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SILICON MATERIALS TASK OF THE LOW COST
SOLAR ARRAY PROJECT (PHASE II)

Eighth Quarterly Report, July 1–September 30, 1977

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Pittsburgh, Pennsylvania

MASTER

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Solar Energy

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Contract No. 954331

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NEW TECHNOLOGY

No new technology is reportable for the period covered by this report.

1. SUMMARY

The objective of Phase II of this program is to investigate the effects of various processes, metal contaminants, and contaminant-process interactions on the performance of terrestrial silicon solar cells so that purity requirements for a solar grade silicon can be delineated.

Briefly, the program approach consists in (1) the growth of doubly and multiply-doped silicon single crystals containing a baseline boron or phosphorus dopant and specific impurities which produce deep levels in the forbidden band gap, (2) assessment of these crystals by a battery of chemical, microstructural, electrical and solar cell tests, (3) correlation of the impurity kind and level with crystal quality and device performance, (4) delineation of the role of impurities and processing on subsequent silicon solar cell performance, and (5) determination of the combined effects of impurities and growth rate on the crystal quality and cell performance of silicon produced by both the dendritic web and Czochralski methods. The central thrust of our activities this quarter was in three areas: the crystal growth of impurity-bearing ingots with different base doping types and concentrations; evaluation of the solar cell performance of n-base and p-base devices; and refinement of techniques for the analysis of solar cells subjected to various contaminants and process variations.

Our comparative study of n- and p-base solar cells doped with metal impurities continues to reveal significant differences in the response of these two types of devices to contaminants. The P^+N devices containing vanadium show substantially better performance than N^+P cells doped to the same metal concentration. For example n-base devices about 70% as efficient as the uncontaminated base devices ($\eta = 10\%$ without AR coating) are readily produced while comparable p-base devices are only about 40% as efficient as the baseline cells. The performance improvement for the vanadium bearing P^+N cells parallels that achieved previously for titanium. For nickel doping the situation is reversed.

N^+P cells with $4 \times 10^{15} \cdot \text{cm}^{-3}$ nickel show little degradation compared to the baseline. However P^+N cells containing similar nickel levels are only 54% as efficient as the baseline devices. The performance degradation in the n-base cells seems to be linked to precipitation effects in the junction rather than base lifetime reductions. Doped with iron n and p-base devices perform in a similar fashion, the P^+N cells being somewhat less efficient.

The first solar cell results for molybdenum-doped p-base material are now available. At an estimated $6 \times 10^{14} \cdot \text{cm}^{-3}$ concentrations molybdenum, a material often used in furnaces and reactors, depreciates cell performance to about 75% of the baseline efficiency. Although the chemical analysis must be refined, this result suggests that the potential effects of molybdenum be kept in mind when it is employed as a material of construction. Phosphorus compensation may be required for some forms of solar grade material; phosphorus may also be present as a contaminant in silicon. As part of this study phosphorus compensation of 4 Ωcm baseline material is being evaluated. For an ingot compensated to about 15% of the boron primary doping level ($6 \times 10^{14} \cdot \text{cm}^{-3}$) phosphorous has little or no effect on cell performance.

During our previous modeling studies we observed that cells containing the impurities copper, nickel, and iron showed a reduction in performance not wholly attributable to a reduction in base lifetime. We have recently developed and tested a method for the quantitative analysis of solar cell I-V data which permits the effects of impurities on junction, base and contact behavior to be separated and accessed. This tool along with precision lifetime measurements will soon be applied to study processing and impurity phenomenon in solar cells.

2. INTRODUCTION

The overall objective of this program is to determine how various processes, impurities and impurity-process interactions affect the performance of terrestrial silicon solar cells. The development of such data permit the definition of the tolerable impurity levels in a low-cost Solar Grade silicon, and also identify what processes mitigate or enhance the effects of impurities in silicon. This information can subsequently be employed in carrying out cost-tradeoff analyses for the application of Solar Grade material.

Specifically under study in Phase II of the program are:

- (1) The effect of heat treatment and gettering on the properties of silicon containing deep level impurities like Ti and Cr.
- (2) The combined effects of metal contaminants and low base resistivity on solar cell performance.
- (3) The relative performance of p-base and n-base solar cells containing similar levels of metal impurities.
- (4) The role of multiple contaminants on solar cell behavior.
- (5) The effect of grain boundaries on metal-contaminated solar cells.
- (6) The interaction of oxygen, carbon, and metal impurities in solar cells.
- (7) Improved techniques for the analysis of impurity effects in silicon and silicon solar cells.

Work this quarter centers primarily in areas (3), (4), and (7). In particular, we present an extended discussion of a refined approach for analyzing solar cell I-V data to quantitatively assess the role of processing and impurities on both the junction and base regions of the device. Initial experimental results in areas (1) and (5) are also described.

3. TECHNICAL RESULTS

3.1 Silicon Growth and Analysis

The concentration ranges of the impurities* under study are illustrated in Table 1. The column headings denote the various substrate doping levels and base types. The choice of 0.2 ohm-cm, p-type material for investigation was made after evaluating the relative performance of cells made on material with resistivity ranging from 0.5 ohm-cm through 4.0 ohm-cm.³ In addition, a total of 17 multiply doped 4 ohm-cm ingots containing two or more of the impurities shown in Table 1 have been prepared. The resistivity of the n-base material was chosen to give comparable carrier concentration to that found in the 4 ohm-cm, p-base silicon.

We reiterate that the upper limit for impurities shown in Table 1 has been established by one of the following criteria: (1) the solid solubility limit, (2) the maximum concentration achievable without producing constitutional supercooling of the melt, or (3) a concentration which degrades solar cell performance beyond any potential utility. The lower limit, where established, is determined as that concentration which does not degrade cell performance. Continued analysis of ingots enhances the data base upon which the impurity concentrations are founded so an updated summary of the best estimate of impurity concentration and actual measured values for all ingots produced during Phase I and Phase II of this program appears in the Appendix.

*The selection of impurities for investigation is based on those elements present in metallurgical-grade silicon and quartzite or the potential impurities introduced during processing.¹

Preparation/characterization of first generation doubly doped n-type ingots is now complete and preparation of low resistivity (0.2 ohm-cm) p-type ingots is also nearly done. Investigation of compensated material was initiated this quarter with ingots doped with phosphorus and boron as well as phosphorus and aluminum. Overall a total of thirteen ingots were grown; the results of the ingot preparation and characterization are presented in the following sections.

3.1.1 Ingot Preparation

All ingots given this quarter were prepared by the Czochralski growth method as described previously.¹ The effective segregation coefficients used to determine appropriate melt concentrations are shown in Table 2. A review of our data for the impurities boron and copper indicate that the effective segregation coefficients should be 0.8 and 8×10^{-4} respectively. These values differ slightly from those reported previously. The breakdown of ingots prepared this quarter is as follows:

- 5 n-type doubly-doped (1.5 ohm-cm): n-base studies
- 3 p-type doubly-doped: 4 ohm-cm matrix extension
- 2 p-type phosphorus compensated (4 ohm-cm): matrix extension
- 3 p-type single doped (0.2 ohm-cm): low resistivity studies

Both compensated n-type and p-type ingots were grown. Aluminum was used as the compensating impurity in Ingot W-084 with a phosphorus to aluminum ratio of approximately 1.4. Two p-type ingots were compensated with phosphorus. The boron/phosphorus ratio of W-080 was 6.6 while the ratio of W-092 was 1.13. The boron concentration in Ingot W-092 is ten times that of W-080.

Table 1. Impurity Matrix Under Investigation

Impurity Element	Approximate Concentration Range Investigated x 10 ¹⁵ atoms per cm ³		
	4 ohm-cm p-type	0.2 ohm-cm p-type	1.5 ohm-cm n-type
Aluminum	3 - 50**		3 - 50
Boron*			
Calcium	0.1		
Carbon	20 - 500 ⁺		
Chromium	0.1 - 1.1	0.5	1.0
Copper	0.4 - 60	2.3	2.5
Iron	0.02 - 1.5		1.0
Magnesium	0.003 - 0.03		
Manganese	0.01 - 1.3	0.7	2.0
Molybdenum			
Nickel	0.4 - 4.0		2.3
Oxygen	500 - 1700 ⁺		
Phosphorus*	1.0 - 28		
Sodium			
Titanium	0.00036 - 0.36		0.36
Tantalum			
Vanadium	0.0004 - 0.4		0.4
Zinc ⁺	<0.001		
Zirconium	<0.015		<0.015

* Boron and phosphorus are electrically active impurities and therefore cause variations in resistivity when used as a secondary impurity.

** Uncertainty in exact range due to discrepancy between electrical and SSMS measurements.¹

⁺ Oxygen and carbon concentrations measured in 50 ingots doped with additional impurities. No effort yet to correlate effects if any.

Table 2. Segregation Coefficients

<u>Element</u>	<u>Segregation Coefficient</u>
Al	3×10^{-2} (2.8×10^{-3})
B	0.8
C	0.05
Ca	?
Cu	8.0×10^{-4}
Cr	1.1×10^{-5}
Fe	6.4×10^{-6}
Mg	3.2×10^{-6}
Mn	1.3×10^{-5}
Mo	$\sim 10^{-6}$
Ni	3.2×10^{-5}
Ph	0.35
Ta	$\sim 10^{-7}$
Ti	3.6×10^{-6}
V	4×10^{-6}
Zn	10^{-5}
Zr	$< 1.5 \times 10^{-7}$

Calcium metal was used successfully as a dopant for p-type, 4 ohm-cm material in Ingot W-087. We note, however, that considerable calcium is evolved from the melt and oxide precipitates form on the melt surface early in the growth cycle which limits single crystal yield. Melt analysis indicates that approximately 90 percent of the calcium is lost from the melt during the growth period.

The yield of single crystal material was also reduced when attempts were made to achieve a high carbon concentrations. Loss of structure consistently occurs at the 4×10^{17} to 5×10^{17} atoms/cm³ concentration. The latter value was achieved in the tang end of Ingot W-086. however, a twin developed prior to achieving this concentration.

As we have reported previously, it is difficult to achieve chromium concentrations of 1×10^{15} atoms/cm³ or greater without precipitation in the melt problems. Due to these growth problems and associated low single crystal yields, the highest Cr concentration achieved in 0.2 ohm cm, p-type first generation material was 0.5×10^{15} atoms/cm³.

3.1.2 Ingot Evaluation

The ingot evaluation process has been discussed previously, e.g. Ref 5. Analytical data, with the exception of SSMS and NAA is up to date on all ingots. Mass spectrographic data is available on all but Ingots W-085 through W-092. Ingots have been selected for neutron activation analysis and analytical efforts will be initiated shortly.

Resistivity and etch pit densities measured on slices from Ingots W-054 through W-092 are tabulated in Table 3. Etch pit densities are shown for both tang and seed ends of the ingots. The first value representing the EPD of the seed is most representative of slices employed in cell analysis. No serious problems have been encountered in meeting resistivity target values. Resistivity of Ingot W-084 is high due to the intended aluminum compensation. Although the resistivity of W-092 is in the 1.7 - 5.6 ohm-cm range, boron concentration in this ingot 3.2×10^{16} atoms/cm³ which in uncompensated material would correspond to 0.55 ohm-cm.

Table 3. Ingot Resistivity and Etch Pit Density

<u>Ingot Identification</u>	<u>TGT Resistivity (ohm-cm)</u>	<u>Actual Resistivity (ohm-cm)</u>	<u>Etch Pit Density (/cm²)</u>
W-054-00-000	4.0 (B)	4.3 - 3.8	0 - 4.25 K **
W-055-Cu-004	4.0 (B)	4.1 - 3.7	0.5 K - 25 K
W-056-Cu-005	4.0 (B)	4.4 - 3.75	2.5 K - 10 K
W*-057-CO-000	0.5 (B)	0.46 - 0.47	0.5 K - 1.25 K
W*-058-00-000	0.2 (B)	0.22 - 0.18	0 - 0.2 K
W*-059-00-000	0.05 (B)	0.05 - 0.053	0 - 2 K
W-060-00-000	1.5 (P)	2.1 - 1.0	0 - 1 K
W-061-Cr/Ti-001	4.0 (B)	5.0 - 4.0	3 K - Clusters
W-062-N/Cu-001	1.5 (P)	2.0 - 0.95	0.4 - 4 K
W-063-N/Cr-001	1.5 (P)	2.2 - 1.7	1 K - 40 K
W-064-N/Mn-001	1.5 (P)	2.2 - 1.35	1 K - 3 K
W-065-N/Ti-001	1.5 (P)	1.9 - 1.7	0 - 2 K
W-066-Ti-005	4.0 (B)	6.0 - 3.9	1 K - 4 K
W-067-Cr/Mn/Ti-001	4.0 (B)	5.5 - 5.2	1 K - 4 K
W-068-Cr-004	4.0 (B)	5.2 - 5.1	1 K - 5 K
W-069-Fe-004	4.0 (B)	5.8 - 5.0	0.4 K - Gross Lineage
W-070-Al-003	4.0 (B)	2.2 - 1.1	0 - 1 K
W-071-CO-000	4.0 (B)	4.1 - 3.3	1 K - 4 K
W-072-Cr-005	4.0 (B)	5.0 - 4.5	0 - 2 K
W-073-Cr/Mn/Ni/Ti/V-001	4.0 (B)	5.0 - 3.8	1 K - 40 K
W-074-Cr/Mn/Ni/Ti/V-002	4.0 (B)	4.4	400 - 30 K
W-075-Ti/V-002	4.0 (B)	4.8 - 3.9	0 - 10 K
W-076-Poly-002	4.0 (B)	4.8 - 3.0	N/A (Poly)

Table 3. Ingot Resistivity and Etch Pit Density (cont.)

