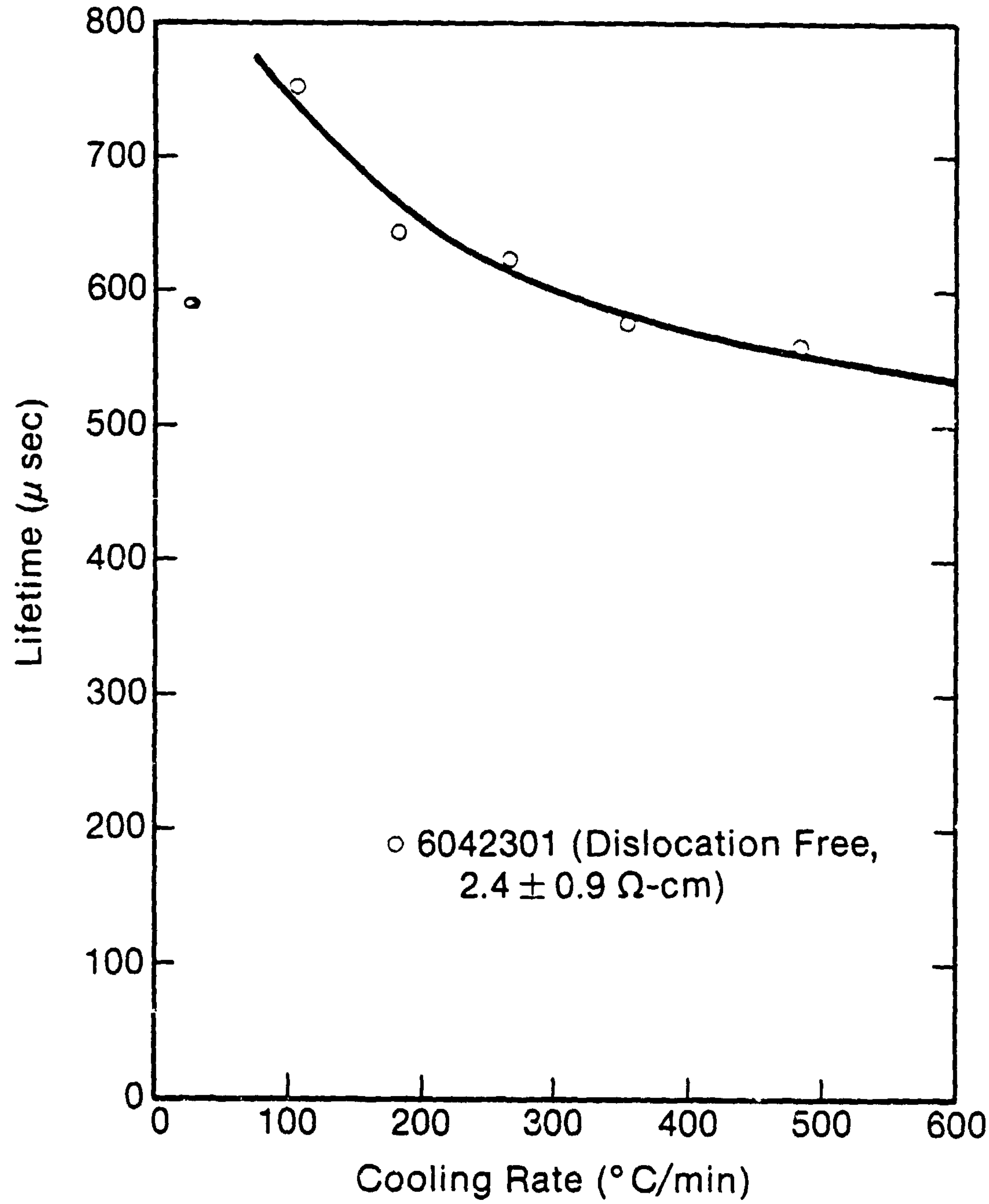




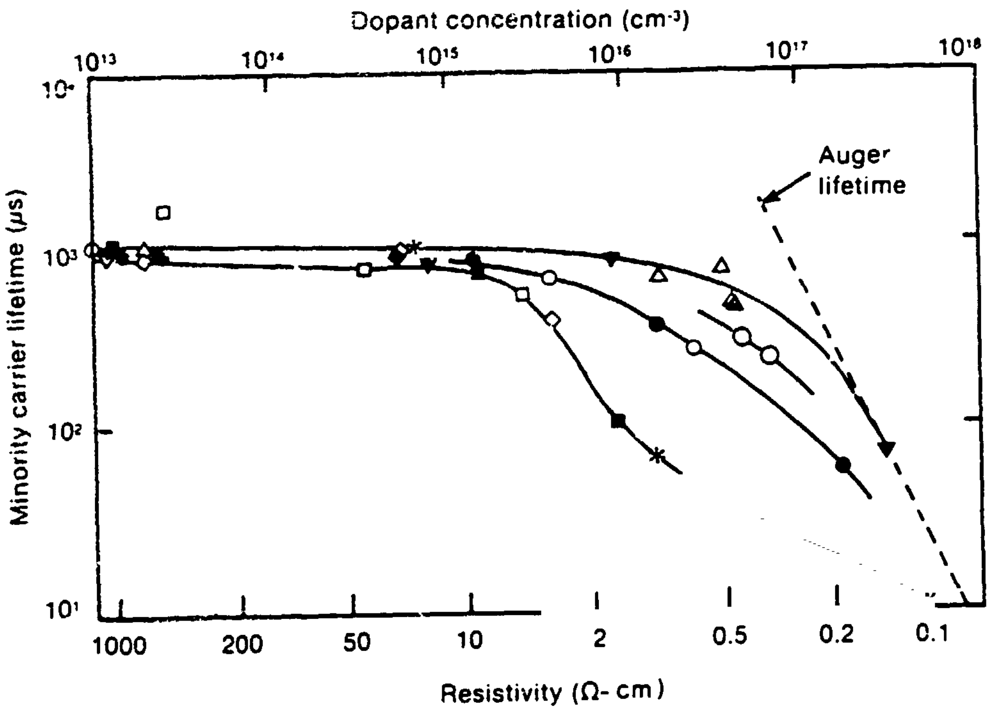
Temperature gradient (°C/mm)
30
25
20
0
10
20
30
(at 3 mm/min
growth rate)
Crystal thickness (mm)



□ 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)

