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

**Effects of Impurities and Processing on Silicon Solar Cells
Sixteenth Quarterly Report, July 1979—September 1979**

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**Westinghouse Research and Development Center
Pittsburgh, Pennsylvania**

U.S. Department of Energy

Solar Energy

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Hemlock Semiconductor Corporation**

Contract No. 954331

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NEW TECHNOLOGY

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

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1. SUMMARY

The overall objective of this program is to define the effects of impurities, various thermochemical processes, and any impurity-process interactions on the performance of terrestrial silicon solar cells. The results of the study form a basis for silicon producers, wafer manufacturers, and cell fabricators to develop appropriate cost-benefit relationships for the use of less pure, less costly Solar Grade silicon.

We have measured the effective segregation coefficients for the partitioning of Ag, Pd, and Sn (three common contact materials) during Czochralski crystal growth. Spark source mass-spectroscopy was used to determine the metal impurity content of the silicon (C_S), while atomic absorption was used to measure the metal content of the residual liquid (C_L) from which the doped crystals were grown. The effective segregation coefficients computed from the relationship $k_{\text{eff}} = C_S/C_L$ were $k_{\text{Ag}} = 1.7 \times 10^{-5}$, $k_{\text{Pd}} = 5.5 \times 10^{-5}$ and $k_{\text{Sn}} = 2.3 \times 10^{-2}$.

Gettering experiments completed on low resistivity silicon (0.2 Ωcm) doped with Ti or Mo indicate that solar cell performance can be enhanced by high temperature HCl or POCl_3 treatment. However, considerable performance variation from cell to cell is observed which is not typical of the results for higher resistivity material. The effect was particularly pronounced for POCl_3 treatment of Mo. We suspect that precipitate or cluster formation near the high field region of the cells is responsible for the low fill factors and open circuit voltages in the affected devices.

We have verified the formation of impurity diffusion profiles during the 1100°C POCl_3 gettering of Mo and Ti. For Ti the variation of impurity concentration extends over two mils deep into the wafer. However, for Mo-doped material even at 1100°C the profile is abrupt

We found no systematic variation in the cell performance or OCD lifetimes across the diameter of large CZ wafers or wide silicon webs doped, respectively, with Cu or Fe and Ti or V. The cell performance maps on the large area wafers are generally consistent with results obtained for small diameter CZ ingots and narrower webs doped with the same impurities. From DLTS data on the impurity-doped webs we estimated segregation coefficients for Ti and V: $k_{Ti}^{web} \sim 4 \times 10^{-6}$ and $k_V^{web} \sim 3 \times 10^{-5}$. The estimates are in fair agreement with values calculated from a theoretical model of the web growth process.

Aging data for Cr-doped solar cells treated at temperatures between 400 and 800°C suggest a more rapid depreciation in performance than for similar cells doped with Ti and Mo. The result may stem from the more rapid diffusion of Cr in silicon compared to the other two metals studied.

2. INTRODUCTION

This is the 15th quarterly report describing activities conducted under JPL Contract 954331. Phase III of this program is entitled "An Investigation of the Effects of Impurities and Processing on Silicon Solar Cells."

The objective of this program is to determine how thermal processes, impurities, and impurity-process interactions affect the properties of silicon and the performance of terrestrial solar cells made from silicon. The development of this data base permits the definition of the tolerable impurity levels in a low-cost Solar Grade Silicon. In addition, the data provide the silicon manufacturer with a means to select materials of construction which minimize product contamination and permit the cost-effective selection of chemical processes for silicon purification. For the silicon ingot, sheet, or ribbon manufacturer, the information indicates what silicon feedstock purity must be selected to produce wafers suitable for cell production and what furnace materials minimize wafer contamination. The cell manufacturer may use the impurity-cell performance relationships to define an acceptable wafer purity for cell fabrication and the heat treatment data to identify processes which minimize impurity impact on efficiency. In short, the impurity data provide a basis for cost-benefit analysis to the producers and users of Solar Grade Silicon.