<u>Ingot Identification</u>	<u>TGT Resistivity (ohm-cm)</u>	<u>Actual Resistivity (ohm-cm)</u>	<u>Etch Pit Density (/cm)</u>
W-077-Mo-001	4.0 (B)	4.3 - 3.8	0 - Gross Lineage
W-078-00-000	4.9 (B)	4.3 - 3.3	0 - 80 K
W-079-00-000	1.5 (P)	2.3 - 1.1	1 K - 10 K
W-080-Ph-001	4.0 (B)	5.2 - 3.8	0 - 5 K
W-081-N/Ni-001	1.5 (P)	2.2 - 1.4	1 K - 4 K
W-082-N/V-001	1.5 (P)	1.8 - 1.5	0 - 6 K
W-083-N/Fe-001	1.5 (P)	2.1 - 1.3	1 K - Gross Lineage
W-084-N/Al-001	1.5 (P)	7.5 - 1.9	1 K - 80 K
W-085-N/Zr-001	1.5 (P)	2.4 - 1.5	1 K - 20 K
W-086-C-001	4.0 (B)	4.0 - 3.5	0 K - 20 K ⁺
W-087-Ca-001	4.0 (B)	3.8 - 3.4	0 ⁺⁺
W*-088-Cr-001	0.2 (B)	0.2 - 0.18	1 K - 20 K
W*-089-Cu-001	0.2 (B)	0.21 - 0.19	0 - 20 K
W*-090-Mn-001	0.2 (B)	0.21 - 0.20	1 K - 3 K
W-091-Zr/Mn-002	4.0 (B)	5.5 - 3.5	0 - Gross Lineage
W-092-Ph-002	4.0 (B)	1.7 - 5.6	0 - 1 K

* Use of asterisk indicates low resistivity p-type ingot.

** The first figure is etch pit density of the seed; second figure etch pit density of extreme tang end of ingot. The first value shown is indicative of dislocation density in slices used for cell fabrication.

+ Twinning due to high carbon concentration occurred after approximately three inches of crystal growth.

++ Multiple crystal Growth due probably to CaO formation.

Twinning problems were encountered in the growth of ingots heavily doped with calcium, carbon, and chromium. To obtain initial data on carbon effects ingot W-086 was forwarded for solar cell fabrication/evaluation with a twinned section extending through approximately one half the slices.

Target impurity concentrations, calculated concentrations based on melt analysis and measured impurity concentrations (SSMS or resistivity where applicable) are summarized in Table 4 for ingots W-054 through W-092. SSMS data is not yet available for Ingots W-085 through W-092. Resistivity measurements were employed for measuring the impurity concentration of Ingot W-092 while infrared transmission was used to determine the carbon concentration in Ingot W-086. It should also be noted that for some ingots shown in Table 4 target and calculated impurity concentrations have been adjusted to be consistent with the effective segregation coefficients shown in Table 2. In general these changes are less than 10 percent for all impurities except copper.

Aluminum concentration as determined by SSMS continues to be significantly higher than that based on resistivity measurements. This difference which has been noted by others² has now been seen on all ingots prepared during this program. Since the aluminum doped ingots are usually compensated with another impurity (for ingots prepared for this program) it has been impossible to establish a firm number for the ratio of total aluminum concentration to electrically active aluminum. Iron continues to pose an analytical problem due to the poor sensitivity of the SSMS to iron in silicon. Future NAA results should provide data on iron concentration.

Agreement among target impurity concentration, calculated concentration and measured concentration continues to be relatively good. The best estimates of impurity concentration for each ingot grown during Phase II are given in Table 5.

Table 4. Ingot Impurity Concentration

Ingot Identification	Target Concentration	Calc. Concentration	Measured Concentration
	10^{15} atoms/cm ³	10^{15} atoms/cm ³	10^{15} atoms/cm ³
W-054-00-000	N/A	N/A	N/A
W-055-Cu-004	0.1	0.06	<1
W-056-Cu-005	60	90	70
W*-057-00-000	N/A	N/A	N/A
W*-058-00-000	N/A	N/A	N/A
W*-059-00-000	N/A	N/A	N/A
W-060-00-000	N/A	N/A	N/A
W-061-Cr/Ti-001	Cr: 1.1 Ti: 0.02	Cr: 1.0 Ti: 0.017	Cr: 1.0 Ti: <1.0
W-062-N/Cu-001	2.5	2.0	2.0
W-063-N/Cr-001	0.83	0.88	1.0
W-064-N/Mn-001	1.0	0.64	2.0
W-065-N/Ti-001	0.37	0.30	0.75**
W-066-Ti-005	0.06	0.048	<0.2
W-067-Cr/Mn/Ti-001	Cr: 0.44 Mn: 0.50 Ti: 0.006	Cr: 0.3 Mn: 0.36 Ti: 0.0039	Cr: 0.3 Mn: 0.7 Ti: <0.2
W-068-Cr-004	1.0	1.0	1.0
W-069-Fe-004	0.98	0.92	<1.5
W-070-Al-003	50 (4.75)*	20 (1.9)	100 (3.0)
W-071-00-000	None	N/A	N/A
W-072-Cr-005	0.4	0.21	0.28
W-073-Cr/Mn/Ni/Ti/V-001	Cr: 0.48 Mn: 0.46 Ni: 2.0 Ti: 0.004 V: 0.004	Cr: 0.34 Mn: 0.31 Ni: 1.3 Ti: 0.005 V: 0.007	Cr: 0.28 Mn: 0.8 Ni: <2.0 Ti: <0.35 V: <0.35

Table 4. Ingot Impurity Concentration (cont.)

Ingot Identification	Target Concentration	Calc. Concentration	Measured Concentration
	10^{15} atoms/cm ³	10^{15} atoms/cm ³	10^{15} atoms/cm ³
W-074-Cr/Mn/Ni/Ti/V-002	Cr: 0.08 Mn: 0.08 Ni: 0.5 Ti: 0.0006 V: 0.0006	Cr: 0.054 Mn: 0.064 Ni: 0.28 Ti: 0.0025 V: 0.0015	Cr: <0.25 Mn: <0.25 Ni: <2.0 Ti: <0.25 V: <0.25
W-075-Ti/V-002	Ti: 0.1 V: 0.1	Ti: 0.075 V: 0.11	Ti: <0.25 V: <0.25
W-076-Poly-002	None	N/A	N/A
W-077-Mo-001	1.0	0.65	<0.3
W-078-00-000	None	N/A	None
W-079-00-000	None	N/A	None
W-080-Ph-001	0.5	0.7	(0.8)**
W-081-N/Ni-001	2.3	0.65	<2
W-082-N/V-001	0.4	0.475	0.85
W-083-N/Fe-001	1.0	0.86	<1.5
W-084-N/Al-001	50 (4.7) *	22 (2.1)	40 (<2.5)
W-085-N/Zr-001	0.007	0.005	Incomp.
W-086-C-001	300	N/A	300-500
W-087-Ca-001	1.0	0.13	Incomp.
W*-088-Cr-001	0.5	0.62	Incomp.
W*-089-Cu-001	2.3	2.13	Incomp.
W*-090-Mn-001	0.45	0.52	Incomp.
W-091-Cr/Mn-002	Cr: 0.5 Mn: 0.3	0.3 0.3	Incomp. Incomp.
W-092-Ph-002	28	N/A	(27-30)**

* Value in parenthesis based on resistivity measurement

** High Ti value possibly due to vacuum leak in M.S.

Table 5. Best Estimate of Impurity Concentration

Ingot Number	Impurity Concentration (10^{15} atoms/cm ³)	
W-054-00-000	N/A	--
W-055-Cu-004	0.05	(<1)
W-056-Cu-005	65	(70)
W*-057-00-000	N/A	--
W*-058-00-000	N/A	--
W*-059-00-000	N/A	--
W-060-00-000	N/A	--
W-061-Cr/Ti-001	Cr: 1.0	(1.0)
	Ti: 0.02	(<1)
W-062-N/Cu-001	2.0	(2.0)
W-063-N/Cr-001	0.8	(1.0)
W-064-N/Mn-001	2.0	(2.0)
W-065-N/Ti-001	0.35	(0.75)
W-066-Ti-005	0.06	(<0.2)
W-067-Cr/Mn/Ti-001	Cr: 0.4	(0.3)
	Mn: 0.5	(0.7)
	Ti: 0.006	(<0.2)
W-068-Cr-004	1.0	(1.0)
W-069-Fe-004	1.0	(<1.5)
W-070-Al-003**	50	(100)
W-071-00-000	N/A	--
W-072-Cr-005	0.4	(0.28)
W-073-Cr/Mn/Ni/Ti/V-001	Cr: 0.4	(0.28)
	Mn: 0.5	(0.80)
	Ni: 2.0	(<2.0)
	Ti: 0.004	(<0.35)
	V: 0.004	(<0.35)
W-074-Cr/Mn/Ni/Ti/V-001	Cr: 0.08	(<0.25)
	Mn: 0.08	(<0.25)
	Ni: 0.5	(<2.0)
	Ti: 0.0006	(<0.25)
	V: 0.0006	(<0.25)
W-075-Ti/V-002	Ti: 0.1	(<0.25)
	V: 0.1	(<0.25)
W-076-Poly-002	N/A	--

Table 5. Best Estimate of Impurity Concentration (Cont.)

<u>Ingot Number</u>	<u>Impurity Concentration</u> (10^{15} atoms/cm ³)	
W-077-Mn-001	~0.1	(<0.3)
W-078-00-000	N/A	--
W-079-00-000	N/A	--
W-080-Ph-001**	0.7	(0.7)
W-081-N/Ni-001	1.7	(<2.0)
W-082-N/V-001	0.4	(0.85)
W-083-N/Fe-001	1.0	(<1.5)
W-084-N/Al-001**	50	(40)
W-085-N/Zr-001	<0.015	
W-086-C-001	400	(300-500)
W-087-Ca-001	?	
W*-088-Cr-001	0.5	
W*-089-Cu-001	2.0	
W-090-Mn-001	0.7	
W-091-Cr/Mn-002	0.5/0.3	
W-092-Ph-002**	28	(27-30)

3.2. Processing Studies

The studies which form most of this task are designed to examine the effects of both crystal growth history and the sequences of heat treatment common to solar cell processing on the performance of devices purposely contaminated with impurities. This information could then be used to develop techniques for minimizing the harmful influence of the contaminants. Much of this work has been held in abeyance pending calibration of the photoconductive decay apparatus since lifetime measurement will be employed as a major tool for assessing the way the silicon responds to the various processes. The equipment calibration is now complete (see section 3.6) and the preliminary processing studies have been initiated.

The first experiments are designed to determine the effects of high temperature cycles on recombination lifetime. Lifetime will be measured on specimens both before and after each high temperature cycle is carried out. The normalized lifetime change will be measured as a function of the maximum temperature, cooling rate from the furnace and quench temperature. Wafers 1.25 mm thick from ingot 078 will be employed to provide baseline data for the study. The thick wafers provide for high accuracy in the PCD measurements when high lifetime material is employed. At this time specimens have been prepared and the heat treatment cycles initiated. Lifetime data on baseline and impurity-doped wafers will be reported during the next quarter.

In parallel with the heat treatment and gettering studies we are also assessing the way in which impurity doped material responds when solar cells are made with back surface fields. It has been conjectured, for example, that impurities may degrade higher efficiency solar cells more severely than conventionally processed devices.

In these initial experiments wafers from ingots purposely doped with Al and Cr were processed to solar cells by two methods: (1) our standard sequence which involves an 825° POCl_3 diffusion for 50 min. giving an N^+/P device and (2) a sequence in which a back surface field

was produced by BBr_3 diffusion at 960°C for 20 min. followed by front junction formation by 825° POCl_3 diffusion giving an $\text{N}^+/\text{P}/\text{P}^+$ structure. The TiPdAg metallizations were made on each type of cell in the same way.

The solar cell I-V characteristics for each type of device can be compared from the data in Table 6, which represent average values for runs of 15 to 20 cells. The raw data for the $\text{N}^+/\text{P}/\text{P}^+$ devices appear in Tables 7 and 8; the data for the N^+/P devices was given previously.^{1,3} The back surface field raised the baseline (uncontaminated) cell efficiency by about 0.5%. With typical SiO AR coatings these devices would yield 14.5 to 15% efficient cells. The Cr containing devices remain about 77% of the baseline for both N^+/P and $\text{N}^+/\text{P}/\text{P}^+$ devices. The Al containing devices are about 72% of baseline for both the standard process cells and the back surface field devices. From these experiments we would conclude that the impurities Al and Cr tend to degrade both the standard and "high performance" devices in about the same way, so that the back surface field would provide efficiency enhancement for the contaminated material.

3.3 N-base studies

The comparative study of impurity effects on p and n-base devices was continued this quarter yielding solar cell data for all but the last two first-generation ingots. The data in Table 9 illustrate how V, Ni, and Fe influence the performance of both device types when the impurity content of the silicon is comparable.

The most striking difference is that for V: n-base devices doped with 4×10^{14} at cm^{-3} , V are about 70% as efficient as the baseline cells. The p-base devices, however, are severely degraded by V, being only about 40% as efficient as the baseline. The improved response of n-base cells to V parallels the improvement noted for Ti.³ The data for Fe indicate a slight decrease in the n-base cell efficiency compared to the p-type counterpart. This is perhaps an effect of the slightly larger Fe content in the n-type ingot. The Ni data is perhaps the most puzzling. Here the n-base devices are degraded to about 55% of the baseline cells.

