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RESEARCH AND DEVELOPMENT OF LOW COST PROCESSES FOR INTEGRATED SOLAR ARRAYS

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ABSTRACT

The current phase of the project is directed toward assembling adequate knowledge to permit the technical and economic feasibility assessment of competing process approaches which are expected to optimally fit into an extremely low cost, large volume process sequence leading to high efficiency solar arrays (Fig. 1). In this endeavor, one of the approaches investigated in the silicon reduction and purification area, namely the upgraded arc-furnace process, has both a much larger background of available information and appears technically and economically exceedingly attractive, so that it has now reached the stage of transition from preliminary feasibility studies to advanced experimentation, with significantly larger requirements for equipment and funding.

The emphasis has continued on the 2 areas of Si reduction and purification and of sheet generation. However, the work has recently been concentrated on gaining information about *one* reduction process combined with purification (higher purity arc furnace with gas blowing and gradient freezing; Dow-Corning) the transport process with purification and polycrystal sheet growth potential (SiF_2), on plastic deformation for sheet generation, and on float zone sheet recrystallization.

The previously unexplored Si transport properties of the SiF_2 reaction at atmospheric pressure have been further investigated. It has been firmly established that the SiF_2 gas can be moved without

decomposition at constant temperature both above 1000° C (see clear zone in deposition tube shown in Fig. 4) and below 100° C, with Si depostion occuring at the intermediate temperatures. Since the rate limiting step has been found to be the SiF_2 formation reaction, which is currently carried out at 1150° C, extrapolation through thermodynamic considerations indicates the possibility of obtaining increased transport rates (up to 0.75 g Si per of gas (STP) moved through the system) by raising the reaction temperature above the Si melting point. Considerable effort was spent in purifying the SiF_4 gas which was found to contain O_2 and other impurity gases, as purchased. This purification eliminated the formation of fluorosilicate byproducts which have been depositing in the piping system, but did not otherwise significantly affect the transport reaction.

Considerable progress was made in the exploration of the high temperature mechanical properties of polycrystalline Si, with the objective of assessing the feasibility of plastic deformation, such as rolling. Data are being accumulated to generate "forming limit diagrams" with temperature and strain rate as parameters. Such diagrams have been recently introduced as design tools in metal forming (Fig. 6). The experiments carried out by axial compression of Si cylinders at temperatures from 1250 to 1350° C have shown that the method of forming limit diagrams is also applicable to silicon. Deformations by up to 70% at strain rates up to 1%/s have indicated that plastic deformation of Si may be a suitable forming method (Fig. 7). Earlier problems with the anisotropic crystal structures in the "polyrods" resulting from the $SiHCl_3$ purification process (Fig. 8) have been overcome by raising temperature and strain. Also, crystallization has been observed to take place, including grain growth by an order of magnitude (Figures 9 and 10).

The float zone recrystallization equipment to be used for the exploration of the conversion of polycrystalline sheet to single crystal sheet by, heating with a planar electron beam is now completed, with experimentation scheduled to begin (Fig. 12).

The investigation of solution growth processes has been tentatively terminated with the finding that the known solvents for properties which do not appear to be conducive to fast growth rates of sheets of high semiconductor quality (Fig. 14).

In preparation for the ultimate economic analysis of competing processes, a thorough economic evaluation, with evolution forecast, of the Czochralski process as a baseline has been carried out, with the result that the primary limiting item is the crucible cost due to the current one time use. Re-use potential may lead to an ultimate single crystal cost near \$13. -/m^2 without cutting or device processing costs, in lieu of approximately \$25. -/m^2 with one time use of the crucible. This assumes the availability of \$4. -/kg polycrystal Si (Fig. 15).

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(PRECEDING: $317,005)

PRINCIPAL INVESTIGATORS

M. WOLF/L. CROSSMAN

OBJECTIVE

DEMONSTRATE FEASIBILITY OF NEW TECHNOLOGY
SUITABLE FOR INTEGRATED PROCESS (QUARTZ SAND TO ARRAY)
YIELDING HIGH EFFICIENCY Si ARRAYS AT $15.00 TO 40.00/$M^2$.

CURRENT PHASE:

ASSEMBLE ADEQUATE INFORMATION TO PERMIT
TECHNO/ECONOMIC ASSESSMENT OF PROCESS ALTERNATES
BEFORE START OF PROCESS DEVELOPMENT.

CARRY OUT EXPERIMENTAL RESEARCH
ON HIGH POTENTIAL APPROACHES, NOT ALREADY UNDER
DEVELOPMENT ELSEWHERE, TO OBTAIN NECESSARY INFORMATION.