The Phase III effort encompasses five major topics, several of which represent new directions for our work: (1) examination of the interaction of impurities with processing treatments, (2) generation of a data base and modeling of impurity effects in n-base solar cells, (3) extension of previous p-base studies to include impurities likely to be introduced during silicon production, refining or crystal growth, (4) a consideration of the potential impact of anisotropic (nonuniform)

impurity distribution in large Czochralski and ribbon solar cells and, (5) a preliminary investigation of the permanence of impurity effects in silicon solar cells.

Important experimental results were obtained in five areas during this past quarter: (1) the impact of HCl gettering on Mo and Ti doped low resistivity silicon was assessed, (2) diffusion profiles were established for Ti and Mo after 1100°C gettering treatments, (3) a correlation was identified between the electrically-active impurity concentration and the metallurgical concentration of several impurities in as-grown ingots, (4) cell and diode measurements verified that no significant anisotropy effects due to Cu or Fe in large diameter CZ ingots, or due to Ti and V in wide silicon web crystals occur, and (5) aging data for Cr indicate a more rapid depreciation in cell performance with time than for Mo or Ti doped cells.

A detailed description of the results and analyses of the observed behavior follow below.

3. TECHNICAL RESULTS

3.1 Silicon Crystal Growth: Impurity Impact and Ingot Evaluation

Major objectives of this activity are to provide ingots purposely contaminated with controlled additions of metal impurities for subsequent electrical and solar cell evaluation and also to assess the effects of impurities on ingot microstructure. During this quarter, we prepared and analyzed nine additional metal-doped Czochralski ingots. The ingot growth task is now complete. We have also completed direct measurements of the segregation coefficients for Ag, Sn, and Pd, and determined the critical impurity concentrations at which the loss of single crystal structure occurs for these and other impurities.

3.1.1 The Segregation of Ag, Sn, Pd and Nb During Czochralski Pulling

Three new segregation coefficients, those for the common grid contacting elements Ag, Sn and Pd, were recently determined. In each case the ingot impurity concentration C_S was measured by spark source mass spectroscopy (SSMS) while the corresponding concentration in the liquid from which the ingot grew C_L was obtained by atomic absorption analysis. The ratio C_S/C_L then gives k_{eff} , the effective segregation coefficient for Czochralski growth, as tabulated below.

TABLE 1

Impurity Segregation Coefficients for Silicon Growth

Element	k_{eff}
Ag	1.7×10^{-5}
Sn	2.3×10^{-2}
Pd	5×10^{-5}

Two SSMS samples were measured to derive the Sn data, four for Ag and two for Pd, so the results are considered preliminary for Sn and Pd. Particularly in the case of Pd additional analyses are planned in order to obtain better line resolution on the photographic plates.

We also carried out some further experiments to better define the Nb segregation coefficient. The best we can do at present is to show that $k_{Nb} < 9 \times 10^{-7}$ based on the mass spectrometer detection limit, $1.5 \times 10^{14} \text{ cm}^{-3}$, for Nb and the fact that the most heavily-doped ingot W167-Nb001 broke down to polycrystalline growth at a melt impurity concentration of $1.7 \times 10^{20} \text{ cm}^{-3}$. Attempts to introduce high Nb concentration by slower growth also failed due to structural breakdown. Thus we have continued use of the estimated value $k_{Nb} \sim 10^{-7}$ which is based on the position of Nb in the Periodic Table and the measured segregation coefficients for the neighboring elements, V and Ta.

Segregation coefficients for all the elements studied so far are Tabulated in Appendix 8.1

3.1.2 Ingot Structure Breakdown Due to Impurities

We have shown previously¹ how to estimate the critical liquid impurity concentration C_l^* at which the impurity-induced transition from single crystal to polycrystalline growth will occur. In Table 2 are compiled the predicted and observed values of C_l^* for a variety of impurities studied as part of Phase III. The agreement between theory and experiment is good despite the fact a key assumption—that the liquid diffusivity is the same for all impurities—cannot be true in detail. We plan to revise these data in a future report to incorporate better estimations of the diffusivity.