TABLE 6

I-V Characteristics of N^+/P and $N^+/P/P^+$ Solar Cells
Fabricated on Silicon Containing Cr and Al

IMPURITY	DEVICE	$I_{sc}/I_{sc0}^* \times 100$	$V_{oc}/V_{oc0}^* \times 100$	$\eta/\eta_0 \times 100$	Baseline Efficiency
Cr	N^+/P	88.2	93.0	77.8	10.1
Cr	$N^+/P/P^+$	85.2	92.3	76.0	10.4
Al	$N + P$	75.4	93.8	70.9	10.09
Al	$N^+/P/P^+$	79.2	94.5	73.8	10.57

TABLE 7

I-V Data for $N^+/P/P^+$ Cells Made on Cr-doped Si

70708 W068CR004 (1E15) W071 00 000

SOL2 10/4 /77 AM1: P0=91.60MW/CM² NO AIR COATING

ID	ISC	VOC	IP	LOG(I0)	N	R	FF	EFF	OCD	PCDA	PCDR
1R*	22.50	.556	20.34	-6.766	1.81	.01	.724	9.58	.00	.00	.00
1B	22.80	.580	20.86	-7.273	1.72	-.27	.750	10.49	15.90	.00	.00
2B.*	22.10	.565	19.84	-6.070	2.14	-1.27	.737	9.73	6.50	.00	.00
3B	22.20	.568	20.30	-7.150	1.73	-.57	.755	10.07	9.75	.00	.00
4B	22.30	.565	20.33	-6.917	1.79	-.74	.753	10.04	9.10	.00	.00
5B	23.40	.580	21.58	-7.803	1.57	-.19	.763	10.95	22.88	.00	.00
1C	19.20	.531	17.42	-6.767	1.76	-.71	.743	8.01	.98	.00	.00
2C	19.50	.528	17.36	-5.803	2.15	-1.48	.725	7.89	.98	.00	.00
3C	19.30	.530	17.37	-6.277	1.94	-1.17	.737	7.97	1.30	.00	.00
4C	19.30	.529	17.09	-5.503	2.33	-2.11	.726	7.84	.98	.00	.00
5C	19.50	.530	17.40	-5.848	2.14	-1.58	.730	7.98	.98	.00	.00
1S	19.20	.531	17.19	-5.990	2.08	-1.50	.733	7.91	.98	.00	.00
2S	19.50	.531	17.51	-6.144	2.00	-1.27	.735	8.05	.98	.00	.00
3S	19.70	.531	17.55	-5.797	2.17	-1.55	.727	8.04	.98	.00	.00
4S	19.50	.531	17.46	-6.048	2.04	-1.29	.731	8.01	.98	.00	.00
5S	19.60	.529	17.41	-5.665	2.23	-1.74	.726	7.96	.98	.00	.00
1T	19.00	.528	16.93	-5.843	2.14	-1.49	.725	7.70	1.04	.00	.00
2T	19.30	.527	17.22	-5.893	2.11	-1.43	.727	7.82	1.00	.00	.00
3T	19.00	.525	16.86	-5.683	2.21	-1.58	.720	7.60	.65	.00	.00
4T	19.00	.527	16.99	-5.959	2.08	-1.50	.732	7.75	.78	.00	.00
5T	19.30	.526	17.29	-6.093	2.01	-1.21	.730	7.84	.65	.00	.00

AVERAGES: 70708 BASELINE W071 00 000

	22.68	.573	20.77	-7.286	1.70	-.44	.755	10.39	14.41	.00	.00
STD	.48	.007	.52	.325	.08	.22	.005	.37	5.56	*	*

70708 W068CR004 (1E15)

	19.33	.529	17.27	-5.954	2.09	-1.44	.730	7.89	.95	.00	.00
STD	.21	.002	.21	.290	.13	.30	.006	.13	.15	*	*

PERCENT OF BASELINE

	85.2	92.3	83.2	118.3	123	*****	96.6	76.0	6.6	*****	*****
STDZ	2.8	1.4	3.1	7.8	14	267.5	1.3	4.0	4.0	*****	*****

TABLE 8

I-V Data for $N^+/P/P^+$ Cells made on Al-doped Silicon

70607 W070AL003 W054 00 000

BLAISS 10/7 /77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(I0)	N	K	FF	EFF	QCD	PCDA	PCDR
1R*	22.50	.555	20.28	-6.578	1.88	-.11	.721	9.52	.00	.00	.00
1B	23.30	.572	21.41	-7.506	1.60	-.06	.753	10.62	3.00	.00	.00
2B*	22.50	.546	20.26	-6.287	1.97	-.88	.735	9.55	3.90	.00	.00
3B	23.60	.561	21.55	-7.081	1.72	-.41	.750	10.50	9.10	.00	.00
4B	23.70	.560	21.78	-7.583	1.57	-.13	.755	10.60	9.10	.00	.00
1C	18.40	.528	16.64	-6.724	1.77	-.43	.732	7.52	.91	.00	.00
3C	18.70	.534	17.07	-7.237	1.60	-.12	.742	7.84	.78	.00	.00
4C	18.90	.535	17.17	-6.990	1.70	-.26	.737	7.88	.78	.00	.00
5C	19.00	.535	17.20	-6.786	1.76	-.37	.733	7.88	.78	.00	.00
1S	18.50	.538	16.96	-7.496	1.56	-.25	.752	7.92	.65	.00	.00
2S	18.50	.535	16.89	-7.292	1.61	-.20	.744	7.79	.78	.00	.00
3S.*	16.80	.517	11.94	-3.086	6.49	-4.44	.496	4.56	.52	.00	.00
4S	18.60	.527	16.65	-6.218	1.96	-.72	.720	7.46	.78	.00	.00
1T	18.50	.531	16.98	-7.628	1.50	-.06	.751	7.80	1.04	.00	.00
2T	18.60	.528	17.00	-7.302	1.58	-.29	.748	7.77	1.04	.00	.00
3T	19.10	.540	17.50	-7.430	1.58	-.30	.752	8.21	.78	.00	.00
4T	18.30	.534	16.76	-7.438	1.56	-.26	.751	7.76	1.04	.00	.00

AVERAGES: 70607 BASELINE W054 00 000

23.53 .564 21.58 -7.423 1.63 -.20 .753 10.57 7.07 .00 .00

STD .17 .005 .15 .242 .06 .15 .002 .05 2.88 * *

70607 W070AL003

18.65 .533 16.98 -7.145 1.65 -.30 .742 7.80 .85 .00 .00

STD .24 .004 .24 .402 .13 .17 .010 .19 .13 * *

PERCENT OF BASELINE

79.2 94.5 78.7 103.8 102 50.9 98.6 73.8 12.0 *****

STD2 1.6 1.6 1.7 8.7 12 258.8 1.6 2.1 7.5 *****

TABLE 9

Comparison of Solar Cell Performance for n and p-base Devices
Containing Similar Metal Contamination Levels.

CELL TYPE	IMPURITY	IMPURITY (10^{15} at cm^{-3})	I_{sc}^*/I_{sc_0} X100	V_{oc}^*/V_{oc_0} X100	η^*/η_0 X100
P	V	0.4	45.5	84.2	30.6
n	V	0.4	81.2	91.6	69.8
P	Ni	3.0	86.4	95.6	83.2
n	Ni	4.0	98	74.6	54.8
P	Fe	.85	89.7	96.3	86.4
n	Fe	1.0	86.2	94.5	74.9

* I-V data normalized to baseline color cells containing no added impurity.

compared to 83% for the p-base devices. Much of the reduction in the n-base cell performance, however, is due to diminished open circuit voltage rather than short circuit current. This suggests that the junction itself rather than base lifetime is effected by Ni. Precipitation, known to occur for Ni^1 , may be the cause. We intend to examine this effect more closely using the quantitative I-V approach described in section 3.6.

The raw I-V data for the n-base devices is presented in Tables 10-12.

3.4 Extension of Data Base for Impurities in 4 Ωcm p-type Silicon.

Three ingots were analyzed as part of this task during the past quarter: W075, a multiply-doped ingot containing Ti and V, W077 doped with Mo, and W080 in which part of the boron was compensated with phosphorus. Ingot W077 was grown to broaden our information on the effects of impurities which may be used as materials of construction in reactors or furnaces. W080 is the first of a series of ingots designed to explore how compensation of the base dopant with electrically active impurities influences solar cell performance. The I-V data for the ingots are compiled in Tables 13 to 15.

The data for ingot W075, Table 13, confirms that the harmful effects of Ti and V on cell performance observed for the individual elements persists when the elements occur together. At the 10^{14} at/cm³ impurity level cell performance is reduced to 56% of baseline. The solar cells doped with Mo, Table 14, also show considerably reduced performance to about 74% of the baseline values, indicating this contaminant can have a significant effect when present in silicon. We estimate the impurity concentration of the ingot at about 6.5×10^{14} at/cm³ on the basis of the assumed segregation coefficient. The concentration is below the detection limits of SSMS so neutron activation analyses are planned for this material. The phosphorus compensation in ingot W080 is about 15% of the boron, and as the data in Table 15 indicate, at this level cell performance is not changed from the baseline values.

TABLE 10

Solar Cell I-V Data for n-base Wafers Containing Vanadium.

70726 W082N-V001 W060 00 000

SOL2 10/4 /77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(I0)	N	R	FF	EFF	OCB	PCDA	PCDF
1R*	22.50	.553	20.21	-6.394	1.95	-.24	.718	9.45	.00	.00	.00
1R.*	21.60	.551	19.30	-5.984	2.13	-.98	.723	9.10	6.50	.00	.00
2B	21.40	.555	19.69	-7.782	1.52	.07	.753	9.45	6.50	.00	.00
3HFB	21.90	.562	20.24	-7.992	1.48	-.16	.766	9.97	9.10	.00	.00
4HFB	21.40	.552	19.61	-7.453	1.59	-.15	.751	9.38	6.54	.00	.00
1CNS	17.20	.511	15.39	-6.333	1.87	-.33	.712	6.62	1.69	.00	.00
3CNS	17.90	.514	16.08	-6.346	1.87	-.80	.727	7.07	.91	.00	.00
4CNS	17.60	.512	15.99	-6.962	1.64	-.40	.739	7.04	.91	.00	.00
5CNS	17.70	.512	15.95	-6.542	1.79	-.61	.729	6.99	1.56	.00	.00
6CNS	17.60	.510	15.72	-6.246	1.90	-.39	.711	6.75	1.56	.00	.00
7C	17.50	.512	15.69	-6.281	1.89	-.86	.725	6.87	.91	.00	.00
8C	17.50	.510	15.44	-5.662	2.18	-1.21	.705	6.65	1.04	.00	.00
9C	17.70	.510	15.88	-6.262	1.89	-.94	.727	6.94	1.30	.00	.00
10C	17.90	.512	16.10	-6.398	1.84	-.83	.730	7.07	1.30	.00	.00
1S	17.60	.513	15.79	-6.478	1.81	-.19	.715	6.83	1.30	.00	.00
2S	17.30	.513	15.61	-6.723	1.73	-.20	.724	6.80	1.04	.00	.00
3S	17.70	.514	15.97	-6.656	1.75	-.35	.726	6.99	1.04	.00	.00
4S	17.60	.513	15.88	-6.678	1.74	-.28	.725	6.92	1.69	.00	.00
1T	17.20	.503	14.83	-5.023	2.58	-1.66	.677	6.19	.78	.00	.00
2T	17.10	.508	14.86	-5.246	2.44	-1.37	.683	6.28	1.30	.00	.00
3T	17.10	.504	14.85	-5.341	2.36	-.81	.675	6.15	.78	.00	.00
4T	17.40	.509	15.51	-6.151	1.94	-.49	.709	6.64	1.82	.00	.00
5T.*	17.30	.508	12.93	-3.692	4.38	.56	.506	4.70	1.56	.00	.00
6T	17.50	.495	14.60	-4.444	3.08	-1.78	.636	5.82	.78	.00	.00

AVERAGES: 70726 BASELINE W060 00 000

21.57 .556 19.85 -7.743 1.53 -.08 .756 9.60 7.38 .00 .00

STD .24 .004 .28 .222 .03 .11 .007 .26 1.22 * *

70726 W082N-V001

17.51 .510 15.56 -6.098 2.02 -.75 .710 6.70 1.21 .00 .00

STD .24 .005 .46 .658 .36 .47 .025 .35 .34 * *

PERCENT OF BASELINE

81.2 91.6 78.4 121.2 132 ***** 93.8 69.8 16.3 ***** *****

STDZ 2.0 1.5 3.5 11.0 28 ***** 4.3 5.7 8.0 ***** *****

TABLE 11

Solar Cell I-V Data for n-base Wafers Containing nickel.

70725 W081-N-NI001 W060 00 000

SOL2 10/4 /77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(10)	N	R	FF	EFF	OCB	PCDA	PCDR
1K*	22.50	.557	20.26	-6.511	1.91	-.18	.721	9.55	.00	.00	.00
1B	21.40	.557	19.42	-7.077	1.72	.30	.724	9.13	7.80	.00	.00
2B	22.10	.568	20.62	-9.078	1.28	.34	.774	10.27	9.10	.00	.00
3B	21.50	.560	19.80	-7.945	1.49	.29	.750	9.55	7.80	.00	.00
4B	21.30	.559	19.57	-7.810	1.52	.32	.745	9.38	6.76	.00	.00
1C	21.20	.541	17.89	-4.407	3.31	-2.34	.660	8.01	1.95	.00	.00
2C	21.10	.540	17.52	-4.140	3.66	-2.70	.644	7.75	1.56	.00	.00
3C	20.90	.294	15.99	-3.727	2.39	.04	.529	3.44	1.69	.00	.00
4C	21.40	.466	17.08	-4.656	2.61	2.62	.536	5.65	1.04	.00	.00
5C	21.30	.372	16.88	-4.159	2.50	.66	.551	4.62	.65	.00	.00
6CNS	20.60	.371	16.30	-4.353	2.32	1.46	.539	4.35	1.30	.00	.00
7CNS	21.00	.369	16.41	-4.087	2.56	.93	.535	4.38	1.30	.00	.00
8CNS	20.80	.357	16.28	-4.140	2.42	1.04	.535	4.20	.91	.00	.00
9CNS	20.80	.360	16.17	-4.089	2.50	1.11	.528	4.18	.91	.00	.00
10CNS	21.30	.414	17.01	-4.298	2.63	.98	.555	5.17	1.56	.00	.00
1S	21.00	.513	17.04	-4.229	3.36	-.22	.587	6.69	1.56	.00	.00
2S	21.50	.447	16.61	-4.309	2.83	2.68	.508	5.16	1.82	.00	.00
3S	21.10	.498	16.79	-4.100	3.43	.28	.562	6.25	.65	.00	.00
4S	21.30	.436	16.61	-4.274	2.80	2.06	.522	5.12	1.17	.00	.00
5S	21.10	.519	16.98	-3.891	3.91	-1.92	.598	6.92	.78	.00	.00
1T	21.90	.335	17.35	-3.798	2.61	-.88	.576	4.47	1.95	.00	.00
2T	21.30	.345	16.56	-3.958	2.52	.54	.536	4.16	1.82	.00	.00
3T	21.20	.411	16.85	-4.401	2.52	1.61	.542	4.99	2.34	.00	.00
4T	21.40	.365	16.64	-4.107	2.50	1.21	.527	4.35	1.30	.00	.00

AVERAGES: 70725 BASELINE W060 00 000

	21.58	.561	19.85	-7.978	1.50	.31	.748	9.58	7.87	.00	.00
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STD	.31	.004	.46	.716	.16	.02	.018	.42	.83	*	*
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70725 W081-N-NI001

	21.17	.419	16.79	-4.164	2.81	.48	.556	5.26	1.38	.00	.00
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STD	.29	.074	.47	.219	.46	1.49	.040	1.26	.47	*	*
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PERCENT OF BASELINE

	98.1	74.6	84.6	147.8	187	153.8	74.3	54.8	17.6	*****	*****
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STDZ	2.8	13.8	4.4	7.7	53	512.3	7.2	16.1	8.5	*****	*****
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TABLE 12

Solar Cell I-V Data for n-base Wafers Containing Iron.