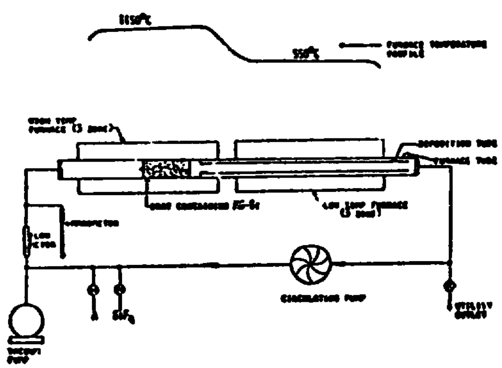
FIGURE 1

PLANNED ACTIVITY-PAST 6 MONTH PERIOD

PLAN	ACTION
1.1 SiF_2 TRANSPORT PROCESS:	
A) DETERMINE OPTIMUM DEPOSITION TEMPERATURE	'RATE(T) DETERMINATION PROGRESSING, NOT RATE LIMITING STEP.
B) DETERMINE TRANSPORT DISTANCE AND TEMPERATURE BEFORE DECOMFOSITION	'EXPERIM'N CONTINUING WITH EQUIPMENT MODIFICATION.
C) ELUCIDATE REACTION KINETICS	'GAS PURIFICATION INSTITUTED. EXPERIMENTATION CONTINUING.
D) DETERMINE IMPURITY SEPARATION	'IN PROGRESS.
1.2 STUDY ARC FURNACE TECHNOLOGY, METAL REDUCTIOM AND ELECTROLYSIS OF SI, SILICATES AS RAW MATERIALS.	'TECHNOLOGY ASSESSED, WORK ON ELECTROLYSIS, METAL REDUCTION. SILICATES TENTATIVELY TERMINATED.
1.3 PRFPARE EQUIPMENT FOR MET-GRADE SI UPGRADING	'EXPERIMENTATION INITIATED.
2.1 COMPLETE MOLTEN ZONE REGROWTH APPARATUS AND START EXPERIMENTATION.	'APPARATUS COMPLETED.
2.2 STUDY SOLUTION GROWTH OF SI LAYERS.	'PROPERTIES OF BINARY SOLUTIONS TABULATED, WORK TENTATIVELY TERMINATED.
2.3 STUDY PLASTIC DEFORMATION (ROLLING OF SI AND GRAIN GROWTH METHOD).	'HIGH TEMPERATURE PROPERTIES OF SI BEING DETERMINED.
2.4 COMPLETE PROCESS EVALUATION METHOD.	'CZOCHRALSKI PROCESS ANALYZED AS BASE LINE.

FIGURE 2

SiF_4/SiF_2 TRANSPORT PROCESS



OB. .TIVE

• DEVELOP LOW COST PROCESS FOR CONVERTING MG-Si TO SOLAR GRADE POLYCRYSTAL SHEET

GOALS

• DETERMINE IF TRANSPORT RATES COMMENSURATE WITH PRODUCTION GOALS ACHIEVABLE

• DETERMINE IF ADEQUATE PURIFICATION ACHIEVABLE

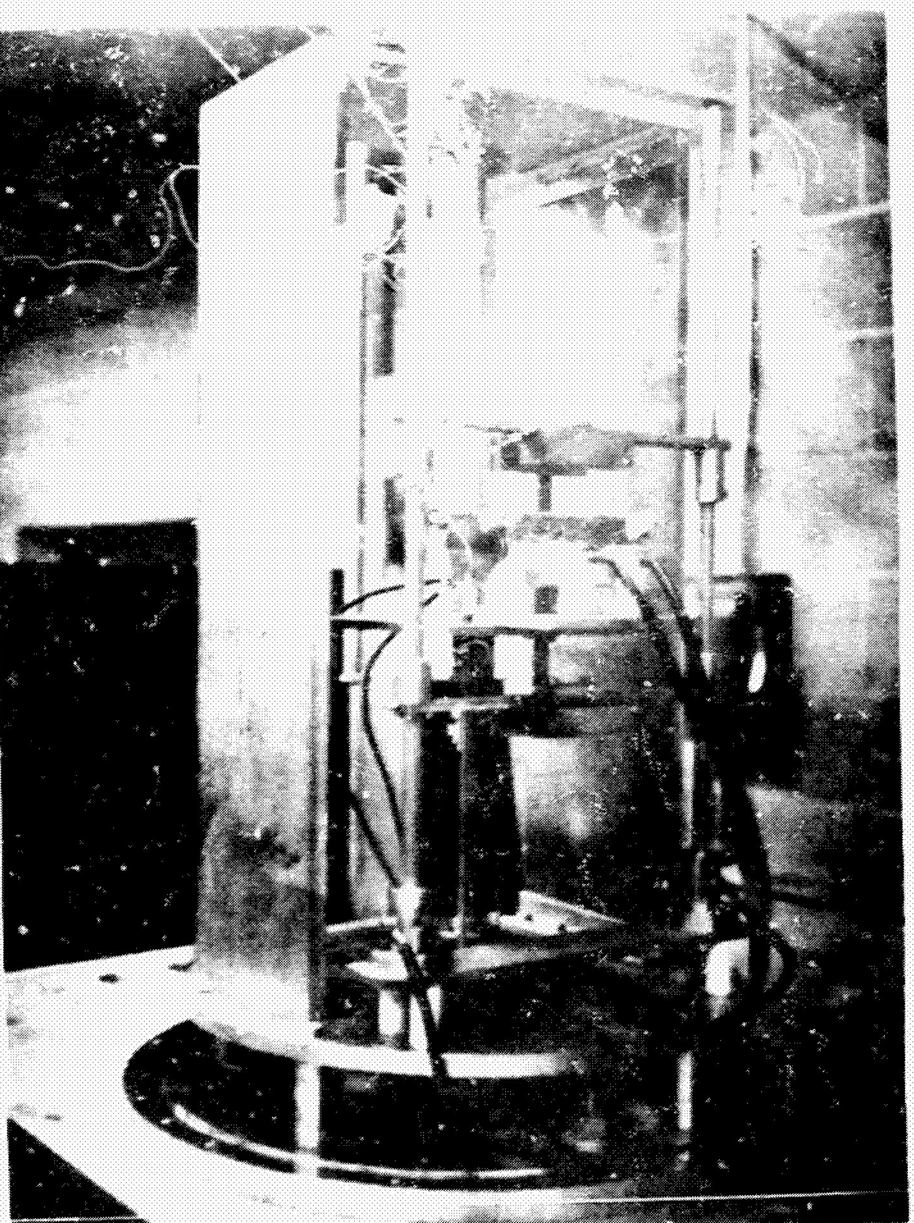
• ESTABLISH OPTIMUM MEANS FOR COUPLING TO SUBSEQUENT PROCESSES (EPITAXIAL GROWTH, ETC.)

