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DEVELOPMENT OF LOW COST THIN FILM POLYCRYSTALLINE SILICON SOLAR CELLS FOR TERRESTRIAL APPLICATIONS

NSF Grant AER 73-07843

(GI-38981)

Period of Grant

June 1, 1973 - November 30, 1976

Value of Grant: $449,000

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Principal Investigator

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I. Objective

The objective of this grant is to develop low-cost thin film polycrystalline silicon solar cells for terrestrial utilization. The technical approaches consist of (1) the deposition, characterization, and optimization of silicon p-n junction structures on graphite and metallurgical silicon substrates, (2) the purification of metallurgical silicon, (3) the fabrication and characterization of solar cells from purified metallurgical silicon, and (4) the fabrication and characterization of large area cells, 30 cm^2 or larger in area.

II. Past Activity

During 1974, major efforts were directed to (1) the deposition and characterization of silicon on graphite and metallurgical silicon substrates by the thermal reduction of trichlorosilane, and (2) the fabrication and evaluation of silicon solar cells on these substrates. The microstructure of silicon deposited on graphite substrates by the trichlorosilane process was optimized, and the average size of crystallites was 20-30 μm. Using appropriate dopants during the deposition process, many solar cells of the configuration n^+-silicon/p-silicon/graphite were fabricated, and their AMO efficiencies were limited to about 1.5%. The grain size of vapor deposited silicon on graphite substrates was improved by rapid melting and solidification, and silicon p-n junction solar cells with AMO efficiencies (no anti-reflection coating) up to 2% were produced.

Metallurgical silicon plates were prepared by unidirectional solidification of the melt in a boron nitride container and were used as substrates for the deposition of silicon by the trichlorosilane process. Silicon deposited on metallurgical silicon plates by the trichlorosilane process was found to be epitaxial with respect to the substrate. Many solar cells of the configuration n^+-silicon/p-silicon/metallurgical silicon were prepared, and their AMO efficiencies (no anti-reflection coating) were up to 2.6%.

III. Current Effort

The recent work has been directed to (1) the improvement in the structural properties of silicon on graphite substrates, (2) the optimization of solar cell characteristics on graphite and metallurgical silicon substrates, and (3) the purification of metallurgical silicon. A zone-melting technique has been developed for the recrystallization of silicon on graphite substrates, and the microstructure of silicon was improved considerably. Silicon p-n junction solar cells on graphite substrates with AMO efficiencies up to 2.5% have been produced. The conversion efficiency of n^+-silicon/p-silicon/metallurgical silicon solar cells appears to be limited by the grain boundaries in the p-layer. This grain boundary effect has been reduced by increasing the dopant concentration in the p-layer, and the AMO efficiency of n^+-silicon/p^+-silicon/metallurgical silicon solar cells was up to 3.5%.

The purification of metallurgical silicon by chemical treatment of the melt and the floating-zone technique has been carried out. The treatment of molten metallurgical silicon with chlorine, chlorine-oxygen mixture, etc., was found to be effective in reducing the concentration of most metallic impurities, except iron. The floating zone technique was found to be effective in reducing the concentration of most impurities, except boron, in metallurgical silicon. Solar cells with AMO efficiencies higher than 4% have been produced from two zone-pass material.

IV. Future Plans

Future work will be directed toward the improvement of conversion efficiencies of solar cells on graphite and metallurgical silicon substrates, including (1) the refinement of the zone-melting technique for the recrystallization of silicon on graphite substrates, (2) the purification and characterization of metallurgical silicon, and (3) the optimization of the thickness and resistivity of the silicon layer.

V. Key Results to Date

The AMO efficiencies (no anti-reflection coating) obtained to date are 2.5% for solar cells deposited on graphite substrates, 3.5% for solar cells deposited on metallurgical silicon substrates, and 4.5% for solar cells fabricate from purified metallurgical silicon.

DEVELOPMENT OF LOW COST THIN FILM POLYCRYSTALLINE SILICON SOLAR CELLS FOR TERRESTRIAL APPLICATIONS

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(GI-38981)

Work performed at

Southern Methodist University and Texas Instruments, Incorporated

Period of Grant

June 1, 1973 - November 30, 1976

Amount of Award: $449,000

Principal Investigator

Ting L. Chu, Southern Methodist University

POLYCRYSTALLINE SILICON SOLAR CELLS

INTRODUCTION

- Overall Objective: To develop low-cost thin film polycrystalline silicon solar cells for terrestrial utilization.

- Approaches:
  - Deposition and characterization of silicon on graphite and metallurgical silicon substrates by the trichlorosilane ($SiHCl_3$) process.
  - Fabrication, characterization, and optimization of solar cells on graphite and metallurgical silicon substrates.
  - Purification of metallurgical silicon.
  - Fabrication and characterization of solar cells from purified metallurgical silicon.

- Key results reported at the last review (December, 1974):
  - The microstructure of silicon deposited on graphite by the trichlorosilane process was optimized. The average size of crystallites was 20-30 μm.
  - Silicon p-n junction solar cells with AMO efficiencies up to 1.5% have been produced on graphite substrates.
  - The grain size of vapor deposited silicon on graphite was improved by rapid melting and solidification. Solar cells with AMO efficiencies up to 2% have been produced.
  - Silicon p-n junction solar cells on metallurgical silicon with AMO efficiencies up to 2.6% have been produced by the trichlorosilane process.

