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POTENTIAL PRODUCTIVITY BENEFITS OF FLOAT-ZONE vs CZOCHRALSKI CRYSTAL GROWTH

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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.

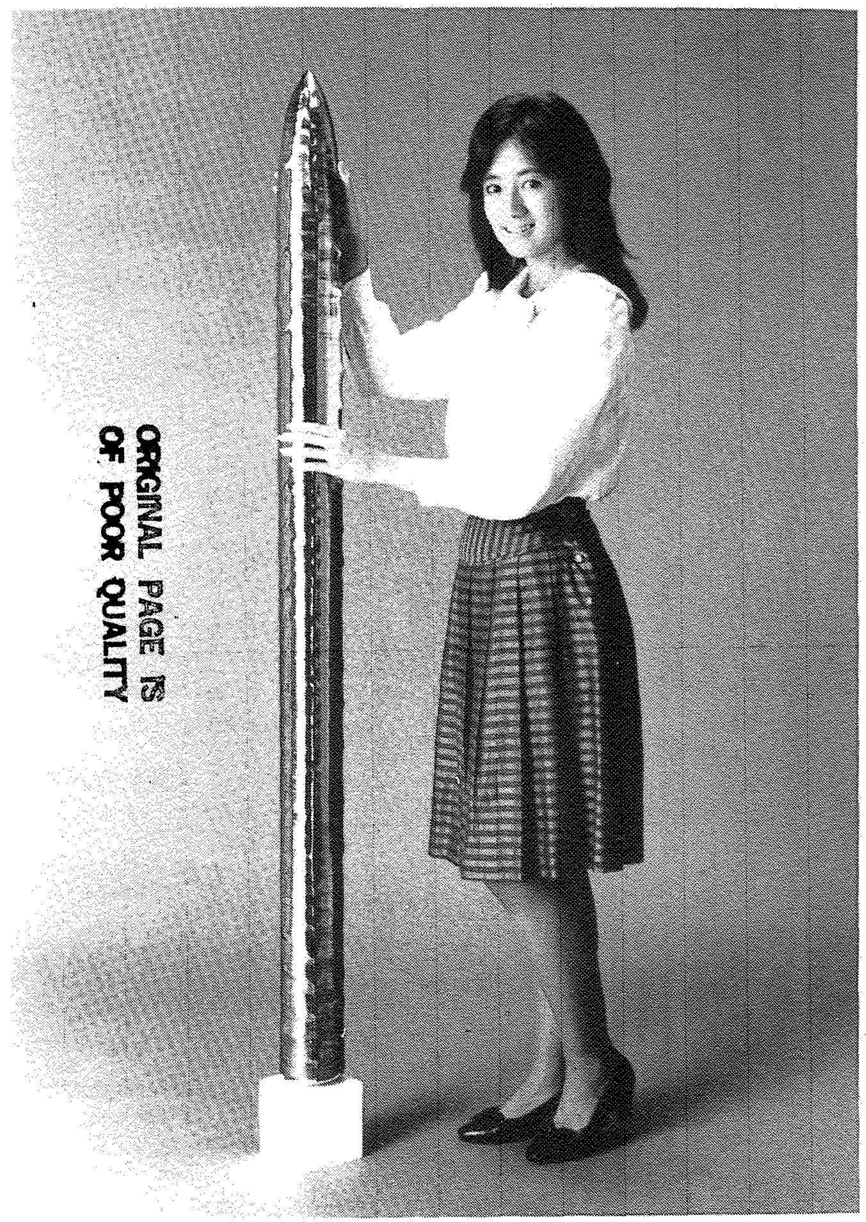
On the other hand, the possibilities of using the FZ method for mass production are described in this paper. Until now, this method has not been heavily used due to the technical and operational issues for growing crystals and the quality issues of the lack of intrinsic gettering (IG) and weakness from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

<u>CONTENT</u>:

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



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

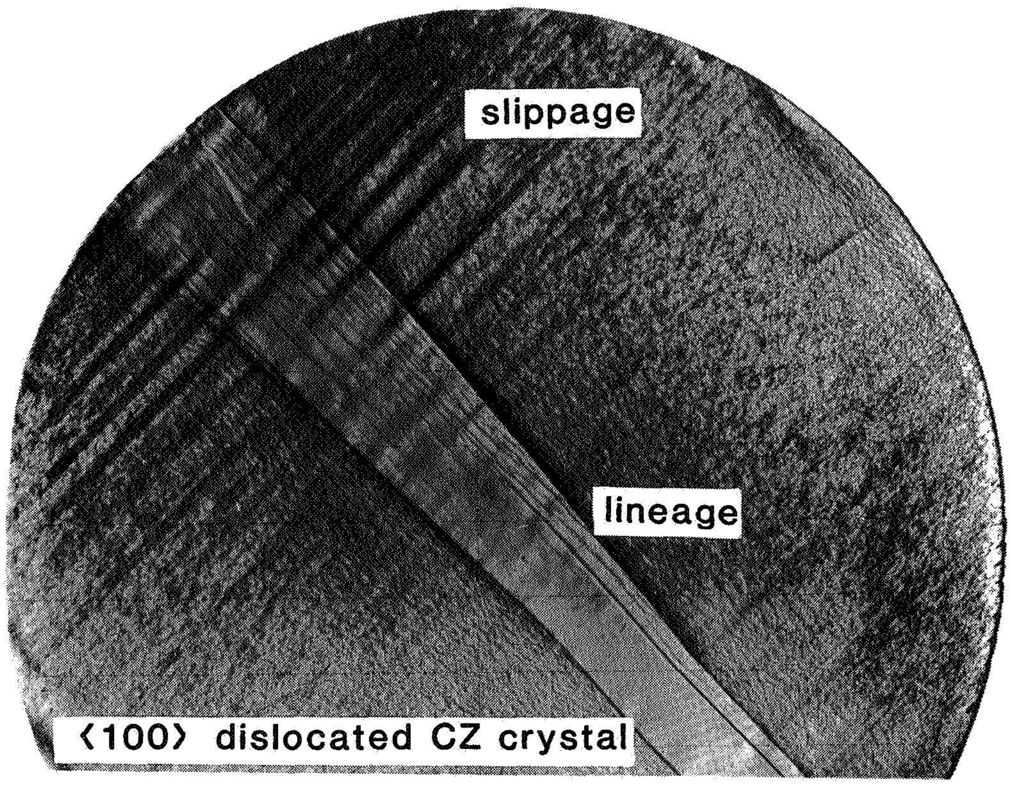
Growth Conditions in 5-in. FZ and Cz Methods