PROGRESS

• EFFECTIVE TRANSPORT POSSIBLE AT ATMOSPHERIC PRESSURE:

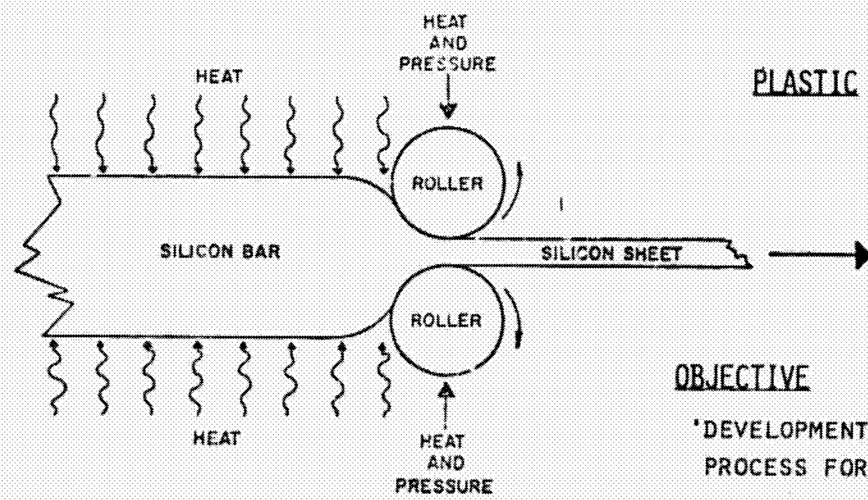
1. Si TRANSPORT RATE $\geq$ 0.05 G/ℓ GAS MOVED
2. NO SiF_2 DECOMPOSITION FOR 3 S ABOVE 1100°C
3. NO SiF_2 DECOMPOSITION OVER 50 CM AT 250°C, FOLLOWED BY DEPOSITION AT 550°C.
4. RATE LIMITING STEP: Si DISSOLUTION
5. WIDE TEMP. RANGE FOR DEPOSITION: 500 - 1000°C
6. DECOMPOSITION INDEPENDENT OF FILM THICKNESS
7. RECRYSTALLIZATION OF AMORPHOUS DEPOSIT OBSERVED
8. DEPOSITION RATE APPROX. EQUAL ON Si WAFERS, SiO_2 WAFERS, HOT TUBE WALLS
9. INFLUENCE OF IMPURITY GASES NOT OBVIOUS.
10. PRELIMINARY IMPURITY ANALYSES INCONCLUSIVE

FIGURE 3



ELECTRON BEAM ZONE MELTING APPARATUS (PIERCE GUN)

PLASTIC DEFORMATION OF SILICON



OBJECTIVE

- DEVELOPMENT OF HIGH SPEED SOLID STATE PROCESS FOR SILICON SHEET FORMATION

GOALS

- INVESTIGATE SI PLASTICITY AT TEMPERATURES BELOW MELTING POINT.
- DETERMINE PROCESS RATE.
- ESTABLISH MATERIALS AND PROCESS PARAMETERS TO DEMONSTRATE WORKING FEASIBILITY.
- DETERMINE PRODUCT CHARACTERISTICS (ELECTRICAL, ETC.)
- OPTIMIZE PRODUCT MORPHOLOGY.

PROGRESS

- FORMING LIMIT DIAGRAM FOR SILICON BEING DETERMINED.
- POLYCRYSTALLINE SILICON UNIAXIALLY COMPRESSED AT DEFORMATION RATES $\leq$ 1% PER SECOND.
- CRYSTALLOGRAPHIC TEXTURE OF POLYCRYSTALLINE SILICON ($SiHCl_3$ PROCESS) DETERMINED - (X-RAY DIFFRACTOMETER).
- GRAIN GROWTH OBSERVED AFTER ANNEALING AND STRAINING, GRAINS UP TO 1MM DIAMETER.