TLC; 2

POLYCRYSTALLINE SILICON SOLAR CELLS

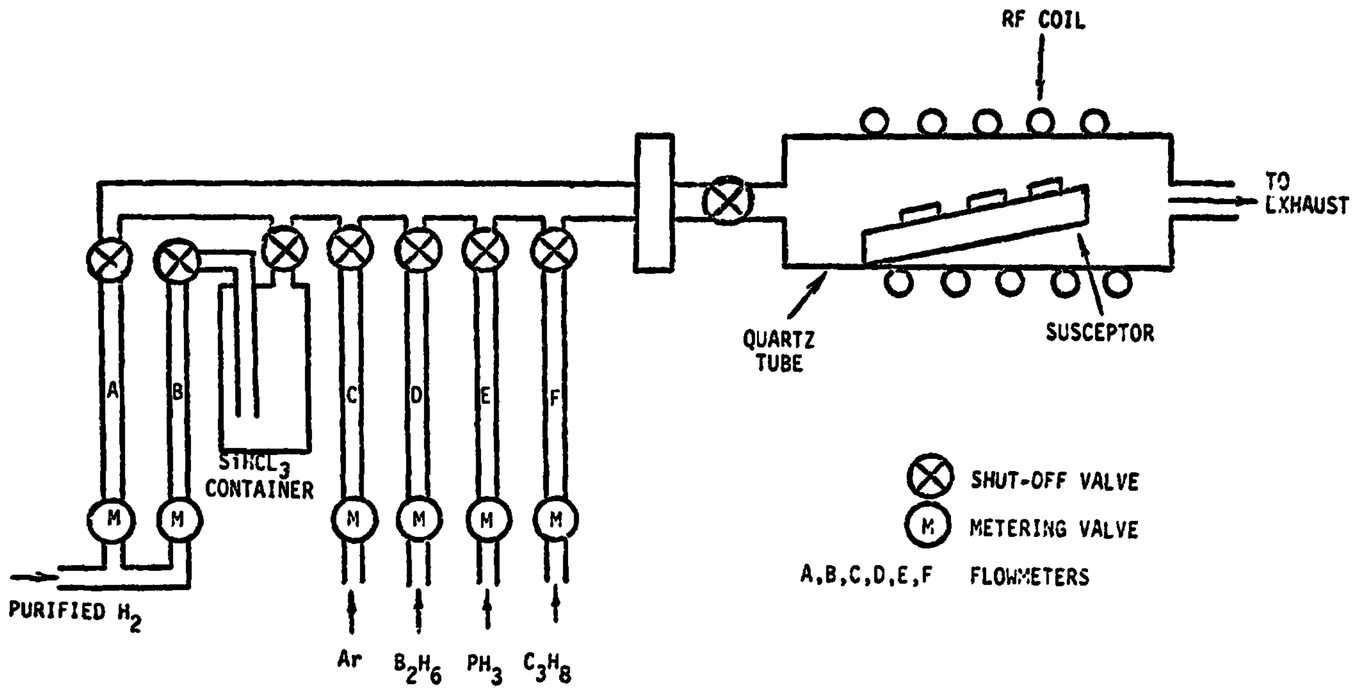
PLANNED ACTIVITY FOR LAST SIX MONTHS

PLAN	ACTION
• Deposition and characterization of silicon on pyrolytic carbon-coated graphite substrates by the thermal reduction of trichlorosilane.	• Silicon layers deposited on carbon-coated graphite substrates under a wide range of conditions, and their microstructure and crystallography evaluated.
• Improvement in structural properties of silicon on graphite substrates.	• Zone-melting technique developed for the recrystallization of silicon.
• Deposition and characterization of silicon solar cells on graphite substrates.	P-n junction solar cells with AMO efficiencies up to 2.5% have been produced.
• Deposition and optimization of silicon solar cells on metallurgical silicon substrates.	• P-n junction solar cells with AMO efficiencies up to 3.5% have been produced.
• Purification of metallurgical silicon and fabrication of solar cells from purified silicon.	• Metallurgical silicon purified by chemical treatment and floating-zone techniques. Solar cells with AMO efficiencies higher than 4% have been produced.

TLC; 3

POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

DEPOSITION OF SILICON ON CARBON-COATED GRAPHITE



Schematic of the Apparatus for the Deposition of Carbon and Silicon

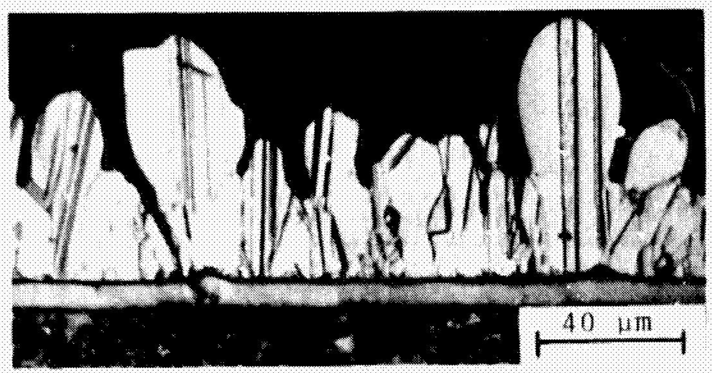
- Reactions: Thermal decomposition of propane for the deposition of carbon.
  Thermal reduction of trichlorosilane for the deposition of silicon.
- Substrate Temperature: 1100° - 1250° C
- Deposition Rate: 0.3 - 0.8 μm/min for carbon
  0.3 - 2 μm/min for silicon