	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).



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

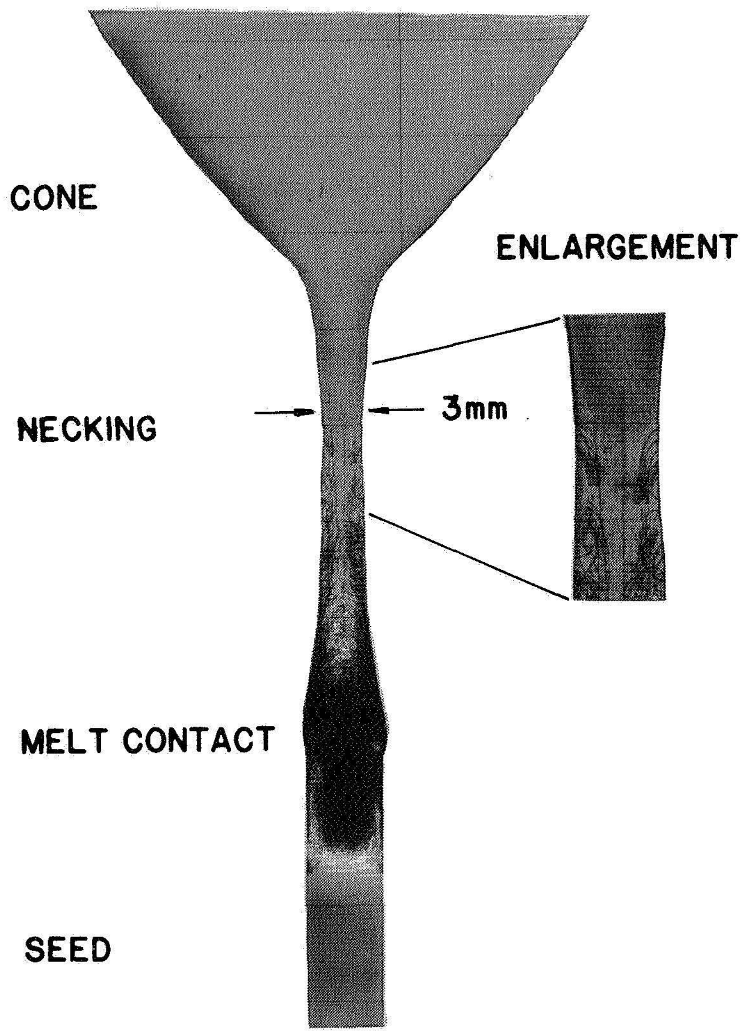
CRYSTAL DIAMETER (INCH)	5	6	7	8	9	> 10
CHARGED WEIGHT (KG)	30	45	60	80	100	>120
CRUCIBLE DIAMETER (INCH)	14	16	18	20	22	> 22