70829 W083NFE001 (8.6E14) <70412> W060 00 000
 SOL2 10/6 /77 AM1: P0=91.60MW/CM² NO AIR COATING

ID	ISC	VOC	IP	LOG(10)	N	R	FF	EFF	QCD	PCDA	PCDP
1R*	22.50	.557	20.09	-6.084	2.10	-.46	.712	9.44	.00	.00	.00
1CB	22.70	.567	21.12	-8.705	1.34	.22	.770	10.48	9.10	.00	.00
2CB	22.60	.561	20.99	-8.550	1.36	.17	.769	10.30	9.10	.00	.00
3CB	22.90	.568	21.41	-9.248	1.25	.30	.779	10.71	3.25	.00	.00
4CB	22.90	.565	21.18	-8.093	1.46	-.03	.765	10.47	9.10	.00	.00
5CB	22.80	.568	21.05	-7.944	1.51	-.07	.762	10.44	9.10	.00	.00
1C	19.50	.535	16.97	-5.098	2.64	-1.88	.694	7.66	1.30	.00	.00
2C	20.00	.539	17.53	-5.400	2.43	-1.20	.696	7.93	2.21	.00	.00
3C	19.10	.534	16.74	-5.394	2.43	-1.40	.698	7.53	1.69	.00	.00
4C.*	18.50	.526	15.50	-4.151	3.63	-4.32	.671	6.91	1.56	.00	.00
5C	20.30	.543	18.39	-6.654	1.83	-.70	.740	8.62	2.34	.00	.00
6C	19.40	.534	17.23	-5.890	2.14	-.83	.710	7.77	1.82	.00	.00
7C	19.30	.529	16.99	-5.726	2.20	-.42	.690	7.45	1.69	.00	.00
8C	20.90	.542	17.88	-4.644	3.05	-2.27	.677	8.11	2.34	.00	.00
9C	20.50	.545	18.70	-7.220	1.65	-.11	.742	8.76	3.51	.00	.00
10C	13.80	.530	16.26	-4.833	2.85	-2.86	.699	7.36	1.04	.00	.00
11C	21.00	.544	19.00	-6.915	1.73	.23	.721	8.71	4.55	.00	.00
12C	21.30	.545	18.59	-5.368	2.46	-.69	.682	8.37	3.77	.00	.00
1S	21.40	.550	19.50	-7.204	1.66	.09	.735	9.15	5.85	.00	.00
2S	21.50	.548	19.54	-7.037	1.70	.03	.732	9.12	4.55	.00	.00
5S.*	21.50	.547	17.29	-3.448	5.11	-6.24	.644	8.01	4.55	.00	.00
1T	17.70	.514	15.43	-5.542	2.27	-.25	.673	6.48	1.69	.00	.00
2T	18.30	.521	16.18	-5.824	2.13	-.61	.698	7.04	.91	.00	.00
3T	18.00	.521	16.07	-6.217	1.95	-.37	.709	7.03	1.95	.00	.00
4T	18.40	.525	16.31	-5.889	2.11	-.73	.705	7.20	1.04	.00	.00
5T	18.00	.523	15.94	-5.911	2.10	-.56	.701	6.98	1.69	.00	.00

AVERAGES: 70829 BASELINE W060 00 000

	22.73	.556	21.15	-8.508	1.38	.12	.760	10.48	7.93	.00	.00
STD	.12	.003	.15	.464	.09	.14	.006	.13	2.34	*	*

70829 W083NFE001 (8.6E14) <70412>

	19.63	.535	17.40	-5.932	2.18	-.81	.706	7.35	2.44	.00	.00
STD	1.24	.010	1.26	.772	.30	.31	.020	.77	1.37	*	*

PERCENT OF BASELINE

	86.2	94.5	82.3	130.3	158	*****	91.8	74.9	30.8	*****	*****
STDZ	5.9	2.3	6.5	13.4	41	*****	3.3	8.4	31.5	*****	*****

TABLE 13

Solar Cell I-V Data for 4 Ω cm p-type Silicon Containing 10^{14} at/cm³
each of Titanium and Vanadium.

SOL2 10/4 /77

70614 W075TI-V002 (1E14-1E14) W054 00 000

SOL2 10/4 /77 AM1: P0=91.60MW/CM² NO AN COATING

ID	ISC	VOC	IP	LOG(I0)	N	R	FF	EFF	OCD	PCDA	PCDR
1K*	22.50	.554	20.33	-6.747	1.81	.01	.723	9.53	.00	.00	.00
1B.*	22.20	.548	19.81	-5.876	2.17	-1.16	.725	9.33	3.38	.00	.00
2B	22.10	.548	20.03	-6.636	1.84	-.68	.742	9.50	3.90	.00	.00
3B	22.20	.549	20.16	-6.682	1.82	-.83	.748	9.65	3.90	.00	.00
4B	22.20	.549	20.42	-7.620	1.54	-.27	.760	9.80	4.16	.00	.00
1C	15.40	.486	13.79	-6.604	1.69	.38	.702	5.56	.22	.00	.00
2C	15.30	.485	13.62	-6.309	1.80	.03	.699	5.49	.13	.00	.00
3C	15.50	.483	13.79	-6.250	1.82	-.09	.700	5.54	.39	.00	.00
4C	15.50	.483	13.70	-5.953	1.95	-.45	.696	5.51	.39	.00	.00
5C	15.40	.482	13.55	-5.923	1.96	.06	.681	5.35	.91	.00	.00
6C	15.40	.479	13.48	-5.732	2.04	-.16	.677	5.28	.65	.00	.00
7C	15.40	.483	13.66	-6.190	1.84	.08	.693	5.45	.91	.00	.00
8C	15.50	.482	13.71	-6.178	1.84	.44	.684	5.40	.91	.00	.00
9C.*	15.40	.478	12.71	-4.214	3.32	-3.15	.634	4.94	.39	.00	.00
10C	15.70	.483	13.91	-6.176	1.85	.24	.689	5.52	.91	.00	.00
11C	15.60	.480	13.66	-5.729	2.04	-.14	.677	5.36	.91	.00	.00
1S	15.70	.483	13.80	-5.747	2.05	-.59	.689	5.53	.91	.00	.00
2S	15.60	.486	13.91	-6.255	1.83	-.36	.707	5.67	.39	.00	.00
3S	15.90	.486	14.12	-6.117	1.88	-.35	.701	5.73	1.04	.00	.00
4S	15.70	.486	13.97	-6.158	1.86	-.41	.705	5.69	.65	.00	.00
1T	15.10	.483	13.51	-6.568	1.70	.30	.703	5.42	.65	.00	.00
2T	15.10	.480	13.40	-6.316	1.78	.47	.689	5.28	.65	.00	.00
3T	15.10	.481	13.51	-6.608	1.68	.46	.700	5.38	.65	.00	.00
4T	15.10	.481	13.22	-5.823	2.01	.23	.672	5.16	.91	.00	.00
5T	15.30	.482	13.68	-6.545	1.70	.31	.702	5.47	.91	.00	.00
6T	15.30	.483	13.68	-6.514	1.72	.17	.704	5.50	.91	.00	.00

AVERAGES: 70614 BASELINE W054 00 000

	22.17	.549	20.21	-6.980	1.73	-.59	.750	9.65	3.99	.00	.00
STD	.05	.000	.16	.453	.14	.24	.008	.12	.12	*	*

70614 W075TI-V002 (1E14-1E14)

	15.43	.483	13.68	-6.185	1.85	.03	.694	5.47	.70	.00	.00
STD	.22	.002	.20	.267	.12	.32	.010	.14	.26	*	*

PERCENT OF BASELINE

	69.6	88.0	67.7	111.4	107	205.2	92.5	56.6	17.6	*****	*****
STD%	1.2	.4	1.6	10.1	16	79.0	2.3	2.2	7.3	*****	*****

TABLE 14

Solar Cell I-V Data for 4 Ω cm p-type Silicon Containing Molybdenum.

70615 W077M0001 (6.5E14) W054 00 000

SOL2 10/4 /77 AM1: PO=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(10)	N	R	FF	EFF	OCD	PCDA	PCDR
1R*	22.50	.551	20.12	-6.149	2.04	-.43	.714	9.37	.00	.00	.00
1B	22.70	.551	20.79	-7.302	1.63	-.32	.753	9.96	5.60	.00	.00
2B	22.00	.548	20.07	-7.072	1.69	-.42	.748	9.54	4.40	.00	.00
3B	22.70	.550	20.98	-7.956	1.46	-.19	.767	10.13	5.20	.00	.00
4B	22.30	.549	20.41	-7.236	1.64	-.45	.755	9.77	5.20	.00	.00
5B	22.60	.549	20.76	-7.672	1.52	.06	.751	9.85	4.55	.00	.00
1C	19.10	.504	17.07	-6.152	1.90	-.66	.718	7.30	.52	.00	.00
2C	18.70	.504	16.74	-6.190	1.89	-.73	.720	7.18	1.04	.00	.00
3C	18.80	.504	16.72	-5.886	2.02	-1.01	.715	7.16	.91	.00	.00
4C	18.80	.503	16.39	-5.214	2.41	-1.60	.694	6.94	.91	.00	.00
5C	18.70	.505	16.78	-6.267	1.86	-.82	.726	7.25	.78	.00	.00
6C	18.80	.505	16.82	-6.100	1.93	-1.02	.725	7.28	.91	.00	.00
7C	18.60	.503	16.24	-5.160	2.45	-2.04	.702	6.95	.91	.00	.00
8C	19.50	.506	17.23	-5.672	2.13	-1.01	.706	7.37	.91	.00	.00
9C	18.70	.503	16.62	-5.912	2.01	-.86	.711	7.08	.65	.00	.00
10C	18.80	.504	16.87	-6.317	1.83	-.64	.723	7.25	.91	.00	.00
1S	18.40	.505	16.51	-6.221	1.88	-1.01	.729	7.17	.65	.00	.00
2S	18.80	.505	16.91	-6.455	1.78	-.52	.725	7.28	.78	.00	.00
3S	19.00	.505	17.03	-6.250	1.86	-.70	.723	7.33	.65	.00	.00
4S	19.00	.503	16.98	-6.099	1.92	-.83	.720	7.28	.78	.00	.00
5S	19.00	.503	17.11	-6.524	1.75	-.44	.726	7.34	.91	.00	.00
1T	19.50	.508	17.47	-6.179	1.90	-.81	.724	7.58	.91	.00	.00
2T	19.30	.508	17.41	-6.533	1.76	-.58	.731	7.58	.91	.00	.00
3T	19.40	.507	17.39	-6.243	1.87	-.71	.723	7.52	.91	.00	.00
4T	19.40	.507	17.42	-6.261	1.86	-.85	.728	7.58	1.04	.00	.00
5T	19.30	.506	17.35	-6.373	1.81	-.63	.726	7.50	1.04	.00	.00
6T	19.40	.505	17.30	-6.046	1.95	-.72	.715	7.41	1.17	.00	.00

AVERAGES: 70615 BASELINE W054 00 000

	22.46	.549	20.60	-7.448	1.59	-.26	.755	9.85	4.99	.00	.00
STD	.27	.001	.32	.321	.09	.18	.007	.19	.45	*	*

70615 W077M0001 (6.5E14)

	19.00	.505	16.97	-6.098	1.94	-.37	.720	7.30	.87	.00	.00
STD	.32	.002	.35	.357	.13	.35	.009	.13	.15	*	*

PERCENT OF BASELINE

	84.6	91.9	82.4	118.1	122	*****	95.4	74.1	17.4	*****	*****
STDZ	2.5	.5	3.0	8.5	19	457.5	2.1	3.4	4.9	*****	*****

TABLE 15

Solar Cell I-V Data for 4 Ω cm p-type Silicon Containing Phosphorus.