TLC; 4

POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

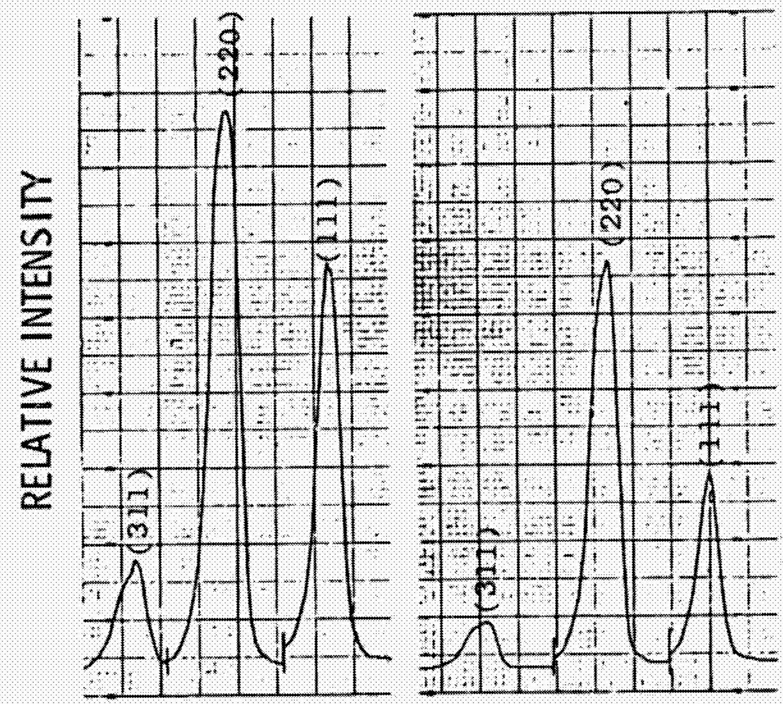
PROPERTIES OF SILICON ON CARBON/GRAPHITE SUBSTRATES

- MICROSTRUCTURE
- CRYSTALLOGRAPHIC PROPERTIES



1250° C, 0.3 μm/min

1250° C, 1.5 μm/min



1000°C, 1 μm/min   1000°C, 0.2 μm/min

- CONCLUSION: Silicon on carbon/graphite is similar to silicon on graphite in microstructure, crystallographic properties, and solar cell characteristics.

TLC; 5

POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

SILICON SOLAR CELLS ON GRAPHITE SUBSTRATES

- BY CONVENTIONAL CVD

0.2 - 0.4 μm, 0.002 - 0.003 ohm-cm N-SILICON
10 - 20 μm, 0.5 - 2 ohm-cm P-SILICON
10 - 40 μm, 0.002 - 0.005 ohm-cm P-SILICON
GRAPHITE SUBSTRATE (OR CARBON-COATED GRAPHITE)

- BY CVD AND RECRYSTALLIZATION

0.2 - 0.4 μm, 0.002 - 0.003 ohm-cm N-SILICON
10 - 20 μm, 0.5 - 2 ohm-cm P-SILICON
VAPOR-DEPOSITED P^+ -SILICON RECRYSTALLIZED
GRAPHITE SUBSTRATE (OR CARBON-COATED GRAPHITE)

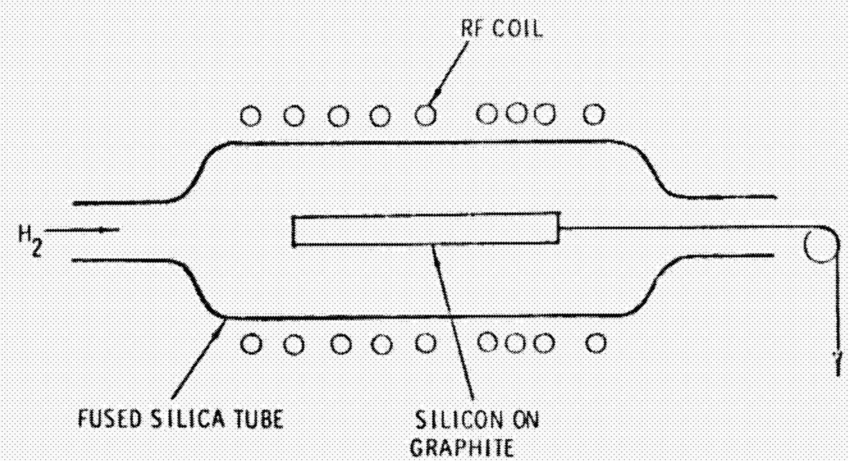
- AVERAGE GRAIN SIZE: 15 - 20 μm
- AMO EFFICIENCY: 1.5%

TLC; 6

POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

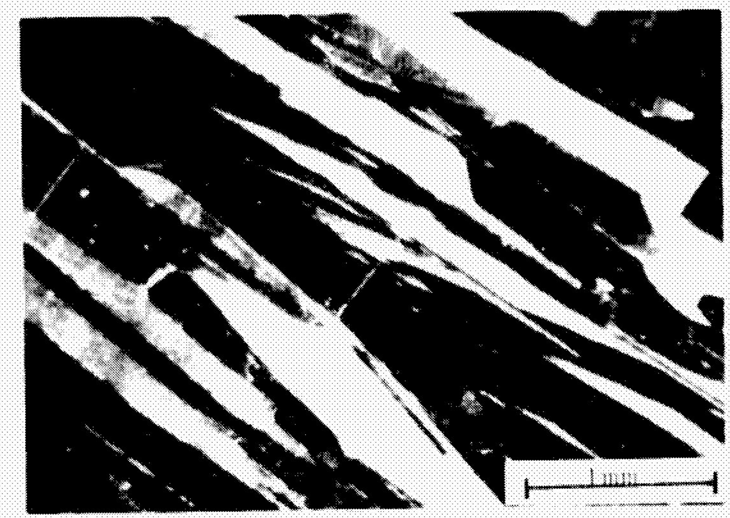
RECRYSTALLIZATION OF SILICON ON GRAPHITE SUBSTRATES