Keys for FZ Mass Production

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

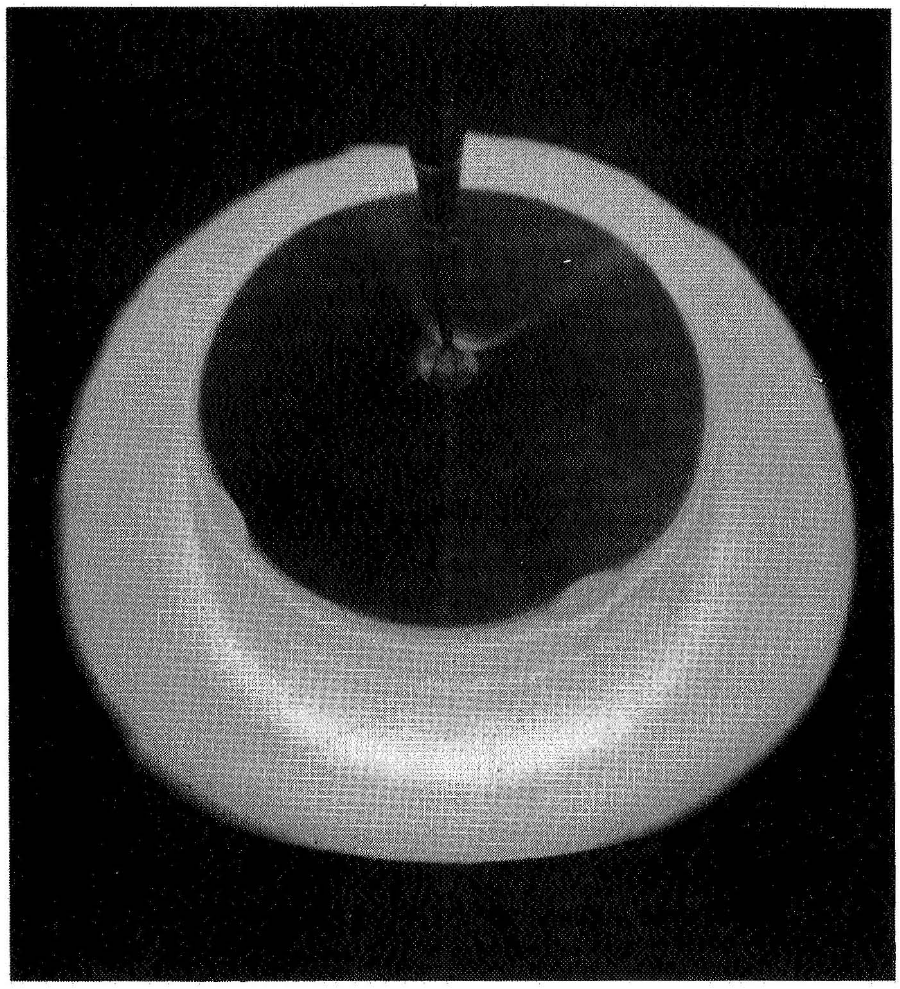
Crystal Quality

	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



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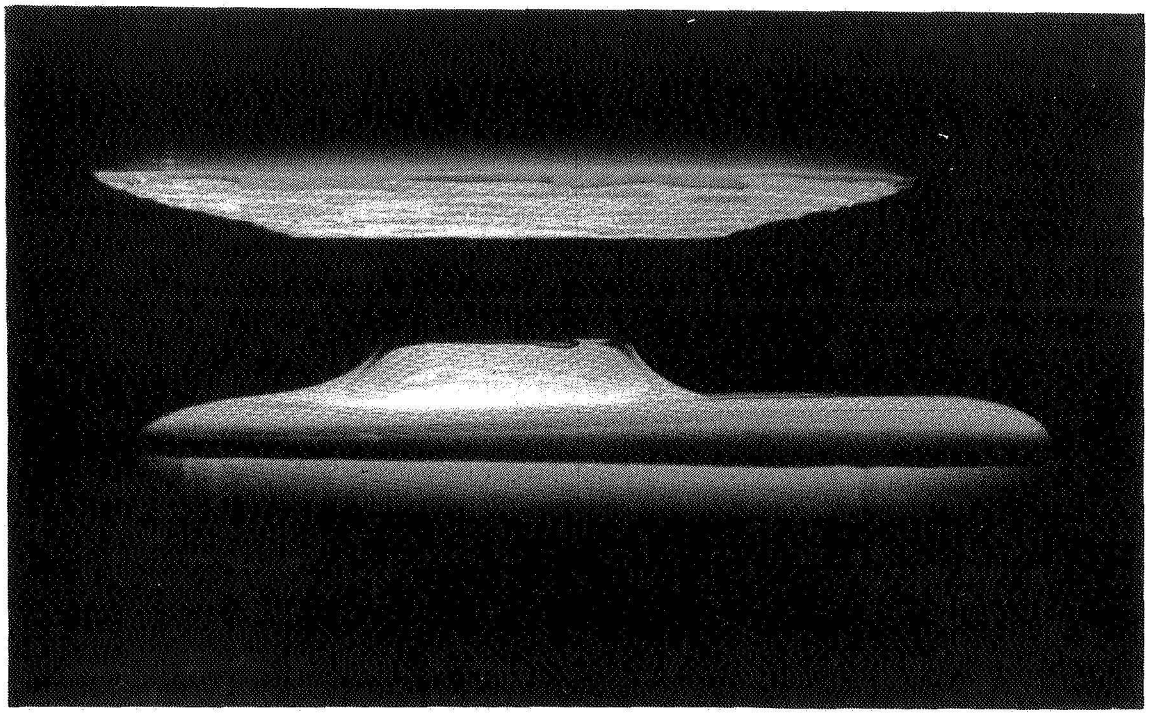
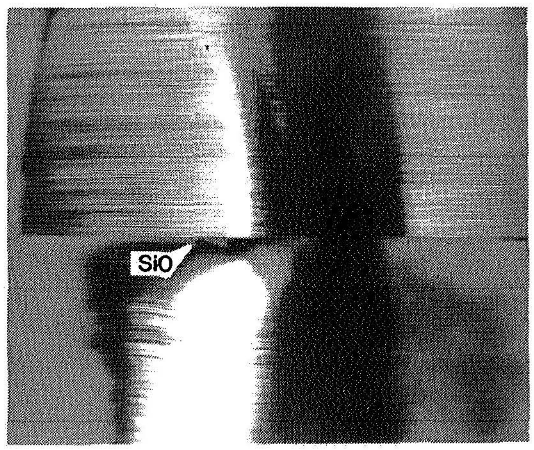
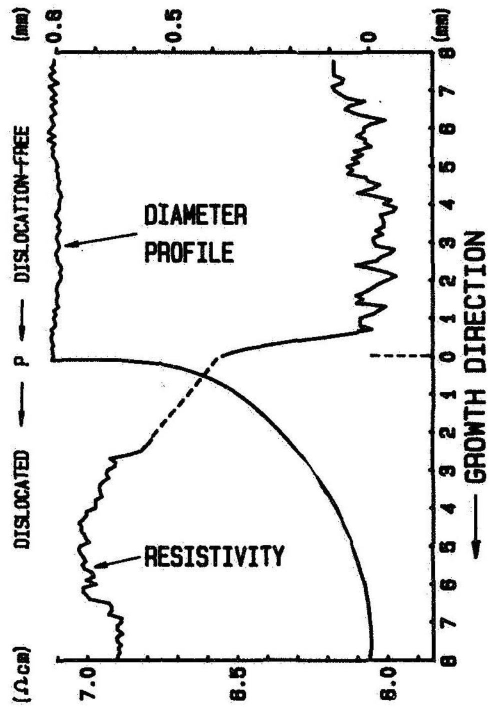