SOL2 10/4 /77

70721 W080PH001 W054 00 000

SOL2 10/4 /77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(I0)	N	R	FF	EFF	OCD	PCDA	PCDE
1R*	22.50	.553	20.18	-6.347	1.97	-.21	.715	9.41	.00	.00	.00
1B	21.50	.547	19.73	-7.456	1.58	-.29	.755	9.39	3.90	.00	.00
2B	21.90	.549	19.82	-6.514	1.89	-.86	.743	9.44	3.90	.00	.00
3B	21.40	.546	19.30	-6.312	1.96	-1.11	.741	9.16	3.25	.00	.00
4B	21.60	.546	19.64	-6.823	1.77	-.64	.747	9.31	3.25	.00	.00
1C	22.30	.550	20.37	-7.120	1.68	-.41	.750	9.73	4.55	.00	.00
2C	22.10	.549	20.13	-6.905	1.75	-.59	.748	9.60	4.94	.00	.00
3C	22.20	.550	20.18	-6.794	1.79	-.64	.746	9.64	5.85	.00	.00
4C	22.30	.549	20.47	-7.540	1.56	-.11	.752	9.74	5.20	.00	.00
5C	22.10	.546	20.03	-6.741	1.79	-.41	.737	9.40	5.46	.00	.00
6C	22.20	.546	19.73	-5.860	2.17	-.69	.709	9.09	4.55	.00	.00
7C	22.10	.549	20.24	-7.245	1.64	-.52	.757	9.72	5.85	.00	.00
8C	22.00	.546	19.66	-5.939	2.13	-1.10	.726	9.22	4.55	.00	.00
9C	22.00	.545	19.87	-6.545	1.86	-.51	.732	9.29	5.20	.00	.00
1S	21.70	.548	19.77	-6.961	1.73	-.53	.748	9.40	4.55	.00	.00
2S	22.10	.550	20.38	-7.973	1.45	.11	.757	9.72	6.50	.00	.00
3S	22.00	.548	20.16	-7.349	1.61	-.35	.755	9.62	5.85	.00	.00
4S	22.00	.546	19.90	-6.570	1.86	-.63	.737	9.37	5.20	.00	.00
5S	21.90	.547	20.05	-7.315	1.62	-.32	.753	9.53	5.85	.00	.00
1T	21.70	.548	19.87	-7.440	1.58	-.04	.747	9.39	5.20	.00	.00
2T	21.90	.548	19.98	-7.101	1.68	-.32	.746	9.46	4.55	.00	.00
3T	21.90	.546	19.92	-6.892	1.74	-.44	.743	9.39	4.81	.00	.00
4T	22.30	.546	20.04	-6.250	1.93	-.71	.728	9.37	4.55	.00	.00
5T	22.30	.547	20.34	-7.162	1.66	-.10	.741	9.55	5.59	.00	.00

AVERAGES: 70721 BASELINE W054 00 000

	21.60	.547	19.62	-6.776	1.80	-.73	.746	9.33	3.58	.00	.00
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STD	.19	.001	.19	.432	.15	.30	.005	.11	.33	*	*
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70721 W080PH001

	22.03	.543	20.06	-6.932	1.75	-.44	.743	9.49	5.20	.00	.00
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STD	.18	.002	.23	.522	.18	.27	.012	.18	.58	*	*
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PERCENT OF BASELINE

	102.1	****	102.2	97.7	97	139.8	99.5	101.7	145.5	*****	*****
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STDZ	1.7	.5	2.2	14.7	19	73.3	2.3	3.1	30.9	*****	*****
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3.5 Impurity/Grain Boundary Interactions

Polycrystalline ingots or forms of silicon sheet containing grain boundaries are potential low cost substrates for terrestrial solar cells. Thus a small part of this program is directed at elucidating the response of solar cells made on polycrystalline silicon to controlled additions of metal contaminants. As a first step in this study a baseline (no added metal impurity) 4 Ω cm p-type ingot was grown from a polycrystalline seed, wafered and then processed to solar cells using our standard sequence for N^+/P devices.

The I-V data for the polycrystalline ingot W076, and concurrently processed single crystal baseline material appear in Table 16. The designations C, S, and T in the left hand column of the data printout refer to wafers from the center, seed and tang positions of the ingot. Overall the cells on the polycrystalline ingot are about 71% as efficient as the baseline material. However, material from the tang end of the ingot appears to give higher cell performance than that from the seed or center sections. This is perhaps consistent with the fact that material from the tang end contains some grains well over a mm in size, Fig 1 (a), while the first part of the ingot to freeze contained a much higher density of twins and associated dislocations, Fig. 1 (b).

TABLE 16

Solar Cell I-V Data for Polycrystalline 4 Ω cm p-type Ingot.

70613 W076POLY002 W054 00 000

SOL1 10/4 /77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(10)	N	R	FF	FFF	OCD	PCDA	PCDE
1R*	22.50	.553	20.18	-6.315	1.98	-.30	.717	9.44	.00	.00	.00
1B*	21.70	.542	18.85	-4.932	2.77	-2.11	.698	8.68	2.99	.00	.00
2B	22.30	.549	20.39	-7.257	1.64	-.23	.748	9.69	5.46	.00	.00
3B	22.30	.550	20.28	-6.777	1.79	-.74	.749	9.72	4.55	.00	.00
4B*	21.70	.543	19.03	-5.208	2.56	-1.88	.710	8.84	3.51	.00	.00
5B	22.10	.548	20.03	-6.636	1.84	-.68	.742	9.50	5.20	.00	.00
1C	18.40	.508	16.24	-6.051	1.97	.43	.680	6.72	1.04	.00	.00
2C	19.00	.505	16.18	-4.936	2.62	-.50	.646	6.55	.78	.00	.00
3C	18.70	.509	15.92	-5.170	2.47	.59	.631	6.35	.91	.00	.00
4C	18.50	.510	16.34	-5.942	2.02	-.07	.690	6.88	1.04	.00	.00
5C	18.80	.506	16.23	-5.452	2.27	.51	.649	6.53	.78	.00	.00
6C	19.40	.507	16.55	-5.092	2.51	.11	.640	6.66	.91	.00	.00
7C	19.30	.512	17.06	-6.040	1.98	.27	.685	7.16	1.04	.00	.00
8C	19.80	.512	17.17	-5.222	2.43	-.80	.674	7.23	1.04	.00	.00
9C	19.00	.504	16.31	-4.927	2.63	-1.33	.668	6.77	.91	.00	.00
10C	19.20	.514	17.05	-6.011	2.00	-.39	.703	7.34	.91	.00	.00
11C.*	19.00	.359	14.12	-4.258	2.36	3.45	.469	3.39	.39	.00	.00
1S.*	18.70	.412	14.40	-4.475	2.50	3.40	.500	4.07	.39	.00	.00
2S	19.30	.514	17.27	-6.241	1.90	-.47	.715	7.51	1.17	.00	.00
3S	19.40	.509	16.15	-4.220	3.39	-2.65	.645	6.74	.78	.00	.00
4S	18.50	.492	15.52	-4.592	2.87	-1.10	.635	6.12	.52	.00	.00
5S.*	17.90	.427	13.47	-4.310	2.78	3.92	.481	3.89	.26	.00	.00
6S	18.60	.416	14.15	-4.211	2.80	2.85	.497	4.06	.26	.00	.00
7S	18.10	.481	14.58	-3.997	3.56	-1.83	.597	5.49	3.90	.00	.00
1T	20.70	.528	18.61	-6.421	1.86	-.37	.722	8.34	1.30	.00	.00
2T	19.70	.519	17.57	-6.170	1.94	-.26	.707	7.64	1.04	.00	.00
3T	20.20	.515	17.50	-5.130	2.50	-1.12	.679	7.47	.78	.00	.00
4T	20.00	.523	17.88	-6.244	1.92	-.28	.711	7.86	1.17	.00	.00
5T	19.50	.514	17.26	-5.894	2.05	-.39	.698	7.40	1.04	.00	.00
6T	19.70	.517	17.50	-5.970	2.03	-.51	.705	7.60	1.04	.00	.00

AVERAGES: 70613 BASELINE W054 00 000

	22.23	.549	20.23	-6.890	1.76	-.55	.746	9.63	5.07	.00	.00
STD	.10	.001	.15	.265	.09	.23	.003	.09	.38	*	*
70613 W076POLY002											
	19.23	.505	16.62	-5.425	2.37	-.35	.666	6.88	1.06	.00	.00
STD	.64	.022	1.03	.731	.48	1.05	.050	.89	.67	*	*
PERCENT OF BASELINE											
	86.5	92.1	82.1	121.3	135	136.8	89.2	71.4	21.0	*****	*****
STD%	3.3	4.2	5.8	14.1	35	293.7	7.1	10.0	15.8	*****	*****

(a) Seed end

(b) Tang end

FIGURE 1 Sirtl Etched Wafers from the Seed and Tang Ends of Polycrystalline Baseline Ingot W076. Reflected Light 32X

3.6 Refinement of Analytical Techniques for Silicon Material and Solar Cells

A major endeavor of this program is to quantify by the use of improved analytical techniques the relations between impurity-process interactions and solar cell performance. The mathematical model used to predict the behavior of solar cells containing single and multiple contaminants is one aspect of this effort.^{1,3} The correlation of data from thermally-stimulated measurements, refined PCD lifetime techniques and quantitative I-V measurement forms a second part of the approach. The following sections describe recent progress in the latter three areas.

3.6.1 Thermally Stimulated Measurements

During this reporting period, apparatus was modified to measure trap density and trapping parameters by both thermally stimulated current and capacitance measurements. Our initial attempts to detect deep level traps in solar cell material have been frustrated for reasons which are attributed to thermal deficiencies in the sample holder. These deficiencies are being corrected in a new sample holder which is now being built. The electronic components of the system have performed satisfactorily and have exhibited sufficient sensitivity to make the anticipated measurements.

3.6.2 Recombination Lifetime Measurements (PCD)

PCD lifetime measurements, as noted in Section 3.2, are being used to track the response of impurity-doped silicon to various thermal and gettering treatments which are employed during cell processing. To be meaningful the measurements must be carried out in a precise and reproducible fashion that provide data which characterize the state of the material before and after processing. Thus we have carried out a sequence of tests to calibrate the laser-excited PCD apparatus and to assess possible error ranges in the measurement technique.

Accurate PCD measurements requires that the surface recombination velocity, s , be known so that proper correction factors can be applied to the measured time constant, τ_r' , in order to obtain the bulk lifetime. In several previous attempts to determine s , scatter in the data limited the confidence level that could be placed on the value of the surface recombination that was deduced.

The technique used to determine s was to measure τ_r' in a single piece of silicon as it was thinned by etching and to mathematically find a value of s which produced the best curve fit to the data. Silicon wafers with an initial thickness of 0.254 mm were used in these experiments since they were readily available. An insufficient number of data points were produced using these thin wafers to achieve good statistical analysis. Recently, silicon wafers with greater initial thickness, 2.01 mm, have been used to refine this technique. The samples were thinned by a combination of lapping and etching. The uncorrected or effective lifetime for this series of measurements is shown in Fig. 2. The effect of higher modes was taken into consideration primarily by obtaining the average time constant between the 1/2 and 1/4 points of the maximum oscilloscope amplitude. As we will show later, this allowance for higher modes is insufficient for wafers with a bulk lifetime of 18.9 μsec and a thickness less than 0.6 mm. The curve in Fig. 2 can also be interpreted as the calculated bulk lifetime where s is equal to zero.

Clearly, s is greater than zero since the curve bends downward for thinner silicon. The flattening of the curve for large values of d is a consequence of the fact that $D_n (\tau_r^2/d^2)$ becomes small compared to $1/\tau_r$. The asymptotic value of the curve is equal to τ_r . The value of τ_r can be bracketed by noting that the calculated value of τ_r ($2d = 2\text{mm}$, $\tau_r' = 16 \mu\text{sec}$) varies between the narrow range of 17.4 to 18.5 μsec as s is mathematically varied over the extreme range of 1×10^3 to $2 \times 10^4 \text{ cm/sec}$.

Fig. 2 Experimental data to be used in mathematically determining the surface recombination velocity, s , on p type silicon

The curve shown in Fig. 3 represents the calculated value of τ_r when s is assumed to be equal to infinity. Theoretically, this value of s should produce a curve which increases monotonically as the thickness decreases. The curve can be analyzed by dividing it into two regions, (1) where surface recombination dominates (thickness greater than 0.5 mm) and (2) where high order modes dominate (thickness less than 0.5 mm). The shape of the curve beyond 0.5 mm indicates that s is much less than infinity.

Fig. 4 was calculated with a surface recombination velocity assumed to be 1.3×10^4 cm/sec. Again, the curve beyond $2d = 0.8$ mm indicates that s is less than 1.3×10^4 cm/sec. Through iteration of the data it was determined that the calculated lifetime became constant with thickness when s was made equal to 5×10^3 cm/sec. Fig. 5 shows the best fit curve obtained for $s = 5 \times 10^3$ cm/sec, considered accurate to +0-30% based on the perception of slope change. The average value ($n=15$) of τ_r obtained for $2d$ greater than 0.8 mm is 18.6 μ sec, and the standard deviation is 1.0 or a probable error of 0.68 μ sec.

The poorer accuracy in lifetime determination for $2d$ values less than 0.7 mm (28 mils) is attributed mainly to the effects of higher modes in the spatial distribution of minority carriers. The effect of higher modes was discussed at length previously.³ In theory the effect can be reduced to insignificance (less than 5%) by measuring the slope of the decay curve on the oscilloscope after the amplitude has decayed to less than 10% of the initial value. As a practical matter this is most difficult to do because of noise in the weak electrical signals. τ_r' is more readily determined when the amplitude has decayed to 1/2 or 1/4 of its initial value. This compromise yields values for τ_r' which are less than the true value for the desired zero order mode. The measurement error may be quite small but because of differential nature of Equation 3.6-1, it may be magnified manifold

$$\frac{1}{\tau_r} = \left[\frac{1}{\tau_r'} - D_n \left(\frac{2}{d^2} \right) \right] \quad (3.6-1)$$

Fig. 3 Calculated bulk lifetime as a function of thickness for the case when s is assumed to be equal to infinity

Fig. 4 Calculated bulk lifetime as a function of thickness for the case when s is assumed to be equal to $1.3 \times 10^4 \text{ cm/sec}$

Curve 692296-A

Fig. 5 Correctly chosen value of $s = 5 \times 10^3 \text{ cm/sec}$ yields a constant value for $\tau_r = 18.6 \mu \text{ sec}$ as thickness is varied above 0.8 mm

and yield large errors in the calculated value of τ_r . This type of error always produces a calculated value of τ_r which is less than the true value as indicated by the curves in Figures 2, 3, and 4. The error increases rapidly for thin wafers with high lifetime, since $D_n (\xi_0^2/d^2)$ may be nearly equal to the value of $1/\tau_r'$. For convenience, the factor $D_n (\xi_0^2/d^2)$ is often referred to as the surface rate of the fundamental mode, $1/r_{ooo}$. Likewise, the factor $1/\tau_r$ is referred to as the bulk rate. The ratio of the bulk rate to the surface rate, $(1/\tau_r)/(1/r_{ooo})$, as described in the last quarterly report,³ was shown by Blakemore and Normura⁴ to be a principal factor in determining the accuracy of PCD measurements. A ratio of 1.0 or greater was recommended by them to achieve accuracies of about +0-50% [$N(\tau)/N(o) = 0.50$]; ratios less than 0.1 are considered to produce unreliable data. Fig. 6 shows a plot of the bulk lifetime, τ_r , necessary to achieve a ratio of 1.0, as a function of wafer thickness for p-type silicon. The curve indicates that a silicon specimen with a thickness of 0.65 mm is necessary for accurate PCD measurements when the bulk lifetime is 18.6 μ sec. This corresponds very closely with the point where large deviations begin to appear in Fig. 5. A superposition of the curve in Fig. 6 over that shown in Fig. 5 shows that the error for thin wafers is almost entirely due to the effects of higher modes. The balance of the error results from the fact that the specimen becomes "pillow" shaped in cross-section after repeated etching. The primary effect of the pillow shape is to enhance the effect of the higher modes since the wafer is thinner than the measured value $2d$ near the edges.