FIGURE 5

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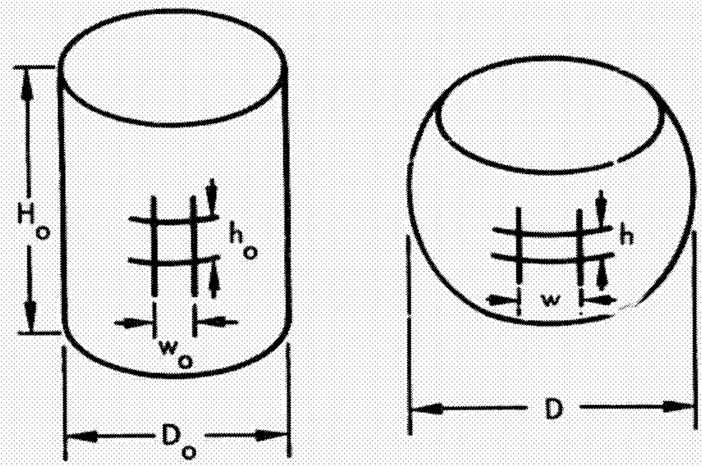
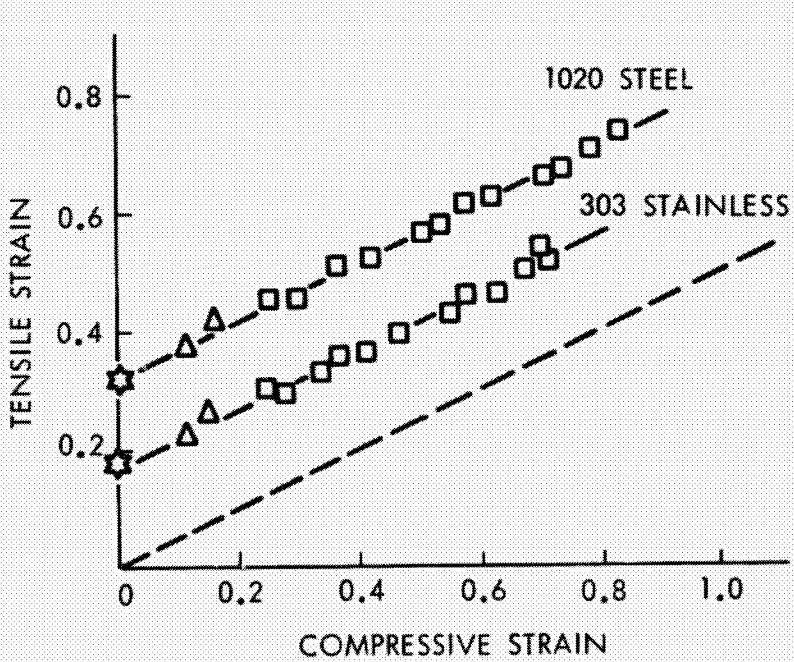
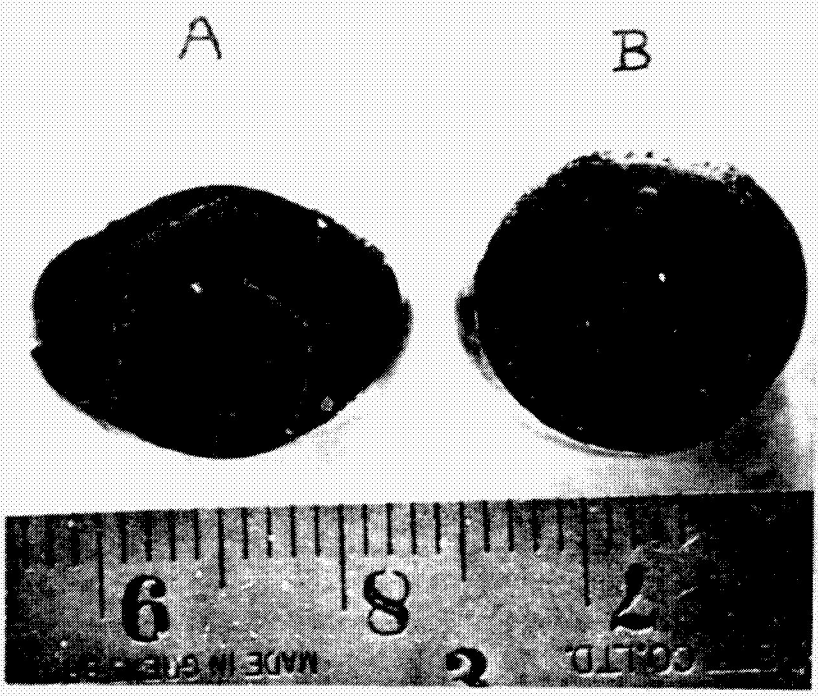