Growing 5-inch-diameter FZ crystal with <100> direction. Diameter is controlled by adjusting both feed and single-crystal movement. The emissivity of the molten zone is lower than that of the solid phase.

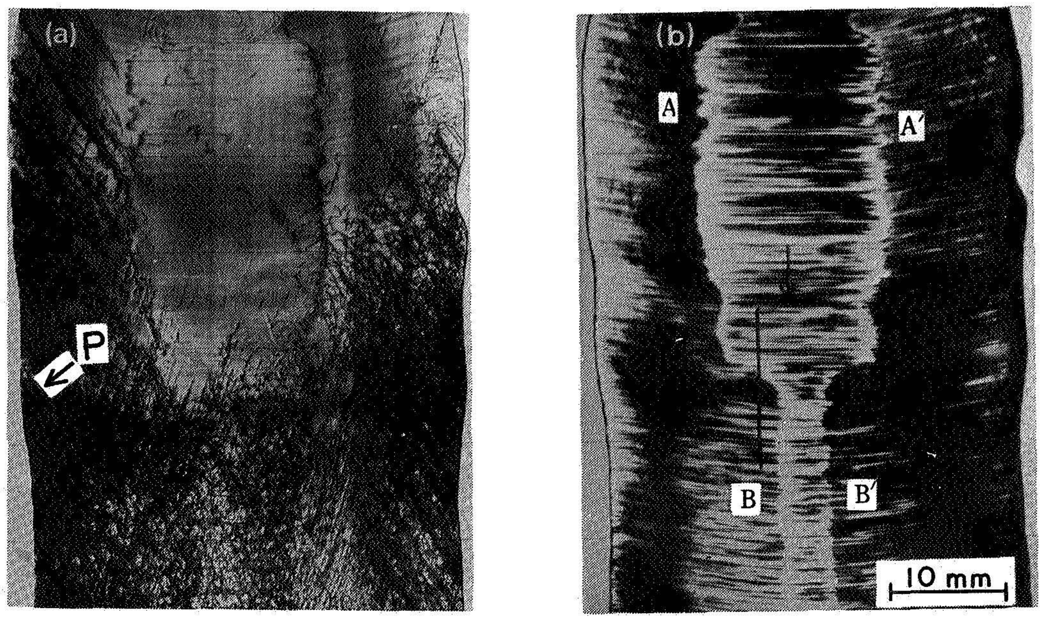
SURFACE MORPHOLOGY CHANGE FROM DISLOCATION-FREE TO DISLOCATED GROWTH



PHOTOGRAPH

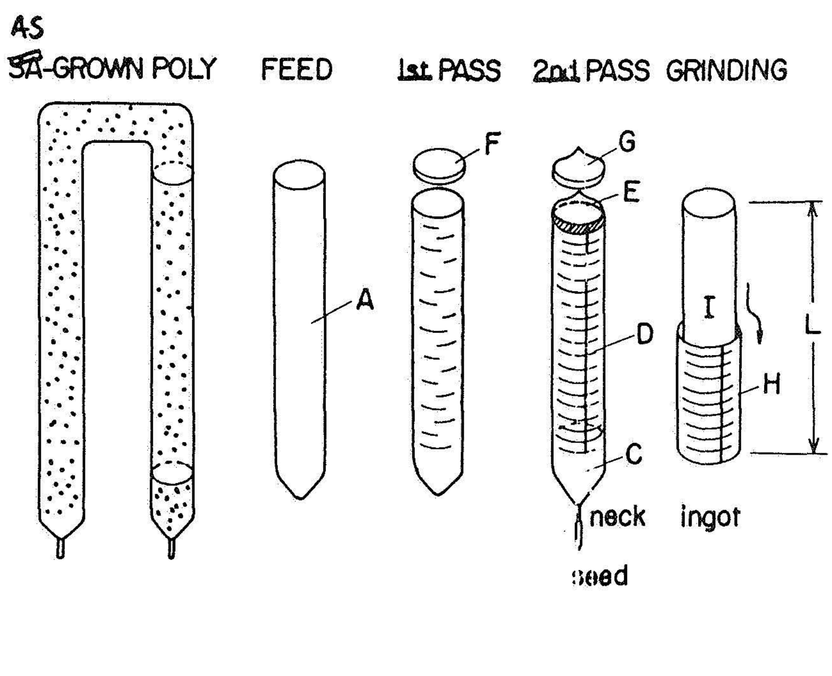


Surface morphology change from dislocation-free dislocated growth in <111> growth crystals with a concave shape interface toward the melt. (a) and (b) X-ray topographs (220 Ref. Moka) showing a crystal diameter (75 mm) with peripheral facet. Both decrease because of dislocation introduction, and lineages 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. MoKα_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