The tentative requirement that $(1/\tau_r)/(1/r_{ooo})$ be equal to or greater than 1.0 resulted from the fact that τ_r' was determined by measuring the time required for the signal to decay from $1/2$ to $1/4$ of its initial amplitude and then dividing by $\ln 2$. A minimum ratio of 0.1 would be more desirable in order to allow measurements of high lifetime on thin specimens. Accurate measurements, with a ratio of 0.1, are possible if the value of τ_r' is obtained after the signal has decayed to less than 10% of the initial value. The ability to make measurements in

Fig. 6 Maximum recombination lifetime which can be accurately measured (ratio = 1.0) on p-type silicon by PCD measurements as a function of sample thickness.

this region of the decay curve is determined by the signal to noise ratio. The signal to noise ratio can be improved by increasing the test current in the specimen, I_t and/or increasing the number of minority carriers at $t = 0$. The effect of increasing these two parameters was investigated experimentally to obtain practical limits for each.

The test current, I_t produces an electric field within the silicon sample which "sweeps" the minority carriers toward the ohmic contacts where they will experience enhanced recombination. The effect of electric field on the corrected recombination lifetime is shown in Fig. 7. The slight increase in the measured lifetime is contrary to that expected by simple theory, which indicates that the measured lifetime should be reduced by the effects of electric field. The deviation from simple theory is due to some rise in the specimen temperature by I^2R heating.

Simple theory predicts that the critical field may be calculated from the expression⁵

$$\vec{E}_x - 1.0 \times 10^4 \ll \sqrt{\frac{4D_n}{\mu_n^2 \tau_r}} \quad (3.6-2)$$

The critical field calculated for the measured sample is 1.98 volts/cm. No curvature is noted in Fig. 7 beyond this critical point. The reason for this behavior is that the ohmic contacts are spaced 1.0 cm apart whereas the laser pulsed light is applied to a length of only 0.5 cm. Therefore, the carriers can experience considerable drift before reaching the ohmic contacts. The calculated lifetime in Fig. 7 for an electric field of zero is 20.3 μsec . This is higher than the value of 18.6 μsec shown in Fig. 5. The reason as discussed below, is that the injection level was increased from 4×10^{-3} to $1.1 \times 10^{-2} \text{ cm}^{-3}$.

Fig. 7 Effect of electric field, $\vec{E}$, produced by the specimen test current, I_t , on photoconductivity decay measurements

The effect of injection level on PCD measurements is shown in Fig. 8. The injection ratio was calculated by⁶

$$\Delta n/n = \frac{b}{b+1} \frac{\Delta v/v}{L/L_0 - \Delta v/v} \quad (3.6-3)$$

Where: $\Delta n/n$ = ratio of injected minority carriers to majority carriers

b = mobility ratio of majority to minority carriers

$\Delta v/v$ = relative change in photovoltage to dark voltage

L/L_0 = ratio of illuminated length to the total electrical length.

A ratio of 1.0 for $\Delta n/n$ is defined as high level injection and τ_r asymptotically approaches $\tau_{no} + \tau_{po}$ as the injection level increases. The shape of the curve in Fig. 8 is typical of that obtained by other experimenters.⁶ This curve has considerable significance for the design of multi-sun solar cells as well as in making accurate PCD measurements.

In summary, the laser-excited PCD equipment is now calibrated for measurements on p-type silicon. Errors due to electric field will be less than 5% when the field is limited to 1.0 volt/cm. Errors due to injection level will be less than 5% when the injection ratio is limited to 5×10^{-3} . Errors due to the effects of higher modes [$\tau_r' = (\tau_{1/2} - \tau_{1/4})/\ln 2$] can be kept in the range +0-50% when the ratio $(1/\tau)/(1/\tau_{ooo})$ is greater than 1.0. The leeway allowed in the electric field and injection level over that used in obtaining Figures 2-5 indicates that τ_r' can be accurately determined after the higher modes have decayed or the signal has decayed to less than 10% of initial signal at $t = 0$. This technique, to be evaluated shortly, will increase the accuracy and/or allow lower ratios of bulk rate to surface rates. The equipment will soon be applied in the processing studies described in section 3.2.

3.5.3 Evaluation of Impurity/Processing Effects on Solar Cell Performance by Means of Quantitative I-V Curve Analysis.

Although the mathematical model we recently developed^{1,3} predicts quite well the effect of multiple contaminants on silicon solar cell efficiency, it cannot, because of its phenomenological nature, be used to analyze a number of process-induced effects which influence solar cell behavior. Nor can the nonlinear effects of impurities such as copper, nickel and iron be completely explained within the context of the model. For this reason we set out to develop a practical analytic and experimental technique which would allow separation of the junction and base region effects from each other and from effects due to contacting and resistance phenomena. The technique, which represents a synthesis of our ideas as well as some which have appeared over the years in the literature, is described below. Because we believe the approach provides a powerful tool for assessing both impurity and process dependent effects on solar cells and because what has been reported in the literature appears in diverse sources, we have discussed the technique in a tutorial fashion, and with considerable detail below. The work was primarily conducted as part of this study but for completeness the description is supplemented by data developed on an internally-funded Westinghouse program.

Fig. 8 Effect of pulsed light irradiance on photoconductivity decay measurements

3.5.3.1 Review of Diode Current-Voltage Characteristics

In a diode, forward bias reduces the barrier height across the junction allowing the majority carriers to cross the junction and diffuse as minority carriers before recombining. This bulk diffusion current is expressed by the equation.

$$I_B = I_{o1} \left(e^{qv/kt} - 1 \right) \quad (3.6.4)$$

where I_{o1} is the reverse saturation current given by

$$I_{o1} = AqN_i^2 \left[\frac{1}{N_A} \sqrt{\frac{D_n}{\pi n}} + \frac{1}{N_D} \sqrt{\frac{D_p}{\pi p}} \right] \quad (3.6.5)$$

In a real diode some carriers are lost in the depletion region as a result of recombination, trapping, and other conduction mechanisms such as, tunneling or field induced emission. This junction excess current is expressed as:^{9,10}

$$I_1 = I_{o2} \left(e^{qv/nkT} - 1 \right) \quad (3.6.6)$$

where n is > 2

There is always an intrinsic series resistance¹¹ present in a diode. In a solar cell the major source of this is the sheet resistance of the diffused region, while other less important sources are resistances of the base region and the contacts. Thus the terminal voltage differs from the junction voltage by IR_s drop.

Shunt or leakage current results from the imperfections which bridge the junction, especially at the edges where ohmic surface conduction paths are easily formed. This effect is represented by a physical shunt-resistance across the junction and a current.

$$I_{sh} = \frac{V_d^2}{R_{sh}} \quad (3.6.7)$$

Figure 9 shows an equivalent circuit of a real diode which includes all the above effects which mathematically are described by equation 3.6.8

FIG. 9 Equivalent circuit of a real diode.

$$\begin{aligned} I_d &= I_B + I_j + I_{sh} \\ &= I_{o1} \left[\frac{e^{q(V-IR_s)/kt}}{e - 1} \right] + I_{o2} \left[\frac{e^{q(V-IR_s)/nkt}}{e - 1} \right] \\ &\quad + \frac{V - IR_s}{R_{sh}} \end{aligned} \quad (3.6.8)$$

When a diode is used as a solar cell the terminal current (I) is given by

$$I = I_L - I_d \quad (3.6.9)$$

where I_L is the current generated by the light. Thus for a given light-source, diode parameters R_s , R_{sh} , I_{o1} , I_{o2} , n and τ control the performance of the solar cell.

3.5.3.2 Procedure for Separating Diode Parameters from the Experimental Dark I-V Data

It should be recognized that equation 3.6.8 is a lumped approximation to the real device in which the distributed parameters may have appreciable anisotropy. Considerable experimental evidence has shown the approximation to be highly accurate except for cases of extreme anisotropy. It is therefore important for our purpose, to be able to dissect the measured current-voltage characteristic into its constituent functions as given in equation (3.6.8).

The first step in this process is to remove the R_s and R_{sh} terms. This is done by transforming the voltage and current variables:

$$V' = V - IR_s \quad (3.6.10)$$

$$I' = I - \frac{V - IR_s}{R_{sh}} \quad (3.6.11)$$

The result of this process is illustrated in Fig. 10a for a device with large R_s and R_{sh} effects. Of course R_s and R_{sh} must be known and the methods of obtaining them are described in the following sections.

The second step¹³ involves separating the functions I_B and I_j . This separation can be carried out exactly by computational methods, however, an acceptably accurate approximation can be obtained by the method illustrated in Fig. 10b. The current data points of $I_B(V)$ are obtained as follows:

Fig. 10a

Fig. 10b

Fig. 10 Schematic Diagram of the Procedure for Transforming the Measured I-V Data to Separate the Bulk (I_B) and Junction (I_j) Components.

$$I_B(V) = I_{X1}(V) - I_{X2}(V) \quad (3.6.12)$$

$$\text{then } I_j(V) = I_{X2}(V) - I_B(V) \quad (3.6.13)$$

As shown in the illustration $\log I_B$ plots as a straight line with slope of q/kt and intercept $\log I_{o1}$ while I_j has a slope q/nkt with $n \geq 2$ and intercept $\log I_{o2}$. Thus we have now determined all the parameters of equation 3.6.8 except R_{sh} and R_s which are dealt with next.

3.5.3.3. Parametric Effects on Cell Performance

The sources of the parameters which influence solar cell performance have been discussed. In this section we consider:

- a) How the parameters influences the solar cell performance.
- b) Quantitative determination of the parameters by I-V measurements.
- c) Discussion of relevant experimental data showing the role of the parameters in "good" and "bad" devices.

A. SHUNT RESISTANCE

Effect of Shunt Resistance on Solar Cell Efficiency

For the purposes of this discussion it is sufficient to describe the solar cell as a single diode, and neglect the effects of I_j and R_s . Figure 11 shows an equivalent circuit of a solar cell with shunt resistance. In the figure $I_d = I_B + I_{sh}$ and $V = V_d$

Fig. 11 Equivalent Circuit of a Diode with Short Resistance Only

$$I_{B1} = I_L - I \text{ with no shunt resistance}$$

$$\text{while } I_{B2} = I_L - I - I_{sh} \text{ with the shunt resistance}$$

For a given terminal current I , $I_{B2} < I_{B1}$,

$$\text{since } I_B = I_o \left[e^{qV_d/nkt} - 1 \right]$$

$$V_{d2} < V_{d1} \text{ or } V_2 < V_1$$

This will move the peak power point inward and reduce the fill factor, open circuit voltage (V_{oc}) and the cell efficiency. Figure 12 depicts solar cell I-V curves with various shunt resistances. These data were obtained by putting various shunt resistance across the device. Figure 12 dictates that shunt resistance will significantly affect the solar cell efficiency only when $R_{sh} \leq 100 \Omega$. For $R_{sh} \geq 300 \Omega$ the effect is negligible. Short circuit current (I_{sc}) is not affected appreciably until $R_{sh} < 1 \Omega$.

Determination of Shunt Resistance

The effect of R_{sh} is more apparent in the low current domain of I-V data. It is quite clear from equation 3.6.8 and Figure 10a that the shunt resistance can be identified as a curvature in the low current segments of the $\log I$ vs. V plot (if the effect of R_{sh} is appreciable). Shunt resistance can be experimentally determined from the reverse dark I-V measurement. In the reverse bias

$$\text{if } R_{sh} = \infty, I = -I_o; \text{ however if } \frac{V}{R_{sh}} \gg I_o$$

$$\text{then } R_{sh} = \frac{\Delta V}{\Delta I} \quad (3.6.14)$$

For this case

$$I_d = I_B = I_o \left[e^{\frac{q(V+IR_s)/kT}{-1}} - 1 \right] = I_o \left[e^{\frac{qVd/kT}{-1}} - 1 \right]$$

while $V = V_d - IR_s$ with series resistance,

and $V = V_d$ without series resistance.

since $I = I_L - I_d$

Therefore for a fixed I , V_d will be the same and the terminal voltage (V) will be smaller by the amount IR_s when the series resistance is present. This will move the peak power point inward and reduce the fill factor and the efficiency of the cell. Figure 14 shows the I - V characteristics of the solar cell with various series resistances. R_s as low as 1Ω tends to affect the cell efficiency. $R_s > 3 \Omega \text{ cm}$ significantly deteriorates the performance of solar cell.

Series resistance does not affect the open circuit voltage (V_{oc}) because there is no voltage drop across R_s ($I = 0$). Series resistance affects I_{sc} because in the short circuit case I_L is divided between R_s and diode impedance.

Identification and Determination of Series Resistance

The series resistance effect is more pronounced in the high current domain. Neglecting (or subtracting) the contribution from I_j and I_{sh} , the diode current is written as

$$I_d = I_B = I_o \left[e^{\frac{q(V-IR_s)/kT}{-1}} - 1 \right]$$

$$\text{Log } I = \text{log } I_o + \frac{q}{2.3 kT} \left[V - IR_s \right] \quad (3.6.15)$$

Fig. 12 The Effect of Shunt Resistance on Solar Cell I-V Characteristics.

Observation of Shunt Resistance in Solar Cells

We found that in good devices ($n > 9\%$ without AR coating) R_{sh} is usually $> 300 \text{ k}\Omega$ and therefore has insignificant influence on the cell performance (section 3.5.3.a). Even in very bad devices shunt resistance was $> 20 \text{ k}\Omega$ and can therefore, not account for the poor efficiency observed. R_{sh} was so high in all the devices and $I_j/I_{sh}/v > 10$ that no curvature in the low current segment was ever observed. Thus our data indicate we can neglect the affect of shunt resistance for all practical purposes.

B. SERIES RESISTANCE

Effect of Series Resistance on Solar Cell Efficiency

Figure 13 shows the equivalent circuit of the solar cell with series resistance. The effect of I_j and I_{sh} are again neglected.