3.1.3 Ingot Preparation

This quarter's activity centered on the preparation of single and multiply-doped ingots for studies of construction materials, elements for solar cell contacts and synergic or coupled impurity behavior. Nine ingots (W188 to W196 inclusive) were grown by Czochralski pulling; the techniques for ingot growth and evaluation were the same as described in earlier reports.^{1,2}

TABLE 2

COMPARISON OF PREDICTED (TH.) AND OBSERVED (EXP)
IMPURITY CONCENTRATIONS FOR STRUCTURAL BREAKDOWN IN PHASE III INGOTS

<u>Ingot Identification</u>	<u>$C_{BD}(\text{Th.}) \times 10^{20} \text{ at/cm}^3$</u>	<u>$C_{BD}(\text{Exp}) \times 10^{20} \text{ at/cm}^3$</u>
W-135-Fe-005	1.7	2.1
W-137-Ti-010	1.7	1.7
W-139-Mo-006	1.8	1.3
W-139-Ti-011	1.7	1.9
W-143-Ti-002	1.9	1.7
W-145-W-001	1.9	1.2
W-146-Co-001	1.8	2.1
W-149-N/Fe-003	1.8	1.3
W-166-Fe-007	1.9	1.9
W-167-Nb-001	2.4	1.7
W-171-W-002	2.4	1.7
W-173-Fe-008	1.4	1.9
W-181-Cr-006	2.3	1.6
W-184-Pd-001	2.3	3.0

As in the past, we have collected the analytical data for all ingots in the Appendix. Listed there are the ingots, the target impurity concentrations, impurity concentrations based on melt analyses and measured impurity concentrations (SSMS). Table 3 lists our best estimate of the impurity concentration in each of the ingots grown for the Phase III study. Note that these estimates have been revised to reflect the new values for the segregation coefficients of Ag, Sn and Pd. The estimated Nb concentrations are based on the assumption $k_{Nb} \sim 10^{-7}$, as noted above.

3.1.4 Ingot Evaluation

The resistivity and etch pit density for each ingot, Table 4, fall close to the norms established in earlier phases of this program.^{1,2} No clear trends due to impurity effects are evident.

The carbon and oxygen concentrations of each odd numbered ingot continue to be measured by infrared absorption at room temperature. The amplitudes of the absorption peaks at 606 cm^{-1} and 1107 cm^{-1} is proportional to the carbon and oxygen concentrations, respectively. The constants of proportionality used in these measurements were 2.2 for carbon and 9.6 for oxygen.² Normal carbon and oxygen concentrations found in Czochralski grown material are in the range of $2.5\text{ to }5 \times 10^{17}\text{ atoms/cm}^3$ for carbon and $5\text{ to }150 \times 10^{16}\text{ atoms/cm}^3$ for oxygen. As usual, no significant deviations from these values were observed this quarter as indicated in Table 5.

3.2 Processing Studies

High temperature treatment of impurity bearing silicon wafers in an ambient bearing POCl_3 or HCl provides one way to electronically deactivate, or getter, the impurities after an ingot is grown. Thus we may improve the performance of solar cells fabricated from solar grades of silicon with an appropriate thermochemical process. We have carried out a series of experiments to delineate the time-temperature and chemical species response for a number of impurities which degrade cell performance. We report here recent results for the gettering of low

Table 3. Best Estimate of Impurity Concentrations

<u>Ingot Identification</u>	<u>Best Estimate of Impurity Concentration ($\times 10^{15}$ atoms/cm³)</u>
W-129-00-000 (7.6 cm)	NA
W-130-00-000 (7.6 cm)	NA
W-131-Mn-008 (7.6 cm)	0.55
W-132-Ta-003	0.000042
W-133-00-000	NA
W-134-Ti-009	0.03
W-135-Fe-005	0.78
W-136-Fe-006	0.24
W-137-Ti-010	0.21
W-138-Mo-005	0.001
W-139-Mo-006	0.0042
W-140-Ti-001 (7.6 cm)	0.18
W-141-Mo/Cu-001	0.004/4.00
W*-142-00-000	NA
W*-143-Ti-002	0.20
W-144-Mo-001	0.004
W-145-W-001	0.00085
W-146-Co-001	1.5
W-147-N/Ni-002	0.33
W-148-N/Mn-002	0.60
W-149-N/Fe-003	0.60
W-150-N/V-003	0.03
W**-151-00-000	NA
W**-152-Ti-001	0.21
W-153-N/Ti-003	0.013