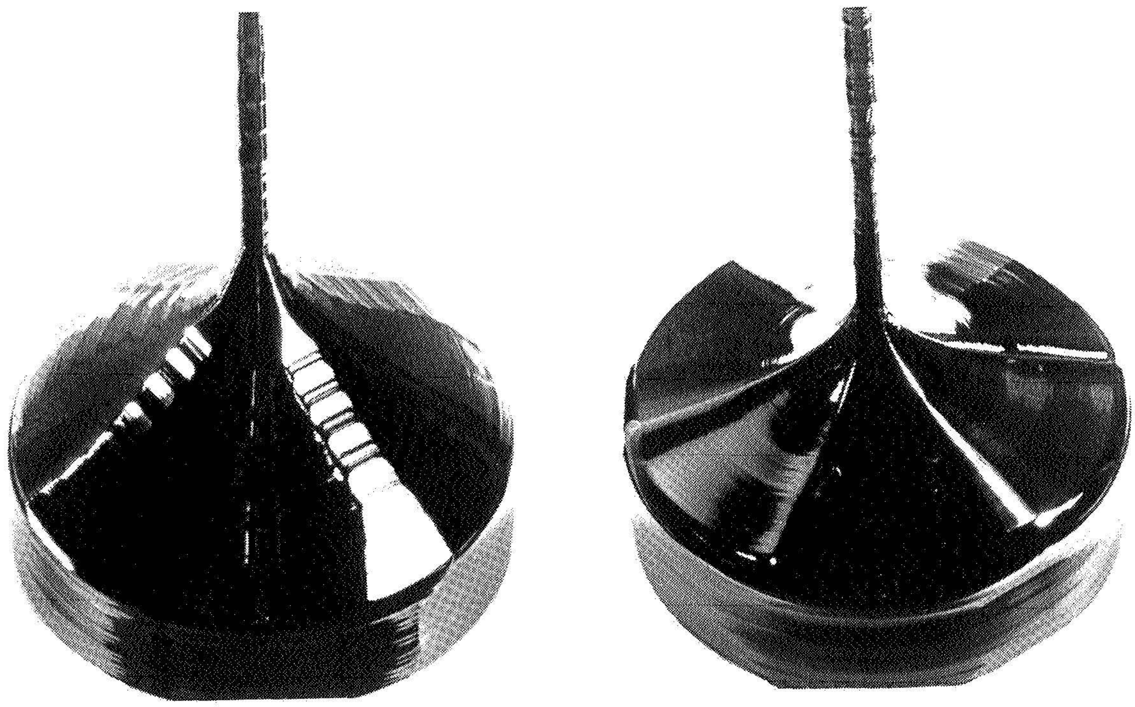
* 2 pass FZ shows higher single crystal yield than that of single pass FZ.

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	1.5 →		
	G	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 →



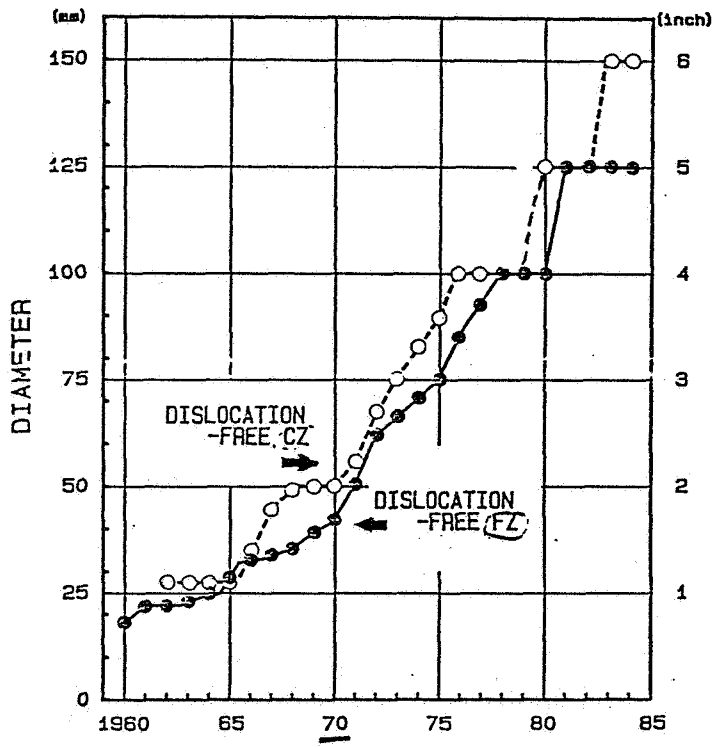
Photographs of necking and conical shaping of (a) <100> orientation and (b) <111> orientation. Dislocation-free grown crystals only give their brilliant crystal habit lines. Maximum weight for 3-mm-diameter necking crystal is estimated as 200 kg.