FIG. 13 Equivalent Circuit of a Diode with Series Resistance Only.

Fig. 14 The Effect of Series Resistance on Solar Cell I-V Characteristics.

$$\frac{d}{dV} (\log I) = \frac{q}{kT} \left(1 - R_s \frac{dI}{dV} \right) \quad (3.6.16)$$

$$\text{Let } \log I = u \quad \frac{dI}{dV} = e^u \frac{du}{dV} = I \frac{du}{dV} \quad (3.6.17)$$

Substituting this in equation (3.6.16) gives

$$\frac{du}{dV} = \frac{q}{kT} \left(1 - IR_s \frac{du}{dV} \right)$$

$$\frac{du}{dV} \left(1 + \frac{qIR_s}{kT} \right) = \frac{q}{kT}$$

which becomes

$$\frac{du}{dV} = \frac{d}{dV} (\log I) = \frac{q}{kT} \left(\frac{1}{1 + \frac{qIR_s}{kT}} \right) \quad (3.6.18)$$

Thus in the presence of R_s the slope of $\log I$ vs V will decrease with the increasing current resulting in a curvature of $\log I$ vs V plot in the current domain. If R_s is very small ($R_s < 1 \Omega$) then curvature will not be visible until high currents ($I > 20 \text{ ma}$), instead the $\log I$ vs V plot will appear to be a straight line with a slope q/nkT .

$$\text{where } \eta = \frac{1}{1 + \frac{qI_{av}R_s}{kT}} > 1$$

For higher series resistances ($R_s > 5 \Omega$) the curvature is seen easily even at low currents ($I < 10 \text{ ma}$).

Figure 15 shows data for samples which were diffused for two different times, 20 min ($R_s = 0.90 \Omega$) and 480 min ($R_s = .45 \Omega$). Since R_s is small the $\log I$ vs V plot appears to be linear with slope = $1/nkT$ and $n > 1$. As predicted by equation (3.6.18) the slope of the

Fig. 15 Partially Transformed I-V Curves for the Samples Diffused 20 and 480 minutes. The Effect of R_s has not been removed.

0.9 Ω sample is smaller than 0.45 Ω sample.

Series resistance can be experimentally determined by a combination of dark and lighted I-V curves. In the high current domain the measured I-V data can be represented by the following equation

$$I_d = I_{o1} \left[e^{\frac{q(V - I_d R_s)}{AkT}} - 1 \right] \quad (3.6.19)$$

-dark I-V

$$I_L - I = I_d = I_{o1} \left[e^{\frac{q(V + IR_s)}{AkT}} - 1 \right] \quad (3.6.20)$$

- lighted I-V

where $A > 1$

For the same diode current (I_d), the terminal voltage (V) will be different in dark and lighted cases because V_d is same but the current (I) flows in opposite directions through R_s .

$$I_d = I_{o1} \left[e^{\frac{q(V_1 - I_d R_s)}{AkT}} - 1 \right] = I_{o1} \left[e^{\frac{q(V_2 + (I_L - I_d) R_s)}{kT}} - 1 \right]$$

$$\text{or } V_1 - I_d R_s = V_2 + (I_L - I_d) R_s$$

$$\text{or } \Delta V = V_1 - V_2 = I_L R_s \quad (3.6.21)$$

$$\text{or } R_s = \frac{\Delta V}{I_L} \quad (3.6.22)$$

Thus a plot of $\log I_d$ vs V in the dark and $\log (I_L - I)$ vs V in the lighted case will show a parallel shift in the voltage (equal to $I_L R_s$) in the high current region. Figure 16 shows the experimental data on dark and lighted I-V for a sample which was diffused for 20 min. ΔV of 20 mv was observed while I_{sc} was 22.2 ma and therefore $R_s = 20/22.2 = 0.9 \Omega$. Figure 16 indicates that a parallel shift is not observed in the low

Fig. 16 The Measured Dark and Illuminated I-V Curves for the Sample Designated SOLEP 134-20C.

current domain. The reason for this is not yet understood. However limited measurement accuracy in that range may be the explanation, especially in the lighted case where the difference of two large numbers ($I_d = I_L - I$) is taken to obtain a very small number. Also, the junction may respond somewhat differently in the presence of light.

C. JUNCTION EXCESS CURRENT

Effect of Junction Excess Current on Solar Cell Efficiency

In a solar cell $I = I_L - I_d = I_L - I_B - I_j - I_{sh}$. Thus if I_j is large enough to be appreciable compared to the diffusion current near the peak power point, then for a given voltage I will be smaller. This will move the peak power point inward and reduce the fill factor and cell efficiency. Since $I_j = I_{o2} (e^{qV/akT} - 1)$, increased I_j shows up either as an increase in I_{o2} or a decrease in n . I_j behaves like a higher impedance diode compared to I_B so I_{sc} will not be affected by junction excess current. However V_{oc} will be reduced if appreciable amount of I_L is lost as junction excess current.

Determination of Junction Excess Current

I_j is obtained by subtracting the contributions of R_{sh} , R_s , and I_B from the measured I-V curve in the low current domain. The procedure is described in detail in section 3.5.3.2, Figure 10. I_j is usually much less than 1 ma in the low current domain ($0.1 < V < 0.4$ volts). In most good devices $R_s < 1\Omega$ so in the low current domain ($V - IR_s \approx V$) an effect of R_s can be ignored. Also the effect of R_{sh} can be neglected ($R_{sh} \geq 30K$) in most cases. Thus, I_j can be obtained simply by subtracting I_B from the measured I-V curve. The intercept of $\log(I_j)$ vs V at $V=0$ gives I_{o2} and the slope gives n ($n = \frac{9}{\text{Slope} \cdot kT}$).

Sintering Studies

The role of junction excess current on the cell performance can be seen from some sintering experiments we conducted using Ti-Pd-Ag contacts. The devices were examined before and after sintering at either 425°C or 550°C in H_2 for 15 minutes. Sintering is usually done to improve the contact resistance and the reliability of the metallurgical bond between the metal and the silicon. In our studies sintering usually resulted in some loss of efficiency in the devices so we analysed the I-V curves to determine the cause of it. Table 17 shows the performance of 10 solar cells before and after sintering at 425°C. Figure 17 shows that sintering primarily increases the junction excess current, hence reducing the cell efficiency. This was found true for all the samples whose performance deteriorated after sintering. Sintering did not affect R_s , I_o , or τ appreciably. The only systematic and significant variation was found in I_j . R_{sh} decreased at times but was found to be greater than 30 K in all cases after sintering. However, if the contact resistance is initially high ($R_s > 5\Omega$) then sintering lowered the series resistance and improved the cell efficiency, Figure 18.

Junction Depth Experiments

In our standard solar cell process diffusion time is 50 minutes which gives approximately a 0.3 μm deep junction. In order to examine the effect of junction depth on cell performance and to further understand the possible adverse effects of sintering, a run was made with diffusion times of 20, 40, 80, 100, 320 and 480 minutes. This should give junction depths in the range of 0.2 to 1 micron. The solar cell response of these samples is shown in Table 18. Contrary to conventional wisdom, no systematic variation in the cell efficiency with the junction depth was observed, instead average efficiency was about 9.9% in all the cases. This suggests that somehow the increase in sheet resistance is balanced by the decrease in dead layer in shallow junctions or vice versa for the deeper junctions. Our light source is somewhat rich in infrared which could be partially responsible for the lack of significant

TABLE 17

RESULTS FROM SINTERING EXPERIMENT

RUN ID SOLEP 133 DIFFUSION TIME = 50 MIN.

SAMPLE NUMBER	SAMPLE STATE	I_{sc} mA	V_{oc} VOLTS	EFFICIENCY
1	Not sintered	21.3	.570	9.49
1	Sintered	20.9	.563	8.85
2	Not sintered	21.7	.565	8.81
2	Sintered	21.3	.569	9.55
3	Not sintered	21.7	.574	9.83
3	Sintered	21.2	.571	9.65
4	Not sintered	22.4	.573	9.67
4	Sintered	21.6	.571	9.62
5	Not sintered	21.1	.572	9.27
5	Sintered	21.2	.564	8.95
6	Not sintered	21.5	.574	9.91
6	Sintered	21.3	.570	9.63
7	Not sintered	21.7	.572	9.37
7	Sintered	21.5	.567	9.59
8	Not sintered	21.7	.576	10.13
8	Sintered	21.5	.567	9.26
9	Not sintered	21.9	.575	9.82
9	Sintered	21.5	.570	9.78
10	Not sintered	21.7	.576	10.09
10	Sintered	21.4	.566	9.56

Fig. 17 Transformed Dark I-V Curves for the Sample SOLEP 133-8: ● Before Sintering, ○ After Sintering at 425°C .

Fig. 18 Measured Dark I-V Curves for the Sample 70714W-13:
• Before Sintering, ○ After Sintering at 425°C .

TABLE 18 Effect of Diffusion Time (Junction Depth)
on Solar Cell Performance. AMI Illumination
No AR Coating.

ID	ISC	VOC	IP	LOG(10)	N	R	FF	EFF	OCD	PCDA	PCDB
1R*	22.50	.556	20.07	-6.037	2.12	-.50	.712	9.41	.00	.00	.00
20A	22.30	.577	20.31	-6.865	1.85	-.73	.751	10.22	3.25	.00	.00
20C	22.50	.571	19.93	-5.581	2.43	-1.35	.715	9.72	2.99	.00	.00
20D	22.40	.575	20.14	-6.170	2.12	-1.09	.735	10.01	2.99	.00	.00
20E	22.40	.572	20.16	-6.284	2.06	-.83	.732	9.92	3.25	.00	.00
40A	21.90	.578	20.10	-7.337	1.70	-.63	.762	10.20	3.90	.00	.00
40C	21.70	.576	19.96	-7.530	1.64	-.49	.764	10.09	3.25	.00	.00
40D	21.80	.551	18.10	-4.360	3.41	-1.12	.624	7.93	.78	.00	.00
40E	21.90	.577	20.07	-7.267	1.72	-.59	.759	10.14	3.45	.00	.00
40F	21.70	.572	19.60	-6.527	1.96	-.60	.733	9.63	2.60	.00	.00
80A	22.00	.576	19.83	-6.257	2.09	-1.16	.740	9.92	3.25	.00	.00
80C	21.90	.573	19.61	-5.953	2.23	-1.39	.734	9.74	2.93	.00	.00
80D	21.70	.577	19.64	-6.422	2.03	-1.26	.750	9.92	3.58	.00	.00
80E	21.80	.575	19.73	-6.428	2.01	-1.21	.748	9.92	3.64	.00	.00
100A	21.50	.580	19.65	-6.954	1.83	-1.08	.763	10.06	3.90	.00	.00
100C	21.70	.577	19.75	-6.799	1.88	-.90	.753	9.97	3.51	.00	.00
100D	22.00	.575	19.80	-6.180	2.12	-1.22	.739	9.88	3.64	.00	.00
100E	21.60	.575	19.76	-7.179	1.74	-.59	.756	9.93	3.64	.00	.00
320A	21.30	.573	19.17	-6.241	2.09	-1.12	.737	9.51	2.60	.00	.00
320C	17.40	.567	15.35	-5.504	2.53	-2.11	.714	7.45	2.60	.00	.00
320D	21.50	.577	19.63	-6.938	1.83	-.98	.760	9.97	3.25	.00	.00
320E	21.10	.572	19.01	-6.204	2.11	-1.41	.743	9.49	3.25	.00	.00
480A	22.50	.577	20.73	-7.658	1.60	-.39	.765	10.50	4.55	.00	.00
480C	22.20	.576	20.38	-7.313	1.70	-.71	.765	10.34	4.42	.00	.00
480D	22.40	.577	20.51	-7.184	1.74	-.67	.760	10.38	3.90	.00	.00
480E	22.60	.580	20.73	-7.278	1.72	-.65	.762	10.57	4.29	.00	.00
480F	22.20	.577	20.20	-6.759	1.89	-.93	.753	10.20	3.64	.00	.00

AVERAGES: 70816 BASELINE
NO BASELINE

	70816 MONSANTO LOT M 9149 MULTI-DIFFUSION EXP										
	21.77	.574	19.69	-6.583	2.00	-.97	.743	9.83	3.35	.00	.00
STD	.96	.005	1.02	.723	.36	.37	.028	.68	.72	*	*

performance variation. Also the syton polished surfaces we used may have mitigated the adverse surface effects on shallow junctions.

In another experiment samples with different junction depths were sintered first at 425°C and then at 550°C. Sintering at 425°C slightly degraded the cell efficiency in most cases. However, 550°C sintering affected the shallow junctions severely while deeper junctions were hardly affected. Results of this experiment are summarized in Table 19. Figures 19 and 20 show a considerable increase in the junction excess current for the shallow junction compared to the deep junction devices. Thus deeper junctions, as expected, are found to be less sensitive to the sintering induced degradation. The reason for this degradation is quite clear, increased I_j . The physical mechanism by which degradation occurs though not fully understood, probably involves titanium diffusion, or migration into the junction region.

LIFETIME

Effect of Lifetime on Solar Cell Efficiency

Reduction in lifetime by processing or impurities diminishes the number of light generated carriers which survive to reach the junction. This produces a decrease of I_L and thereby I_{sc} . Reduction in lifetime increases I_0 and since ^{12,14}

$$V_{oc} = \frac{q}{kT} \ln \left(\frac{I_L}{I_0} + 1 \right) \quad (3.6.23)$$

therefore V_{oc} is also reduced. Both these effects reduce the solar cell efficiency.

TABLE 19 Effect of Sintering Parameters on Solar Cell Performance.