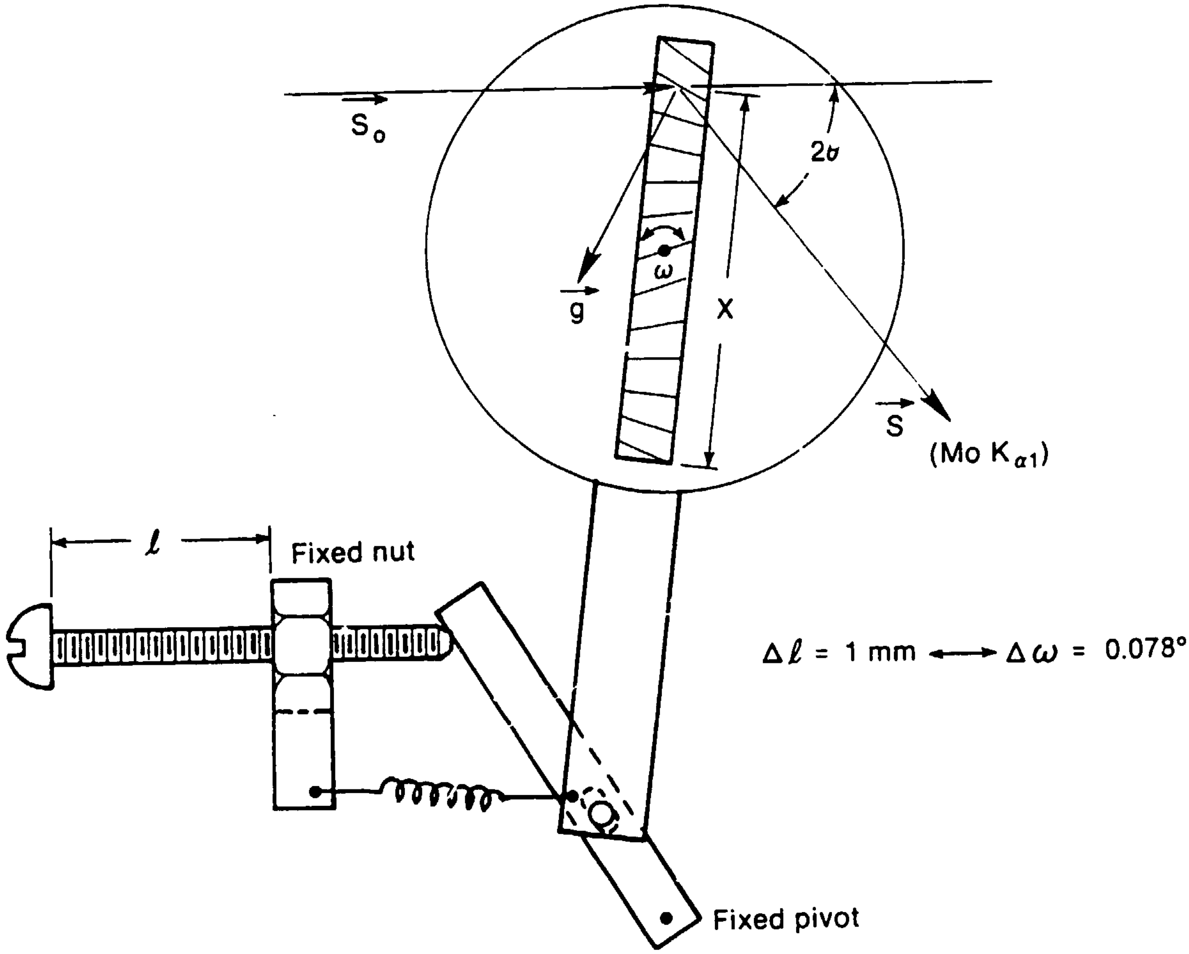


800
700
600
500
400
300
200
100
0
Lifetime (μ sec)
0
100
200
300
400
500
600
Cooling Rate (°C/min)
○ 6042301 (Dislocation Free,
2.4 ± 0.9 Ω-cm)