Summary

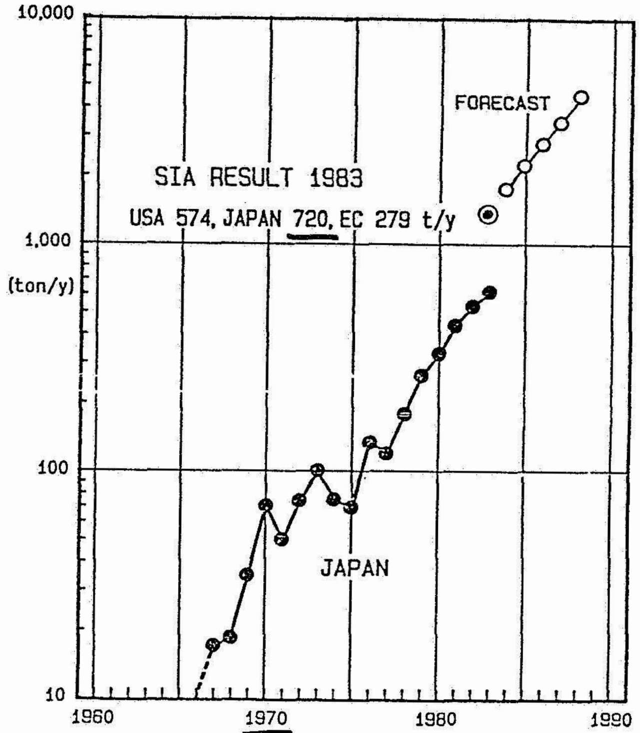
1. SINGLE CRYSTAL MASS PRODUCTION
   N-TYPE FOR C-MOS/MOS EPI

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

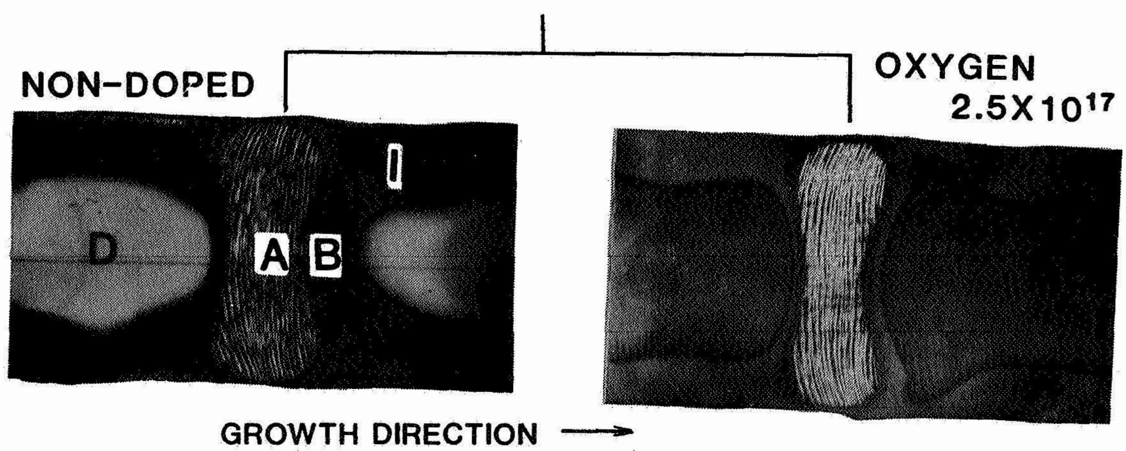
Maximum Diameter Trend in Production



Results and Forecast of Si Crystal Production

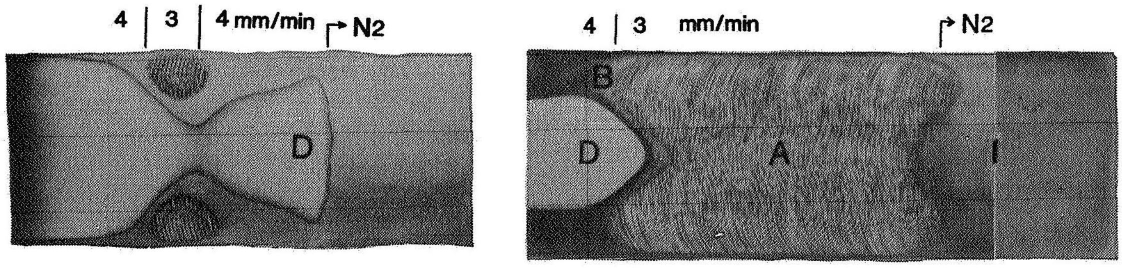


Swirls and D-Defects Formation: In-Situ Annealing (2 min)



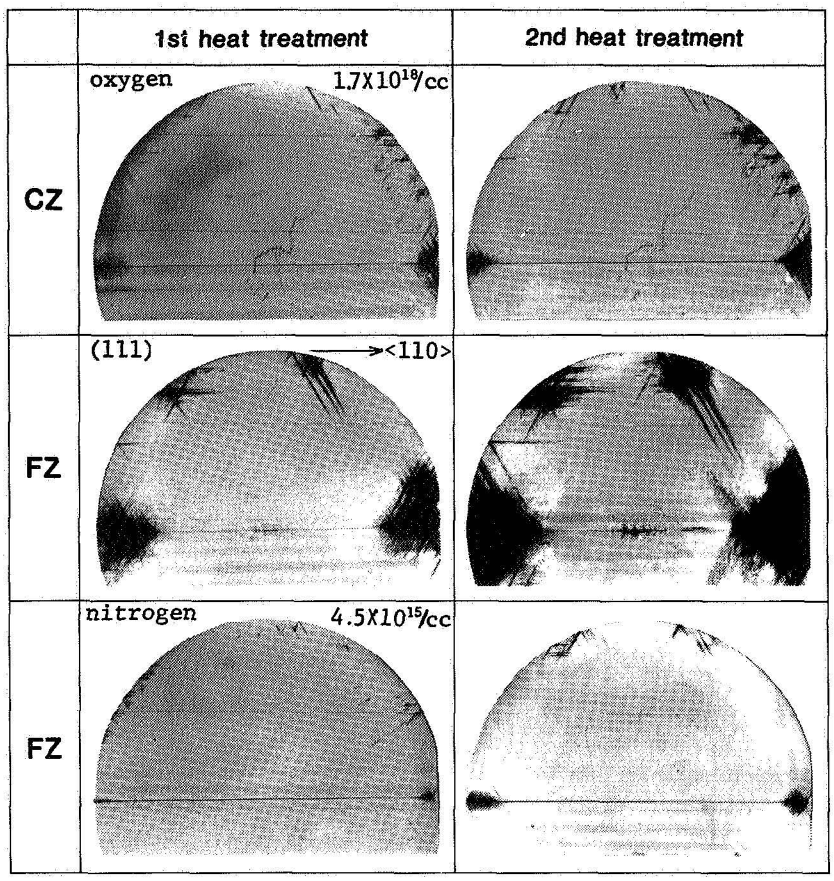
X-ray topographs of copper-decorated FZ crystals that were in situ annealed during growth. Right-hand crystal is oxygen doped with silica plate insertion into the melt.