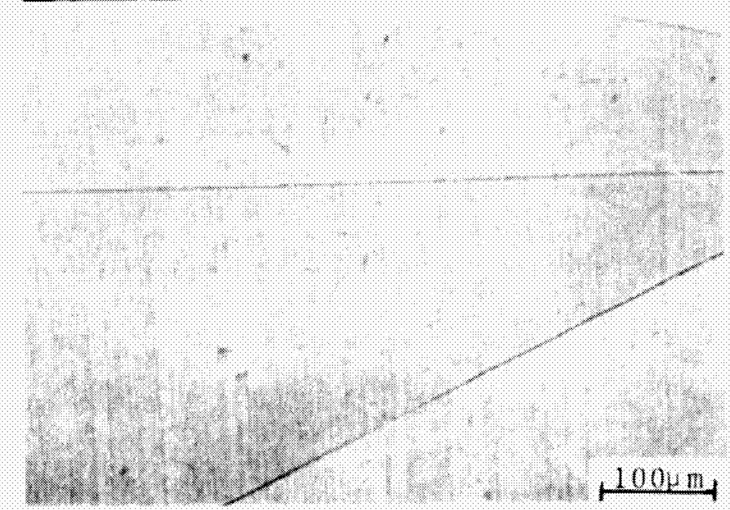
- APPROACHES
  - Rapid Melting and Solidification
  - Zone-Melting



Scnematic of the Zone-Melting Apparatus

- SILICON BY ZONE-MELTING



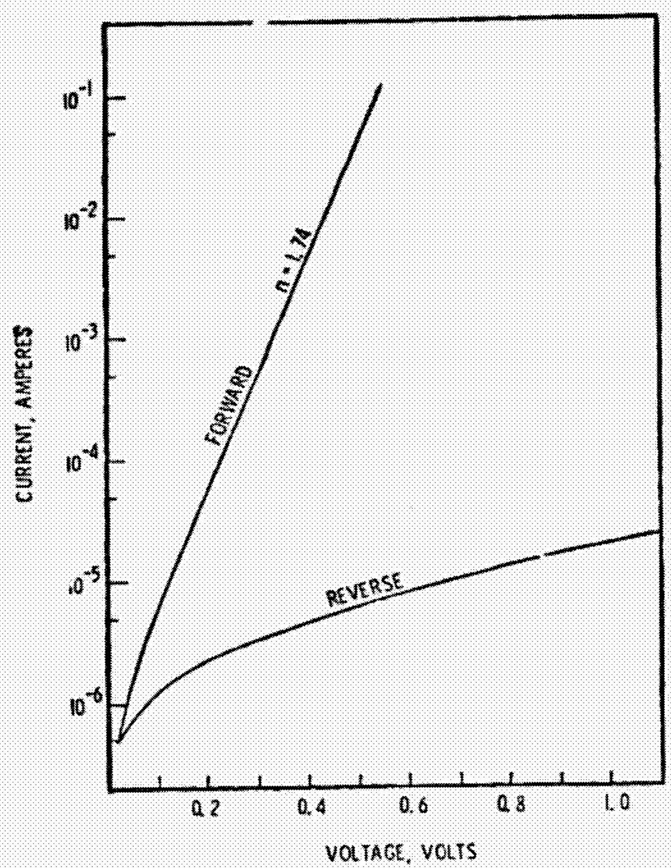


TLC; 7

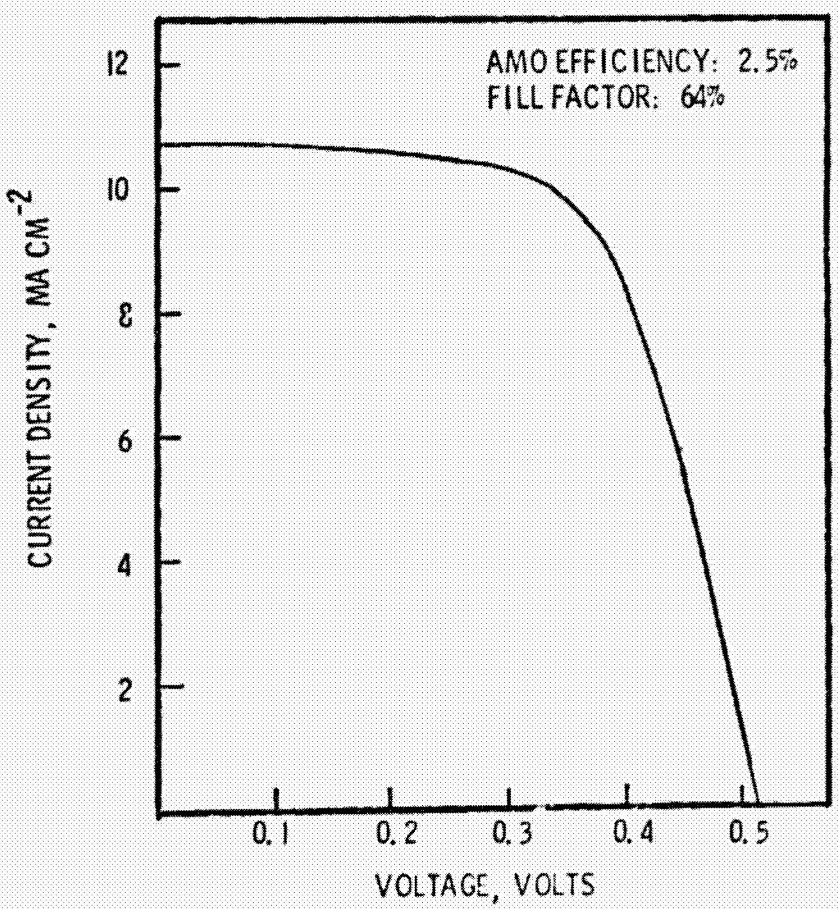
POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

SILICON SOLAR CELLS, 2.5 CM X 2.5 CM, ON GRAPHITE SUBSTRATE

- Dark Characteristics



- Characteristics under Illumination at 135 mW/cm^2.