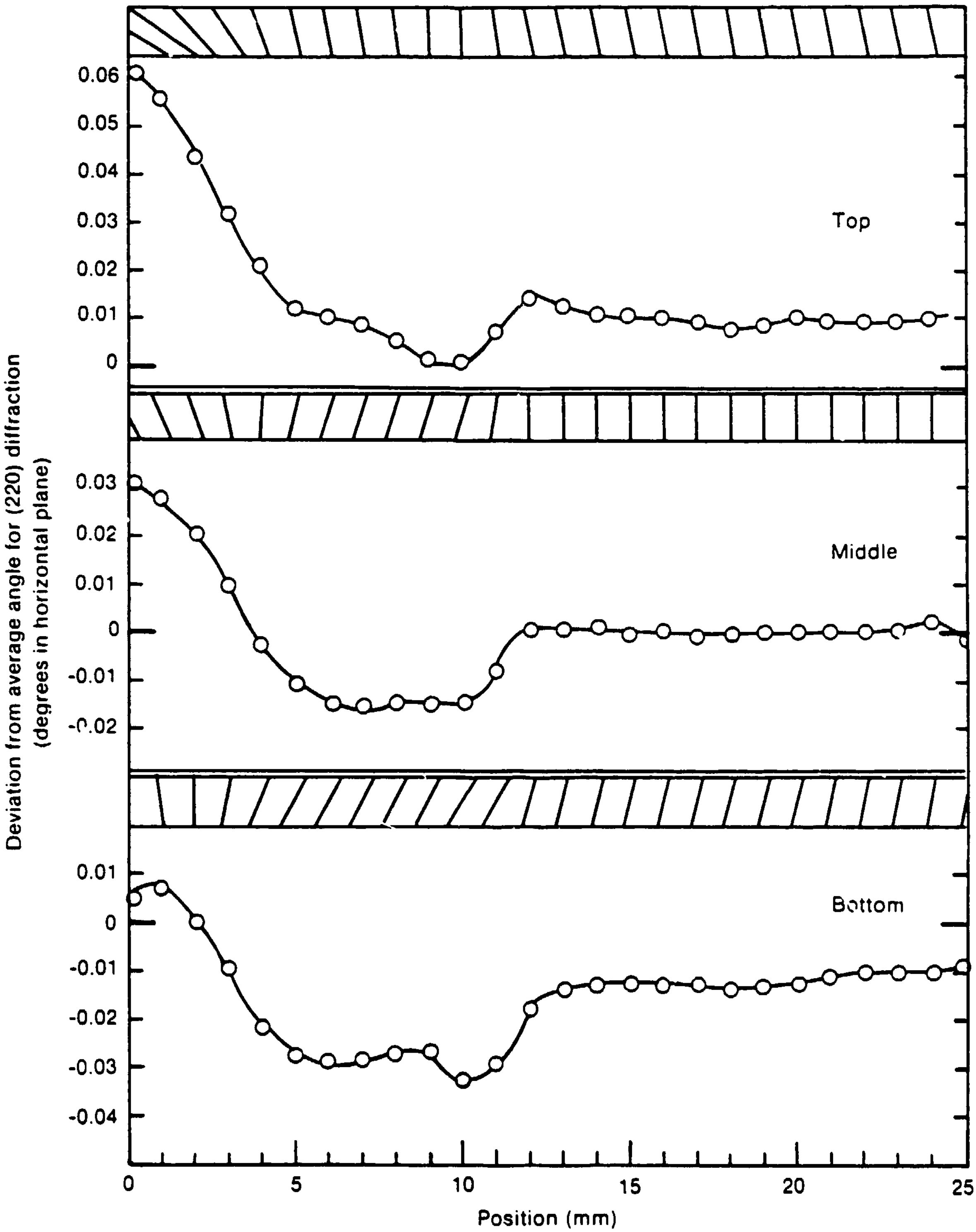


■ Al, 20 mm dia. poly Si vendor A
□ Al, 20 mm dia. poly Si vendor B
▼ B, 20 mm dia. poly Si vendor A
△ B, 20 mm dia. poly Si vendor B
● Ga, 20 mm dia. poly Si vendor A
○ Ga, 20 mm dia. poly Si vendor B
C Ga, 34 mm dia. poly Si vendor B
◆ In, 20 mm dia. poly Si vendor A
◇ In, 20 mm dia. poly Si vendor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

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



$\vec{S}_o$
2θ
ω
$\vec{g}$
X
$\vec{S}$
(Mo $K_{\alpha 1}$)
ℓ
Fixed nut
$\Delta\ell$ = 1 mm ⟷ $\Delta\omega$ = 0.078°
Fixed pivot


0.06
0.05
0.04
0.03
0.02
0.01
0
Top
0.03
0.02
0.01
0
-0.01
-0.02
Middle
0.01
0
-0.01
-0.02
-0.03
-0.04
Bottom
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.