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].)

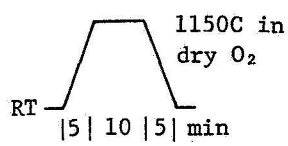
Effects of Nitrogen on Dislocation Nucleation and Movement in Silicon



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.

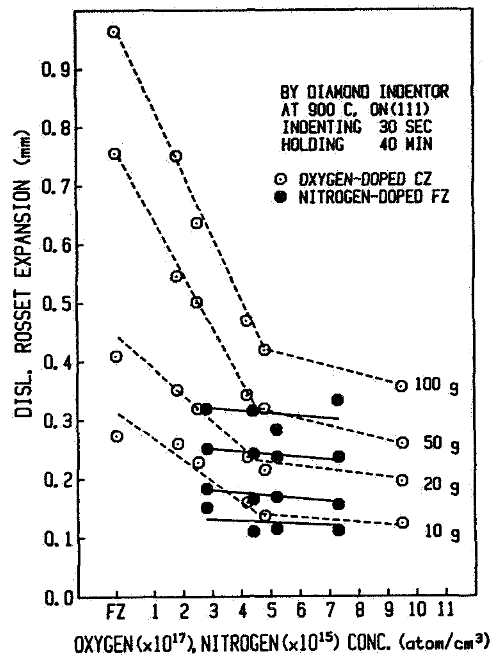
Real Problems for Mass Production

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

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

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

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

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

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

$d=2.33$ (g/cm)