SAMPLE ID	SINTERING CONDITION	I _{sc} mA	V _{oc} V	OCD LIFETIME τ (μ sec)	EFFICIENCY η
20A	Unsintered	22.3	.577	3.25	10.22
20A	425°C, 15 min, H ₂	22.1	.570	3.25	9.89
20A	550°C, 15 min, H ₂	22.4	.562	1.56	8.70
40A	Unsintered	21.9	.578	3.9	10.20
40A	425°C, 15 min, H ₂	21.6	.571	3.9	9.99
40A	550°C, 15 min, H ₂	21.4	.551	.26	6.67
80A	Unsintered	22.0	.576	3.25	9.92
80A	425°C, 15 min, H ₂	21.6	.566	3.90	9.62
80A	550°C, 15 min, H ₂	21.6	.563	1.17	7.81
100A	Unsintered	21.5	.575	3.9	10.06
100A	425°C, 15 min, H ₂	21.4	.572	4.29	10.01
100A	550°C, 15 min, H ₂	21.2	.562	1.04	7.60
320D	Unsintered	21.5	.577	3.25	9.97
320D	425°C, 15 min, H ₂	21.2	.572	3.9	9.59
320D	550°C, 15 min, H ₂	21.2	.574	2.60	9.32
480F	Unsintered	22.2	.577	3.64	10.20
480F	425°C, 15 min, H ₂	21.7	.575	4.55	10.21
480F	550°C, 15 min, H ₂	21.7	.575	2.99	9.78

Fig. 19 Transformed Dark I-V Curves for the Sample SOLEP 134-80A: ● Before, ○ After Sintering at 550°C.

Fig. 20 Transformed Dark I-V Curves for the Sample SOLEP 134-480F: • Before, ○ After Sintering at 550°C.

Determination of Lifetime from I-V Data

Reduction in lifetime increases I_0 which mainly effects the bulk diffusion current.

$$I_B = I_0 \left(e^{\frac{qV}{kT}} - 1 \right)$$

or $\text{Log } I_B = \text{Log } I_0 + \frac{qV}{kT}$ in the high current domain

For a fixed I_D

$$\Delta V = - \frac{kT}{q} \Delta (\text{Log } I_0) = \text{constant} \quad (3.6.24)$$

This reduction in lifetime will move I_B parallel and to the left in Figure 21.

After subtracting the contributions of I_j and I_{sh} from the measured I-V data in the high current segment one gets

$$I = I_0 \left(e^{\frac{q(V-IR_s)}{kT}} - 1 \right)$$

$$\text{or } \text{Log } I = \text{Log } I_0 + \frac{V}{2.3 kT} (V-IR_s)$$

If R_s is known then any point (V, I) can be used to get I_0 . However if R_s is not known a point at lower current (≈ 1 ma) should be used so that $V-IR_s \approx V$. For example, let us determine the lifetime of the baseline sample ($[\pi_1] = 0$) in Figure 21 by using a point (1 ma, .48 V) from I_B .

$$\text{Log } 1 = \text{Log } I_0 + \frac{1}{2.3 \times 25} \quad (480)$$

IR_s is neglected because $V - IR_s = 480 - 1 \approx 480$

$$\text{Log } I_o = 8.347$$

or $I_o = 4.49 \times 10^{-9} \text{ ma}$

$$I_o \approx \frac{A q n_i^2}{N_A} \sqrt{\frac{D_n}{\tau_n}} \quad 3.6.25 \quad \text{for } N^+P \text{ device}$$

$$N_A = 6 \times 10^{15} \quad A = 1 \text{ cm}^2, \quad D_n = 25$$

$$I_o = \frac{1.3.33 \times 10^{-15}}{\sqrt{\tau}}$$

Fig. 21 Transformed Dark I-V Curves for Titanium-doped 4 Ω cm Silicon.

$$\text{or } \sqrt{\tau} = \frac{13.33 \times 10^{-15}}{4.49 \times 10^{-12}} = 2.969 \times 10^{-3}$$

$$\text{or } \tau = 8.8 \text{ } \mu\text{sec.}$$

The measured OCD lifetime on this sample was 4.55 μsec which is somewhat smaller because of surface recombination at the back surface which is not taken into account in equation (3.6.25). Test devices fabricated with back surface fields actually show OCD lifetime of $\approx 9\text{--}10 \text{ } \mu\text{sec}$.

Observations for Ti-doped Solar Cells

The data for Ti-doped silicon, Table 20, indicate how the technique can be applied to evaluate impurity effects. Here, solar cell efficiency is significantly and systematically reduced with the increase in Ti concentration in the substrate. Analysis of I-V data Figure 21 shows that Ti addition does not significantly alter R_{sh} , R_s , or I_j to account for the degradation. However, a systematic and significant increase in I_o is observed with the addition of Ti Figure 21. Thus, here the impurity addition primarily reduces the bulk lifetime, confirming a conclusion drawn from the impurity effect modeling as discussed in the previous quarterly reports.^{1,3} This is not necessarily the mechanism of cell degradation for all impurities viz, Copper.

Table 20

Effect of Titanium Concentration
on Solar Cell Parameters

RUN ID	SAMPLE ID	Ti CONC. atoms/cm ³	I _{sc}	V _{oc}	OCD Lifetime	Efficiency n
60608	3B	0	22.5	.555	4.55	10.46%
60608	2C	0.36X10 ¹³	20.2	.544	1.69	8.71%
60820	1S	7X10 ¹³	16.6	.494	.26	5.97%
60205	1S	36X10 ¹³	7.80	.445	.07	2.71%

3.5.3.4 Summary of I-V Curve Analysis Studies

The measurement and characterization technique described above has provided us with the ability to separate and analyze various process and impurity dependent mechanisms which influence solar cell performance. We can now quantitatively measure the effect of impurities and or processes on the junction region as compared to their effect on base region. It is also possible to distinguish impurity induced effects on the control interface resistance should such occur.

On-going experiments are being conducted to examine the behavior of impurity contaminated cells. The data obtained for titanium shows the degradation to be primarily the result of lifetime loss in the base as had been deduced from the impurity modeling analysis. Of particular interest are cells containing iron, nickel or copper since, in the impurity model, these metals seem to display a non-linear effect on lifetime. It is conjectured that this may be a consequence of precipitate formation, known to occur for these metals and which are expected to affect junction properties more strongly than base properties.

4. CONCLUSIONS

P^+N solar cells appear to be more resistant to the harmful effects of Ti and V than do conventional p-base devices. For example, at comparable vanadium contamination levels (4×10^{14} at cm^{-3}) n-base devices exhibit efficiencies about 70% of the uncontaminated baseline cells while p-base devices are only 40% as efficient. Nickel, on the other hand, degrades the cell performance of n-base devices to about 54% of the baseline value while having little effect on N^+/P cells. Lifetime reduction seems to be the primary mechanism by which Ti and V reduce cell performance. Nickel, however, influences solar cell output through changes in junction properties. The detailed influence of nickel will be examined shortly by a newly developed quantitative I-V technique which facilitates separation of impurity effects in the base and junction regions of the device.

In 4 Ω cm p-base material molybdenum degrades cell performance to about 75% of the baseline value when the metal content is about 6×10^{14} at cm^{-3} . Phosphorus at a similar concentration has essentially no effect on efficiency. The effect of high compensation levels will be examined in future work. Solar cells fabricated on silicon containing twins and grain boundaries introduced purposely (grain sizes up to about 1 mm) exhibit about 70% the efficiency of the single crystal baseline material. This metal-free polycrystalline material will be used for comparative studies with polycrystalline ingots containing selected impurities.

5. PROGRAM STATUS

5.1 Present Status

The program is essentially on schedule, Figure 22, although chemical analysis of the ingots lags because of downtime on the mass spectrometer.

During this quarter we have:

- Completed the growth of thirteen new ingots; all first generation n-base ingots and half the first generation low resistivity crystals are grown.
- Completed growth of ingots containing the new impurities C, Ca, and P as secondary dopants in 4 Ω cm p-type silicon.
- Completed solar cell evaluation of the first ingots containing Mo and P and also evaluated baseline polycrystalline material for grain boundary/impurity studies.
- Calibrated the laser-excited PCD equipment and determined the conditions for precision recombination lifetime measurements.
- Initiated the study of processing effects on solar cell performance.
- Developed and tested a quantitative method for dissecting the effect of impurities and processing on the base, junction, and contact behavior in contaminated solar cells.

5.2 Future Activity

During the next quarter all first generation low resistivity ingots will be grown and characterized as will most second generation n-base ingots. Polycrystalline metal-doped ingots will be prepared. The variation of impurity concentration and cell performance as a function of growth rate will be investigated. Processing studies will be extended to encompass impurity-bearing silicon. The solar cell performance of all first generation n-base ingots will be measured and the evaluation of

FIG. 22 Program Schedule

about half the first generation low resistivity ingots will also be finished. Detailed I-V measurements will be carried out to determine the way in which impurities like Cu, Fe, and Ni degrade device performance.

6. REFERENCES

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7. APPENDIX

BEST ESTIMATE OF IMPURITY CONCENTRATION
IN ALL INGOTS PRODUCED TO DATE

APPENDIX

Best Estimate of Impurity Concentrations

<u>Ingot Identification</u>	<u>Best Estimate of Impurity Conc. (10¹⁵ atoms/cm³)</u>	
W-001-00-000	--	
W-002-00-000	--	
W-003-00-000	--	
W-004-Cr-001/1286	1.0	(1.0)**
W-005-Mn-001/1288	1.3	(1.3)
W-006-Ni-001/1292	0.5	
W-007-Cu-001/1294	2.0	(1.8)
W-008-Ti-001/1298	0.36	(0.36)
W-009-V-001/12100	0.4	(0.4)
W-010-Ni-002/12101	3.0	(4.0)
W-011-Zr-001/12105	<0.015	(<0.015)
W-012-Cr-002/1285	0.2	--
W-013-Mn-002-1287	0.25	--
W-014-00-000/12103	--	--
W-015-Zn-001/12108	<0.001	(<0.3)
W-016-Fe-001/12112	0.85	(0.9)
W-017-Cu-002/1295	19	(32)
W-018-Fe-002/12114	1.7	(1.7)
W-019-Cu-003/1293	0.4	(0.4)
W-020-00-000/1289	--	--
W-021-Mg-001/12116	0.003	--
W-022-00-000/12109	--	--
W-023-00-000/12122	--	--
W-024-Mg-002/12117	0.03	--
W-025-00-000/12120	--	--
W-026-Mn-003/12123	0.012	--
W-027-Mn/Cu-001/12125	1.3/1.7	(1.0/1.0)
W-028-Al-001/01-18A	26	(26)
W-029-Cr-003/12127	0.012	--
W-030-Cr/Cu-001/12129	1/1.7	(1.0/1.0)

<u>Ingot Identification</u>	<u>Best Estimate of Impurity Conc. (10¹⁵ atoms/cm)</u>	
W-031-Cr/Mn-001/12130	1.0/1.3	(1.0/2.5)
W-032-Mg-003/12132	0.32	(0.32)
W-033-Ti-002/12135	0.0036	--
W-034-00-000/12137	--	--
W-035-V-002/12138	0.004	--
W-036-Zr-002/12145	<0.025	(<0.025)
W-037-Zr/Ti-001/12146	<0.015/0.40	(0.015/0.36)
W-038-Al-002/01-22	60	(34)
W-039-Ni-003/12147	8	(4)
W-040-Cr/Ni-001/12151	0.8/2.4	(1.0/3.5)
W-041-Ni/Cr/Cu-001/12153	2.4/0.8/1.7	(3.0/1.7/2.3)
W-042-Ti-003/1297	0.07	--
W-043-Fe/Ti-001/12158	0.56/0.06	--
W-044-Fe-003/12156	0.017	--
W-045-Cr/Fe/Ti-001/12159	0.65/0.43/0.06	(0.2/0.5/0.06)
W-046-Fe/V-001/12160	0.57/0.07	--
W-047-Cu/Ni/Zr-001/12165	2.0/1.0/<0.015	(<2.4/<1/<1)
W-048-Ti-004/12167	0.00036	--
W-049-V-003/12168	0.0004	--
W-050-Ti/V-001/12169	0.00036/0.0004	
W-051-Cu/Ti-001/12170	2.0/0.36	(4/0.36)
W-052-Ni-004/01-36	4.5	(4.0)
W-053-Poly/12166	--	--
W-054-00-000/12182	--	--
W-055-Cu-004/12189	0.05	(<1)
W-056-Cu-005/12190	65	(70)
W-057-00-000/12184	--	--
W-058-00-000/12188	--	--
W-059-00-000/12198	--	--
W-060-00-000/12202	--	--
W-061-Cr/Ti-001/12191	1.0/.02	1.0/<1
W-062-N-Cu-001/12203	1.7	(2.0)
W-063-N-Cr-001/12211	1.0	(1.0)

W-064-N-Mn-001/12212	2.0	(2.0)
W-065-N-Ti-001/12218	0.36	(0.75)
W-066-Ti-005/12222	0.06	(<0.2)
W-067-Cr/Mn/Ti-001/12229	0.4	(0.3)
	0.5	(0.7)
	0.006	(<0.2)
W-068-Cr-004/12228	1.0	(1.0)
W-069-Fe-004/12232	1.0	(<1.5)
W-070-Al-003/12234	50	(100)
W-071-00-000/05-07	--	--
W-072-Cr-005/12237	0.4	0.25 (0.28)
W-073-Cr/Mn/Ni/Ti/V-001/12238	0.5	0.28
	0.5	0.80
	2.0	2.0
	0.004	<0.35
	0.004	<0.35
W-074-Cr/Mn/Ni/Ti/V-002/12239	0.08	<0.25
	0.08	<0.25
	0.5	<2.0
	0.0006	<0.25
	0.0006	<0.25
W-075-Ti/V-002/12240	0.1	<0.25
	0.1	<0.25
W-076-Poly-2/12236	--	--
W-077-Mo-001/12241	~0.1	(<0.3)
W-078-00-000/12244	--	--
W-079-00-001/12248	--	--
W-080-Ph-001/12254	0.7	(0.7)
W-081-N/Ni-001/12256	1.7	(<2.0)
W-082-N/V-001/12258	0.4	(0.85)
W-083-N/Fe-001/12260	1	(<1.5)
W-084-N/Al-001/12263	50	(40)
W-085-N/Zr-001/12265	<0.015	
W-086-C-001/12268	400	(300 500)
W-087-Ca-001/12269	?	
W*-088-Cr-001/1H0524	0.5	
W*-089-Cu-001/H0526	2.0	
W*-090-Mn-001/H-0529	0.7	
W-091-Cr/Mn-002/H-0530	0.5/0.3	
W-092-Ph-002/H-0533	28	(27-30)

** Quantity in parenthesis is measured concentration.