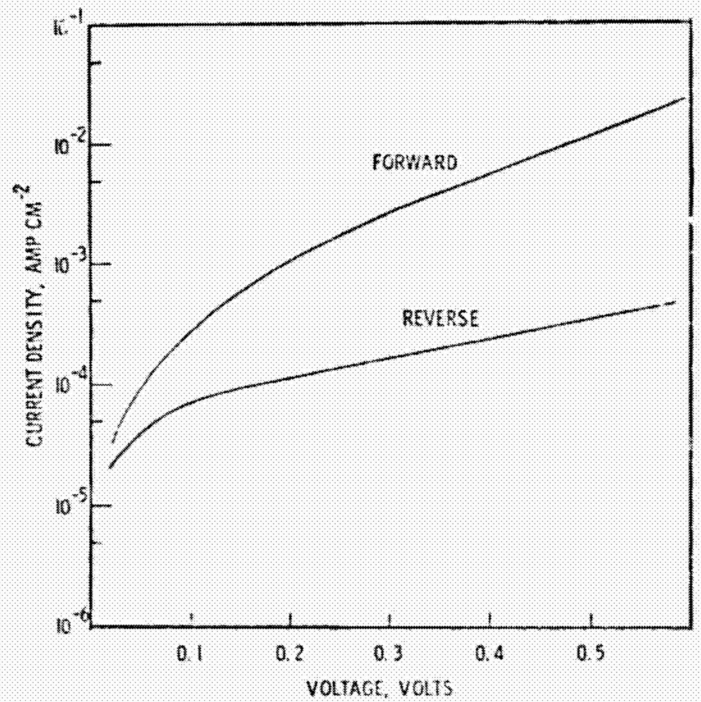


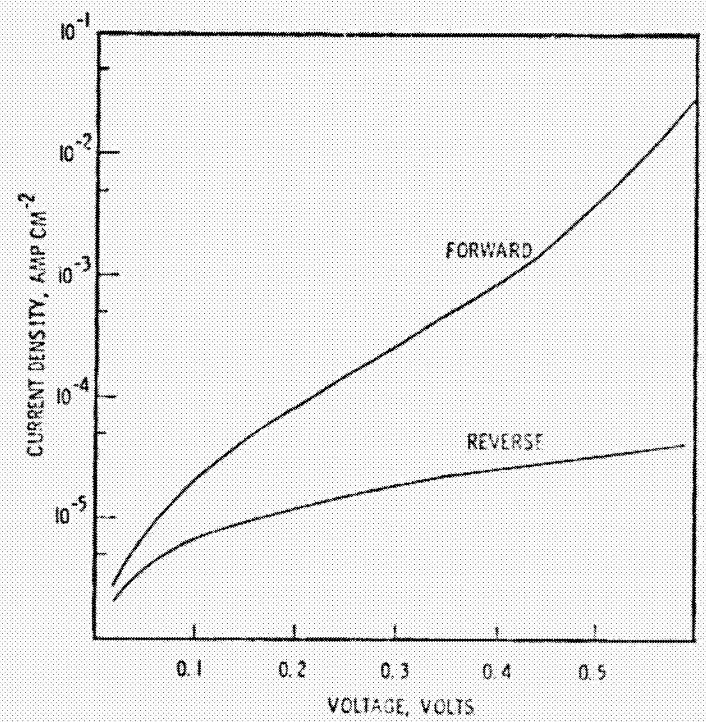
TLC, 8

POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

SILICON SOLAR CELLS ON UNIDIRECTIONALLY SOLIDIFIED METALLURGICAL SILISON

DARK CURRENT-VOLTAGE CHARACTERISTICS





0.4 μm	0.005 OHM-CM	N-SILICON
20 μm	1 OHM-CM	P-SILICON
P^+ SUBSTRATE		

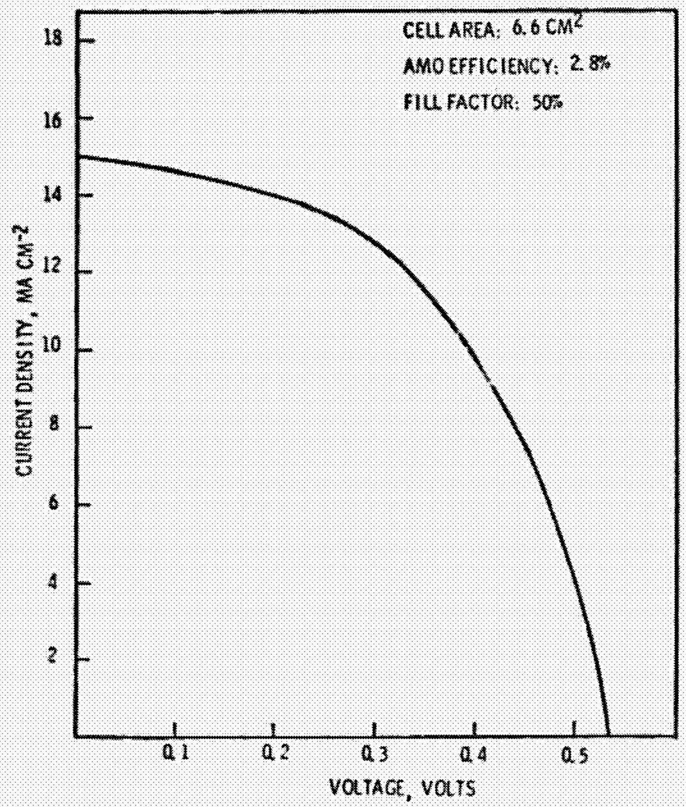
0.4 μm	0.005 OHM-CM	N-SILICON
5 μm	0.06 OHM-CM	P-SILICON
P^+ SUBSTRATE		