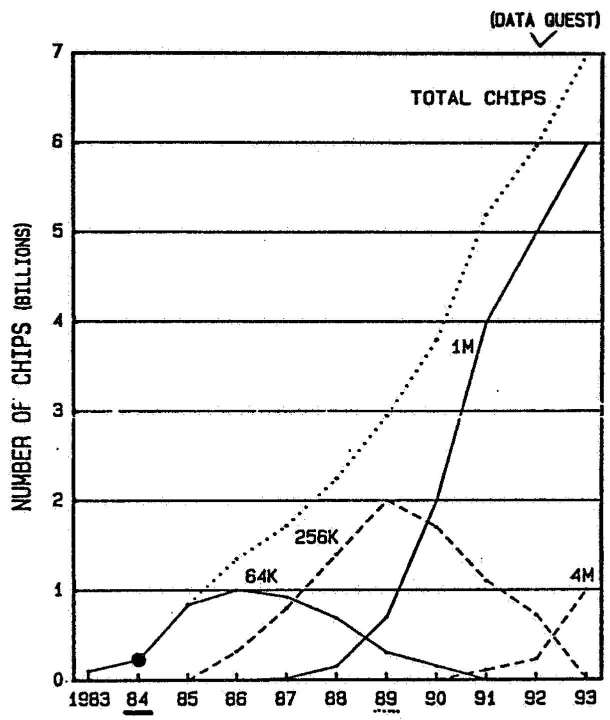
M = charged weight 30kg

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

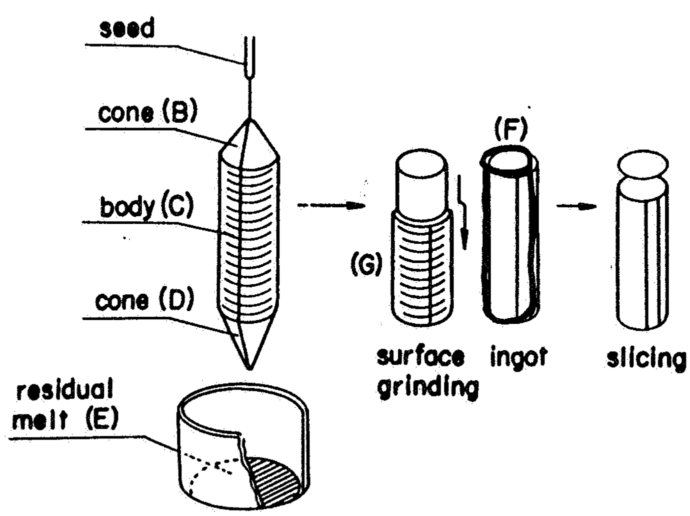
Dia x 0.7 = cone(B) length

Dia x 4 = cone (D) length

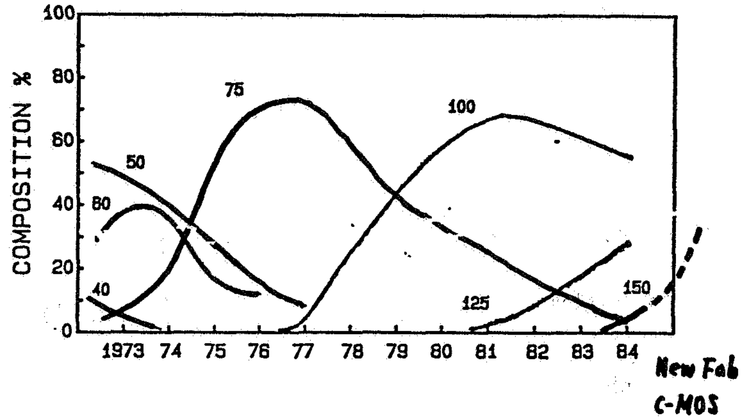
Worldwide D.RAM Demand Forecasts



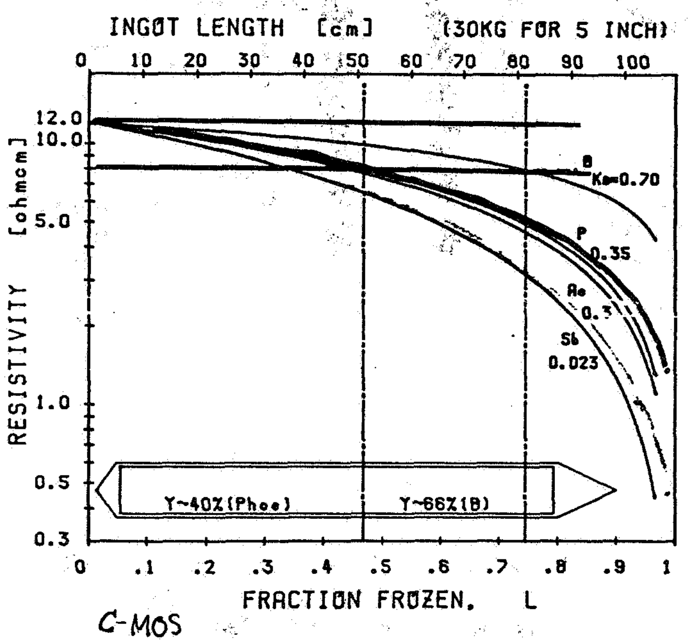
Cz Processing and Silicon Losses

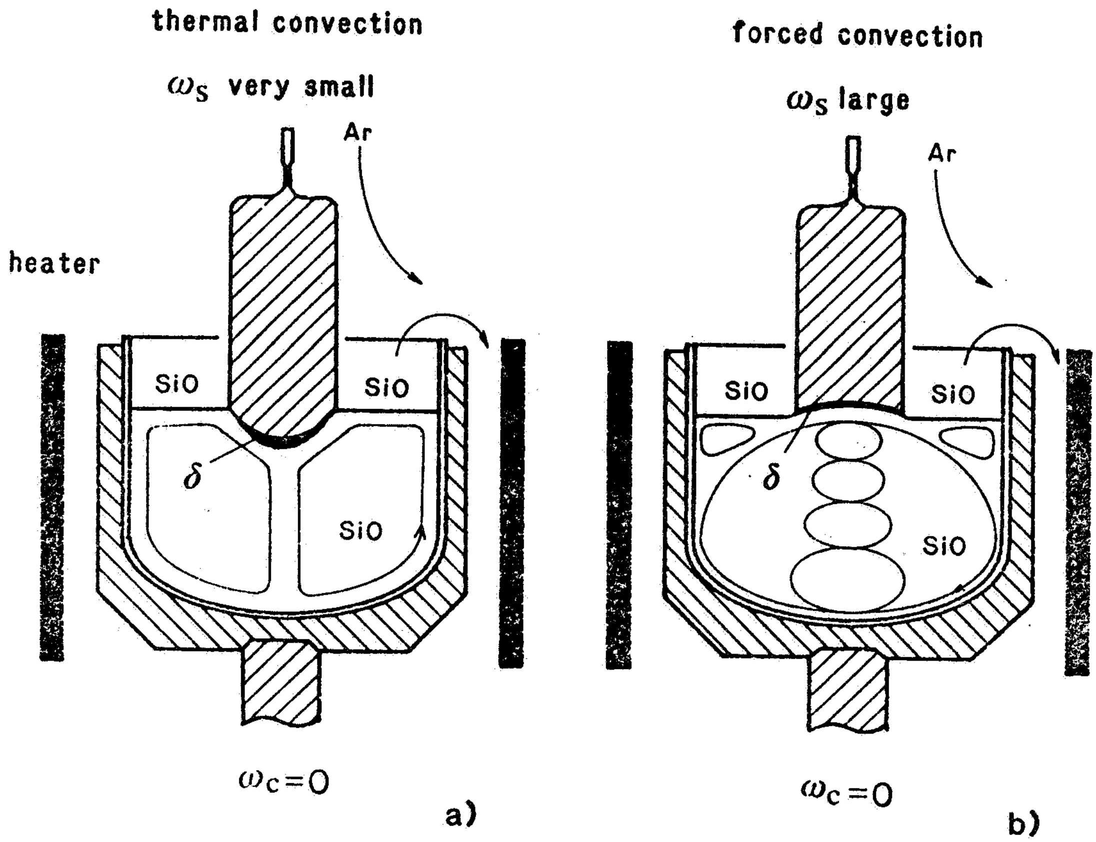


Silicon Wafer Diameter Trend (Area Gain)



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.