AXIAL STRAIN $\epsilon_z = \ln (h/h_o)$

HOOP STRAIN $\epsilon_\theta = \ln (w/w_o)$ or $\ln (D/D_o)$

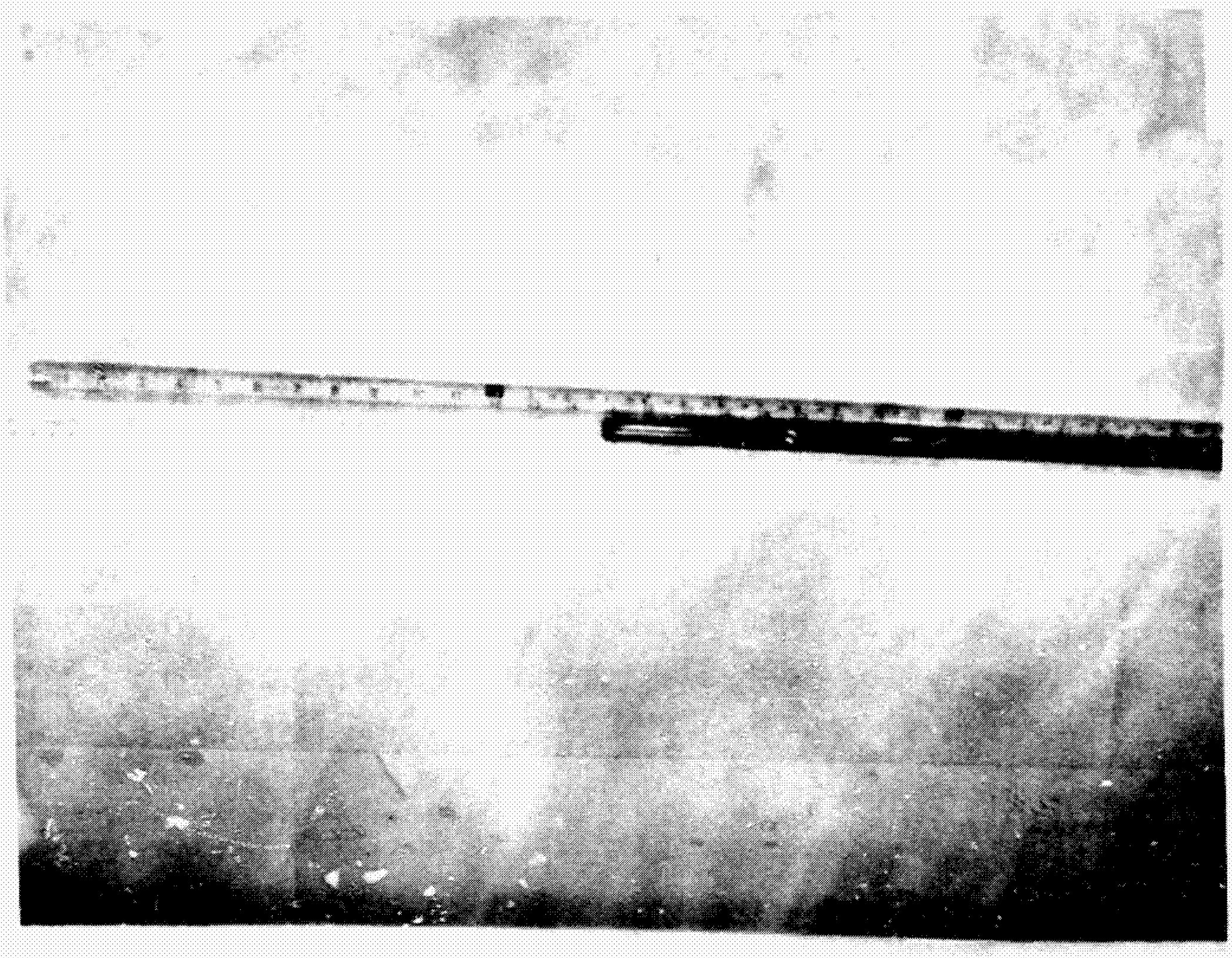




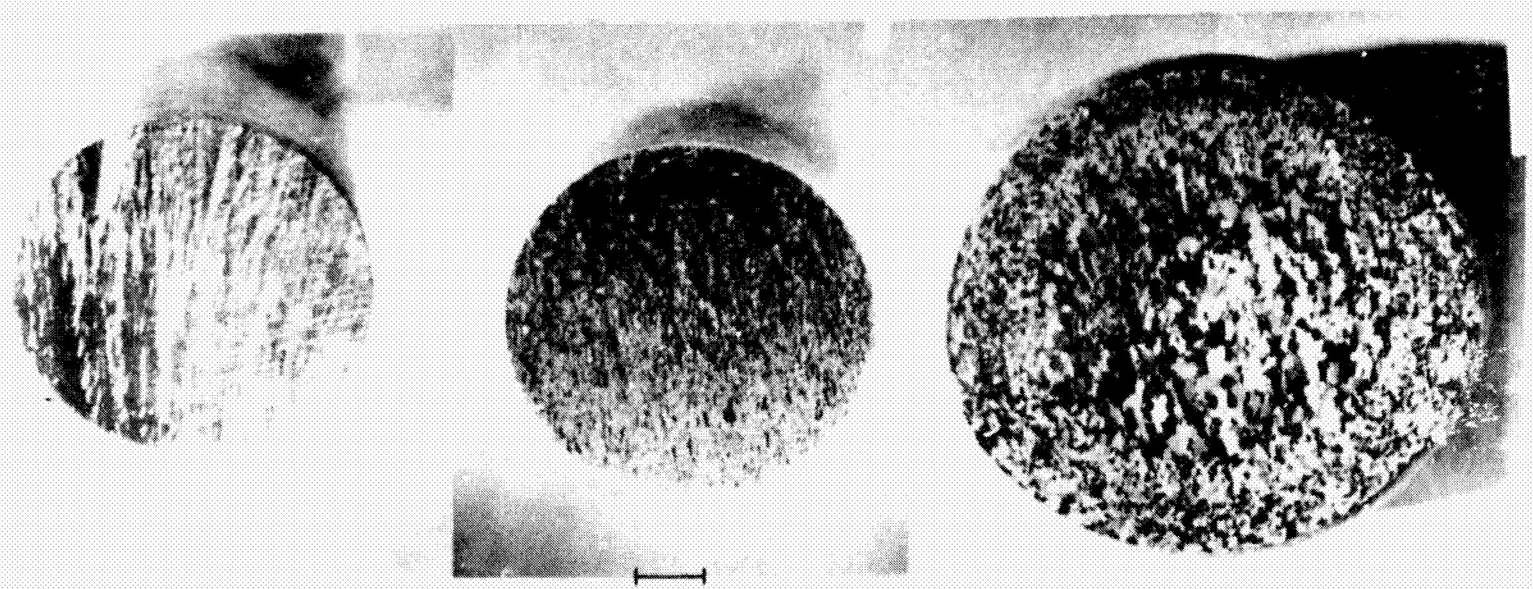
ANISOTROPIC DEFORMATION

A. 40% DEFORMATION AT 1280°C