TLC; 9

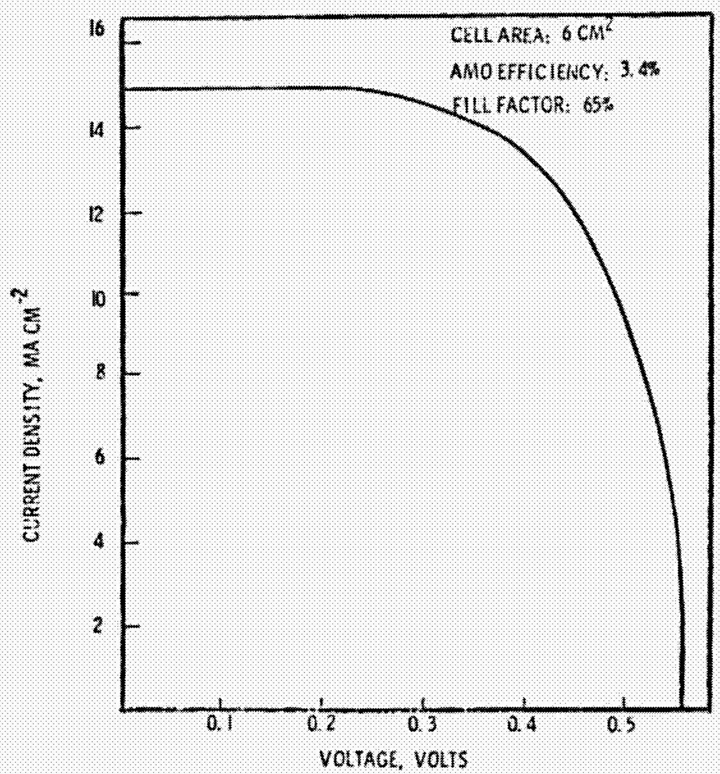
POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

SILICON SOLAR CELLS ON UNIDIRECTIONALLY SOLIDIFIED METALLURGICAL SILICON

- Characteristics under illuminations at 135 MW/cm^2



N$^+$-SILICON/P-SILICON/SUBSTRATE



N$^+$-SILICON/P$^+$-SILICON/SUBSTRATE

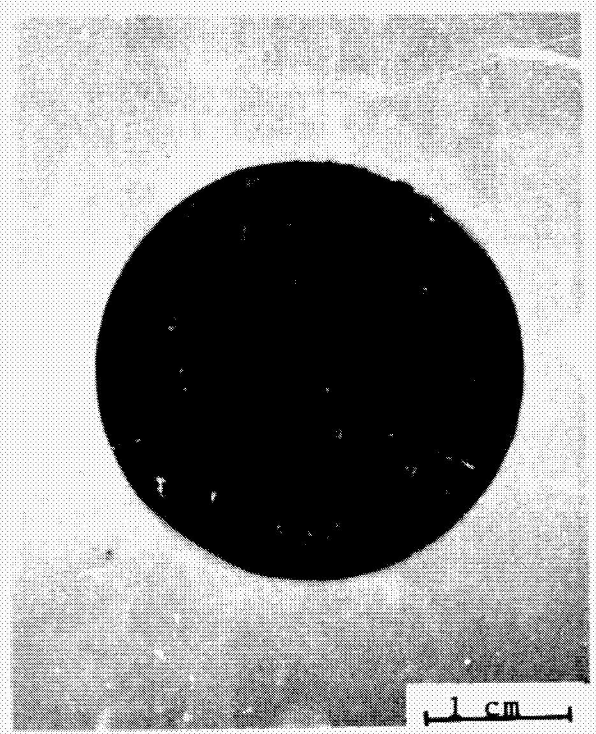
- CONCLUSION: Grain boundary effects in polycrystalline silicon can be reduced by doping.

TLC; 10

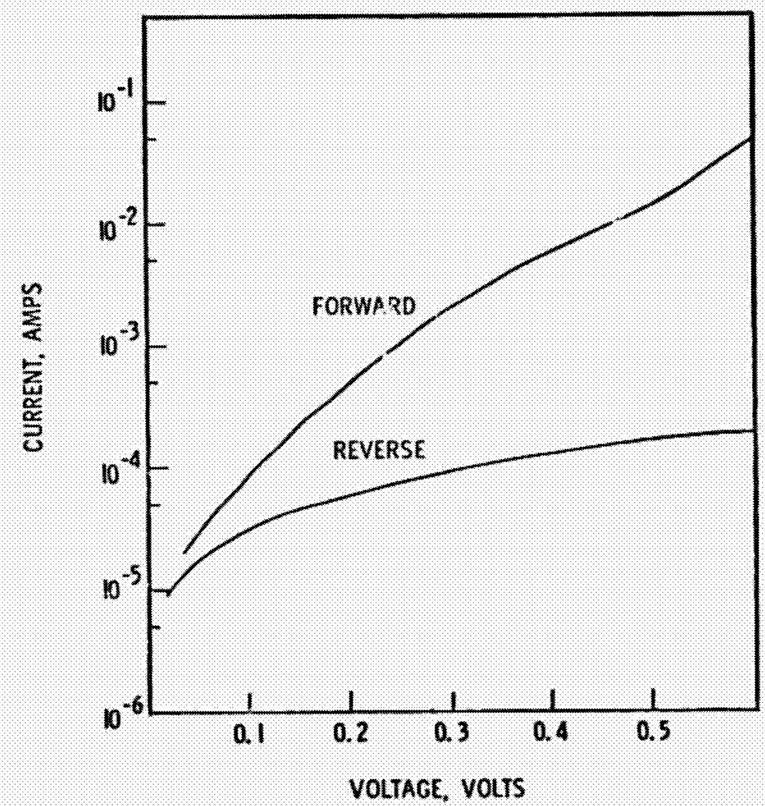
POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