Table 3. Best Estimate of Impurity Concentrations (Continued)

<u>Ingot Identification</u>	<u>Best Estimate of Impurity Concentrations (X 10¹⁵ atoms/cm³)</u>
W-154-N/Cr-003	0.50
W-155-N/Mo-001	0.001
W-156-N/Mo-002	0.004
W-157-N/Ti/V-001	0.08/0.12
W-158-N/Ti/V/Cr-001	0.05/0.05/0.55
W-159-N/Cr/Mn/Ti/V-001	0.35/0.32/0.02/0.02
W*-160-Ti-001	0.17
W**-161-Ti-002	0.03
W-162-Ni/Ti-001	1.21/0.16
W-163-Ni/V-001	1.0/0.44
W-164-Ni/Mo-001	1.23/0.004
W-165-Co-002	0.3
W-166-Fe-007	1.06
W-167-Nb-001	0.01++
W*-168-Ph-002	1101
W*-169-Ph-004	136+
W-170-Ph-005	150+
W-171-W-002	0.0015
W-172-Cu-006 (7.6 cm)	24
W-173-Fe-008 (7.6 cm)	0.51
W-174-Ta-004	0.00084
W-175-W-003	0.00027
W-176-00-000	NA
W-177-N/Cr/Mn-001	1.20/1.26
W-178-N/Mn/Ti-001	0.86/0.08
W*-179-Ph-006	NA
W*-180-Ti-001	0.13
W-181-Cr-006	1.04
W-182-Cr-007	0.45
W-183-Nb-002	0.002++

Table 3. Best Estimate of Impurity Concentrations (continued)

<u>Ingot Identification</u>	<u>Best Estimate of Impurity Concentrations ($\times 10^{15}$ atoms/cm³)</u>
W-184-Pd-001	6.5
W-185-Cu/Ti-004	Cu: 1.2 Ti: 0.15
W-186-Co-003	0.027
W-187-Co-004	0.14
W-188-W-004	0.0002
W-189-Nb-003	0.0003
W-190-Cu/Zr-001	Cu: 2.0 Zr: 0.0012
W-191-Cu/Ta-001	Cu: 1.74 Ta: 0.00068
W-192-Ag-001	2.08
W-193-Sn-001	4846
W-194-Ti-012	0.003
W-195-Ti/V/Mo-001	Processing
W-196-Ti/V-Mo-Ta-001	Processing

* Asterisk indicates low resistivity p-type ingot (≤ 1 ohm-cm)