B. 40% DEFORMATION AT 1350°C



HIGH TEMPERATURE (>1000°C)
SiF_2 TRANSPORT

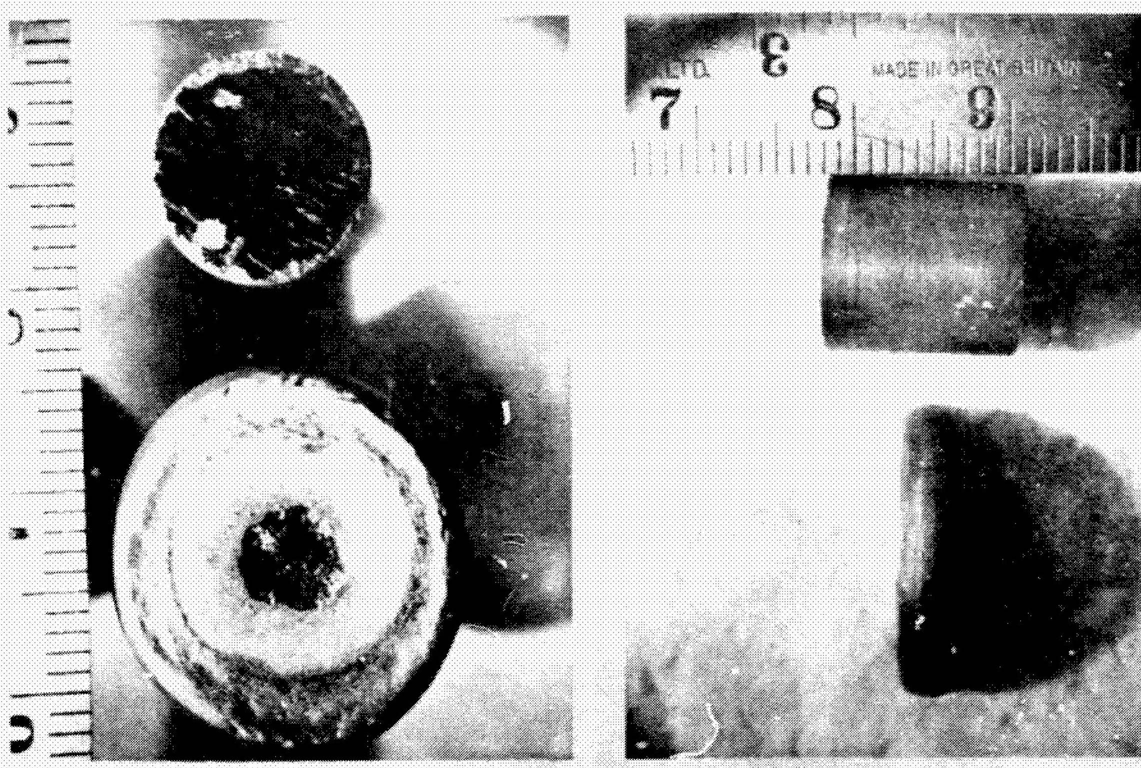


RECRYSTALLIZATION

AS RECEIVED

(b) ANNEALING
OF (a)
T= 1350°C
Δt= 4 HRS.

(C) ANNEALING AF[illegible]
PLASTIC
DEFORMATION
T = 1350°C
Δt = 4 HRS.