SILICON SOLAR CELLS ON CZOCHRALSKI METALLURGICAL SILICON

- SUBSTRATE



- DARK CURRENT VOLTAGE CHARACTERISTICS



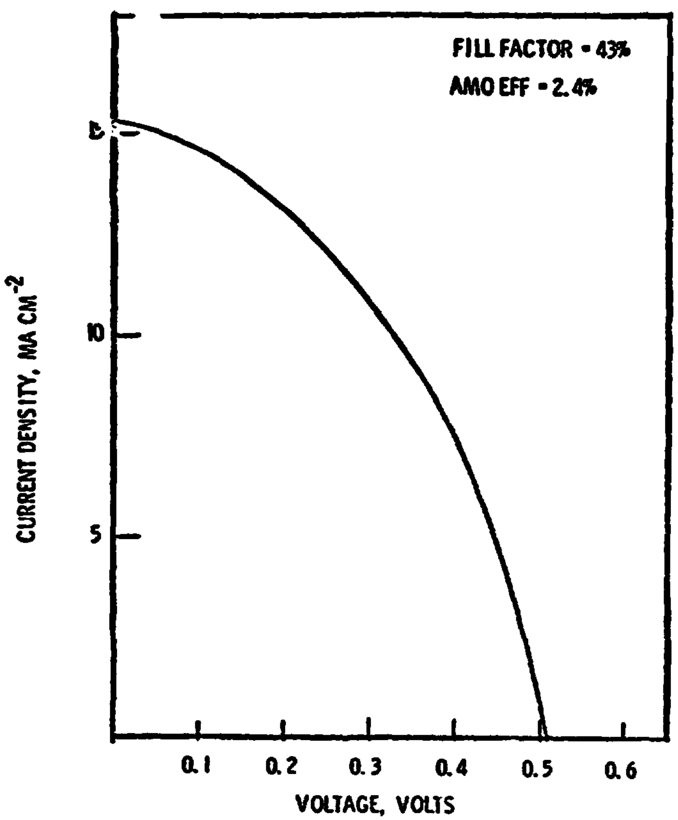
N^{+}-SILICON/P-SILICON/CZOCHRALSKI METALLURGICAL SILICON

TLC; II

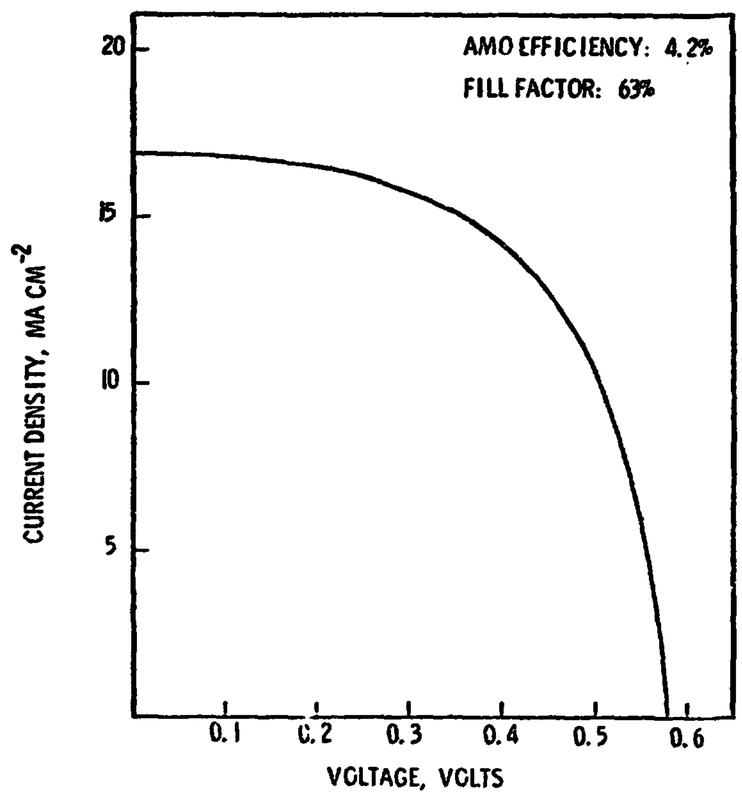
POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

SILICON SOLAR CELLS ON CZOCHRALSKI PULLED METALLURGICAL SILICON

- Characteristics under illuminations at 135 MW/cm^2



DIFFUSED CELL



N^+-SILICON/P-SILICON/SUBSTRATE

TLC; 12

POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

PURIFICATION OF METALLURGICAL SILICON

- TECHNIQUES: Floating-zone and chemical treatment of melt
- RESULTS:

IMPURITY CONCENTRATION, PPM BY WEIGHT

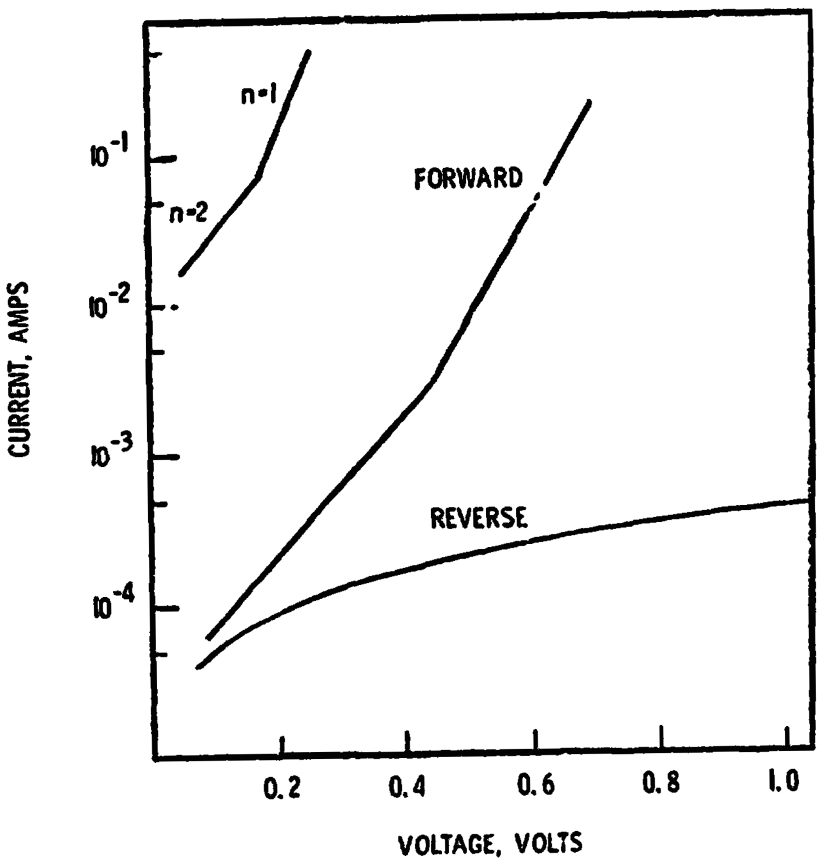
	Metal. Silicon	2 Zone Passes	Cl_2 Treat.	Cl_2+O_2 Treat.	GeO_2-SiO_2 Treat.
Al	>>5,000	1-10	10-100	1-10	10-100
Fe	>>1,000	1-10	>>1000	>>1000	300-3000
B	10-100	10-100	1-10	1-10	1-10
V	100-1000	N. D.	10-100	30-300	10-100
Cu	10-100	<0. 1	1-10	10-100	1-10
Ti	30-300	N. D.	10-100	30-300	10-100
Mn	30-300	N. D.	30-300	30-300	30-300
Mg	10-100	0. 1-1	0. 1-1	3-30	0. 1-1
Cr	30-300	N. D.	1-10	10-100	1-10
Ni	10-100	N. D.	10-100	10-100	10-100

TLC; 13

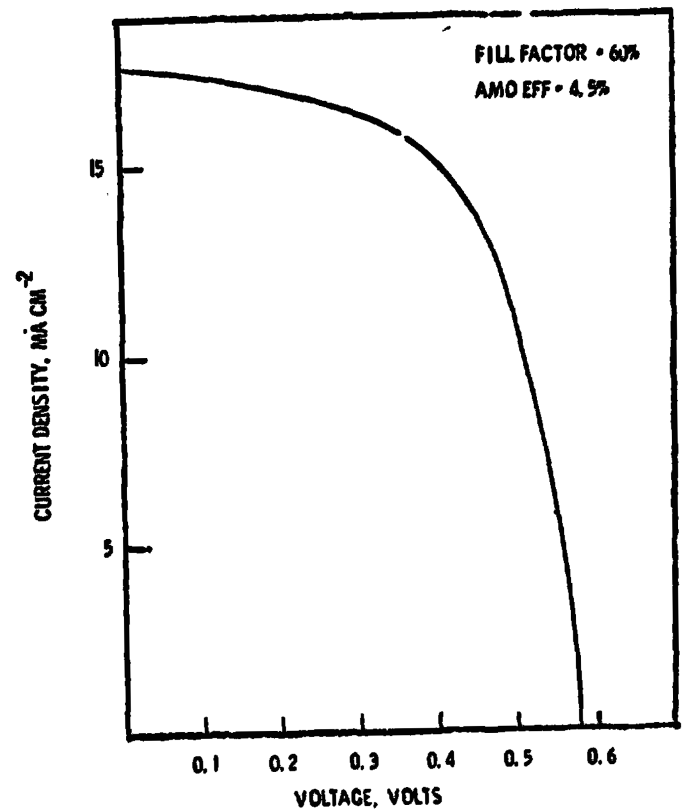
POLYCRYSTALLINE SILICON SOLAR CELLS - PROGRESS TO DATE

SILICON SOLAR CELLS FROM TWO ZONE-PASS METALLURGICAL SILICON BY DIFFUSION

- Dark Characteris..cs



- Characteristics under Illumination at 135 mW/cm^2.



TLC; 14

POLYCRYSTALLINE SILICON SOLAR CELLS

SUMMARY OF KEY RESULTS

- Silicon deposited on carbon/graphite substrates is similar to silicon deposited on graphite substrates in structural and crystallographic properties and solar cell characteristics.

- A simple zone-melting technique has been developed to improve structural properties of silicon on graphite substrates. Solar cells with AMO efficiencies of up to 2.5% have been produced.

- Grain boundary effects in silicon on metallurgical silicon substrates can be reduced by doping. Silicon solar cells with AMO efficiencies up to 3.5% have been produced.

- Chemical treatment of the melt is effective in reducing the concentration of most metallic impurities, except iron, in metallurgical silicon.

- Zone-refining is effective in reducing the concentration of most impurities, except boron, in metallurgical silicon. Solar cells with AMO efficiencies higher than 4% have been produced.

TLC, 15

POLYCRYSTALLINE SILICON SOLAR CELLS

MAJOR PROBLEMS

- Silicon Solar Cells on Graphite
  - Non-reproducible structural properties of silicon
  - High series resistance of solar cells
- Silicon Solar Cells on Metallurgical Silicon
  - Casting of silicon substrates with large crystallites
  - Relatively high cost of casting
- Purification of Metallurgical Silicon
  - Removal of iron by chemical treatment
  - Relatively high cost of zone-refining

TLC; 16

POLYCRYSTALLINE SILICON SOLAR CELLS

PLANNED ACTIVITY FOR NEXT SIX MONTHS

- Further improvement in the recrystallization of silicon on graphite.
- Preparation of substrates from purified metallurgical silicon.
- Optimization of solar cell characteristics on graphite and metallurgical silicon substrates.
- Critical evaluation of the purification of metallurgical silicon by zone-refining.
- Characterization of metallurgical silicon purified by chemical treatment.

TLC; 17