(a) TOP VIEW (b) SIDE VIEW

PLASTIC DEFORMATION

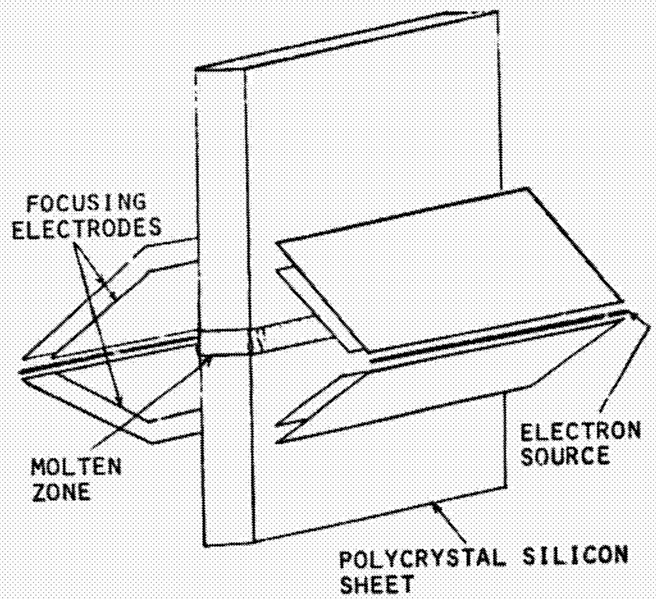
$\dot{\varepsilon} = 10^{-3}\ SEC^{-1}$

$T = 1350^{\circ}\ C$

$\sigma = 10\ Kg \cdot mm^{-2}$ (15×10^{3} P.S.I)

$\Delta L \cdot L^{-1} = 70\ \%$

FLOATING MOLTEN ZONE RECRYSTALLIZATION



OBJECTIVE

- PRODUCE SINGLE CRYSTAL SHEET FROM FINE GRAIN POLYCRYSTALLINE SI SHEET.

GOALS

- PRODUCE STABLE FLOATING MOLTEN ZONES IN SHEET DOWN TO 100 µM THICKNESS.
- DEMONSTRATE ADEQUATE RECRYSTALLIZATION RATE WITH ACCEPTABLE MORPHOLOGY.
- DEMONSTRATE COMPATIBILITY OF PROCESS WITH CONTINUOUS FLOW CONCEPT.

PROGRESS

- MAXIMUM THEORETICAL RECRYSTALLIZATION RATE AND CORRESPONDING E-GUN OPERATIONAL PARAMETERS DETERMINED.
- CONSTRUCTION OF MOLTEN ZONE REGROWTH APPARATUS COMPLETED.

FIGURE 11

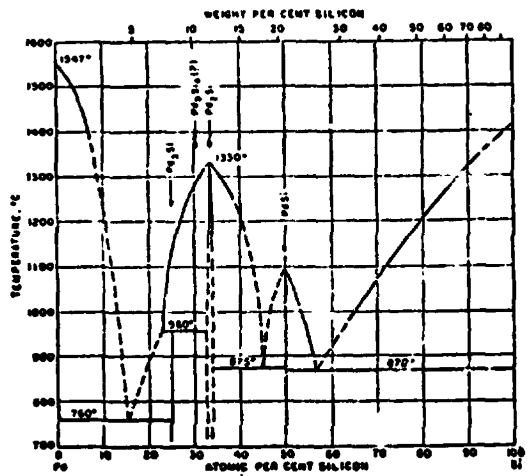
GRAIN SIZE

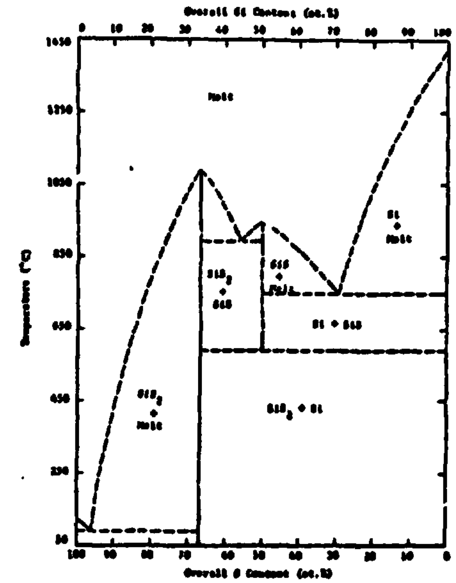
(a) AS RECEIVED

(b) ANNEALING OF (a)
T = 1350°C
Δt = 4 HRS.

(C) ANNEALING AFTER PLAS. DEFORMATION
T = 1350°C
Δt = 4 HRS.

BINARY SOLUTION GROWTH OF SILICON





OBJECTIVE

- LOW TEMPERATURE GROWTH OF SILICON SHEET

GOALS

- SURVEY POTENTIAL BINARY SYSTEMS, DETERMINE SUITABILITY
- DETERMINE IF ACCEPTABLE GROWTH RATES ACHIEVABLE
- DETERMINE IF ACCEPTABLE MATERIAL PROPERTIES ACHIEVABLE
- ESTABLISH OPTIMUM BINARY SYSTEM

PROGRESS

- PROPERTIES OF POTENTIAL SOLUTIONS TABULATED AND GROUPED.
- EXPERIMENTAL WORK POSTPONED.

FIGURE 13

CANDIDATE MATERIALS FOR SILICON SOLUTION GROWTH

I M.P. ≤ 6?0°C LIQ. SOL'Y. ≤ 5% AT M.P.	II M.P. ≥ 950°C LIQ SOL'Y. HIGH	III M.P. ≤ 950°C; LIQ. SOL'Y. HIGH ELECTR. ACTIVE OR LIFETIME KILLER
Bi In Pb Sn Zn	As Cr Ni Th B Fe O Ti Ba Hf P U Be Hg Pt V C Mg Pu W Ca Mn Re Y Ce Mo Sr Zr Co Nb Ta	Ag Al Au Cu Ga Li Sb

600° ≤ M.P. ≤ 950°C LIQ. SOL'Y. HIGH, NEUTRAL	Si ALLOYS NOT CHARACTERIZED
S (?) Pd	Cd N Pr Se Cs Na Rb Sm Ir Nd Rh Te K Np Ru Tl La Os Sc Yb

FIGURE 14

ATTRIBUTE	CURRENT DATA	PROJECTED DATA		
CRYSTAL DIAMETER, INCHES	3	4	6	8
WAFER THICKNESS, MM	0.4	0.24	0.20	0.20
KERF, MM	0.28	0.16	0.12	0.12
QUARTZ CRUCIBLE COST, $/KG	19.19	12.00	12.00	12.00
REPLACEMENT PARTS, $/KG	11.96	5.60	3.60	3.45
CAPITAL COSTS, $/KG	9.81	4.68	3.00	2.87
ALL OTHER DIRECT COSTS, $/KG	6.68	3.78	1.96	1.43
SILICON AT $4/KG	5.50	5.50	5.50	5.50
COST OF CYL. SILICON, AFTER 20% G&A	62.79	36.77	30.17	29.20
WAFER COST, $/M^2	113.65	42.44	25.64	24.82

FIGURE 15. CZOCHRALSKI GROWTH COST SUMMARY

PROBLEMS

1. LOW SUPPLIER INVENTORIES AND LONG DELIVERY TIMES CAUSE DELAYS.
2. SiF_4 AND SI PURITY
3. SHORT GRANT PERIODS PREVENT PH.D. THESIS USE.

STAFF

	SiF_2 TRANSPORT		PLASTIC DEFORMATION		RECRYSTALLIZATION	
FACULTY	MACDIARMID WOLF	0.2 0.15	GRAHAM POPE	0.1 0.15	WOLF ZEMEL	0.15 0.1
RE. SPEC.	NOEL	0.5	-	-	NOEL	0.4
POST. DOC.	-	-	KULKURNI	1.0	STARTING SEPT.	-
TECHN.	GORMAN	0.7	-	-	GORMAN	0.3
STUDENT	2	1.0	1	0.3	1	0.6

SUMMARY OF KEY RESULTS

1.1.1 PRELIMINARY EVALUATION COMPLETED:

- COMMERCIAL MG-SI PROCESS SELECTED FOR UPGRADING
- SiF_2 POTENTIALLY USEFUL WITH MG-SI UPGRADING FOR TRANSPORT/PURIFICATION
- AL REDUCTION OF SiO_2 AND SIO REACTIONS POTENTIALLY FEASIBLE ROUTES

1.2.1 SiF_2 TRANSPORTABLE AT ATMOSPHERIC PRESSURE W/O DECOMPOSITION ABOVE 1100°C AND BELOW 100°C.

1.2.2 SILICON TRANSPORT RATE DETERMINED BY SiF_2 FORMATION REACTION.

1.2.4 MG-SI UPGRADED

- USING GAS BLOWING
- USING UNIDIRECTIONAL SOLIDIFICATION
- 10.7% (AMO) EFFICIENT CELL PRODUCED

2.1.1 EQUIPMENT FOR MOLTEN ZONE RECRYSTALLIZATION COMPLETED.

2.2.1 MATERIALS FOR BINARY MELT SOLUTION GROWTH TABULATED AND GROUPED.

2.2.2 SILICON PLASTICALLY DEFORMED $\geq$ 1250°C UP TO 70% AT DEFORMATION RATES $\leq$ 1%.

2.3.1 STRAIN-ANNEALING OBSERVED, GRAIN GROWTH BY FACTOR ~ 10 TO 1MM DIA.

PLANNED ACTIVITY-NEXT 6 MONTHS

1. SiF_2 TRANSPORT PROCESS:

   A) COMPLETE PRELIMINARY INVESTIGATION OF TRANSPORT PARAMETERS.

      INITIATE STUDY OF REACTION KINETICS.

   B) EVALUATE IMPURITY SEPARATION CAPABILITIES.

2. EXPERIMENTAL STUDY OF FLOATING MOLTEN ZONE PROCESS IN THIN SI SHEETS.

3. CONTINUE CHARACTERIZATION OF HIGH TEMPERATURE MECHANICAL PROPERTIES OF SILICON.

   COMPLETE AT LEAST ONE FORMING LIMIT DIAGRAM.

4. EXTEND PROCESS EVALUATION METHOD AND ECONOMIC ANALYSIS.