** 30 ohm-cm p-type ingot

+ Value based on resistivity measurement

++ Assumed k value near 1×10^{-7}

Table 4. Resistivity and Etch Pit Density
of Phase III Ingots

Ingot Identification	TGT Resistivity (ohm-cm)	Actual Resistivity (ohm-cm)	Etch ⁺ Pit Density (/cm ²)
W-129-00-000 (7.6 cm)	4.0 (B)	4.7-3.0	1 K-Gross Lineage
W-130-00-000 (7.6 cm)	4.0 (B)	4.7-3.7	OK-Gross Lineage
W-131-Mn-008 (7.6 cm)	4.0 (B)	6.0-3.8	OK-Gross Lineage
W-132-Ta-003	4.0 (B)	3.8-3.4	1-20K
W-133-00-000	4.0 (B)	4.3-3.7	OK-Gross Lineage
W-134-Ti-009	4.0 (B)	4.9-4.4	0-10K
W-135-Fe-005	4.0 (B)	5.3-2.1	0-Gross Lineage
W-136-Fe-006	4.0 (B)	3.3-2.7	1K-Gross Lineage
W-137-Ti-010	4.0 (B)	4.6-4.4	0-Gross Lineage
W-138-Mo-005	4.0 (B)	5.0-4.1	0-5K
W-139-Mo-006	4.0 (B)	4.0-2.3	0-Gross Lineage
W-140-Ti-011 (7.6 cm)	4.0 (B)	3.6-1.7	5K-Gross Lineage
W-141-Mo/Cu-001	4.0 (B)	4.7-3.0	2K-Gross Lineage
W*-142-00-000	0.2 (B)	0.22-0.20	0-3K
W*-143-Ti-002	0.2 (B)	0.21-0.15	0-Gross Poly
W*-144-Mo-001	0.2 (B)	0.23-0.19	0-Gross Poly
W-145-W-001	4 (B)	4.5-4.0	2K-Gross Poly
W-146-Co-001	4 (B)	4.7-4.2	1K-Gross Poly
W-147-N/Ni-002	1.5 (P)	1.9-1.4	2-15K
W-148-N/Mn-002	1.5 (P)	2.5-2.1	1K-Gross Poly
W-149-N/Fe-003	1.5 (P)	2.0-1.6	3K-Gross Poly
W-150-N/V-003	1.5 (P)	2.0-1.5	1-5K
W**-151-00-000	30 (B)	35.6-18.1	0-5K
W**-152-Ti-001	30 (B)	31.9-25	0-Gross Poly
W-153-N/Ti-003	1.5 (P)	2.1-1.1	0-10K
W-154-N/Cr-003	1.5 (P)	2.1-1.4	3K-10K
W-155-N/Mo-001	1.5 (P)	1.9-1.8	1-4K
W-156-N/Mo-002	1.5 (P)	1.7-1.3	3K-Gross Poly
W-157-N/Ti/V-001	1.5 (P)	2.0-1.6	1-10K
W-158-N/Ti/V/Cr-001	1.5 (P)	2.1-1.6	1K-gross Lineage
W-159-N/Cr/Mn/Ti/V-001	1.5 (P)	2.0-1.8	1-2K

Table 4. Resistivity and Etch Pit Density
of Phase III Ingots (Continued)

<u>Identification</u>	<u>TGT Resistivity (ohm-cm)</u>	<u>Actual Resistivity (ohm-cm)</u>	<u>Etch+ Pit Density (/cm²)</u>
W*-160-Ti-001	1.0 (B)	1.3-1.0	2-8K
W*-161-Ti-002	30 (B)	31.8-21.7	1-15K
W-162-Ni/Ti-001	4.0 (B)	4.5-4.0	OK-Clusters
W-163-Ni/V-001	4.0 (B)	4.8-4.4	1K-Clusters
W-164-Ni/Mo-001	4.0 (B)	4.7-3.2	OK-Clusters
W-165-Co-002	4.0 (B)	4.5-3.8	0-5K
W-166-Fe-007	4.0 (B)	4.7-3.0	OK-Gross Lineage
W-167-Nb-001	4.0 (B)	4.0-5.7	OK-Poly
W*-168-Ph-002	0.5 (B)	0.41-0.50	3-10K
W*-169-Ph-004	1.0 (B)	0.9-1.4	OK
W-170-Ph-005	2.9 (B)	1.1-2.5	1-3K
W-171-W-002	4.0 (B)	4.3-4.1	0-2K
W-172-Cu-006 (7.6 cm)	4.0 (B)	3.4-2.7	0-10K
W-173-Fe-008 (7.6 cm)	4.0 (B)	5.9-3.6	3K-Poly
W-174-Ta-004	4.0 (B)	4.3-3.8	OK-Twin
W-175-W-003	4.0 (B)	4.1-3.3	0-10K
W-176-00-000	2.0 (P)	2.0-1.3	OK
W-177-N/Cr/Mn-001	2.0 (P)	2.2-1.4	OK-Poly
W-178-N/Mn/Ti-001	2.0 (P)	2.1-1.7	2K-Poly
W*-179-Ph-006	0.35 (B)	0.3-0.3	0-2K
W*-180-Ti-001	0.5 (B)	0.51-0.49	2-5K
W-181-Cr-006	4.0 (B)	5.4-4.0	OK Clusters
W-182-Cr-007	4.0 (B)	4.2-3.6	0-4K
W-183-Nb-002	4.0 (B)	3.6-2.9	0-5K
W-184-Pd-001	4.0 (B)	4.2-3.9	0-4K
W-185-Cu/Ti-004	4.0 (B)	4.7-4.6	0-Poly
W-186-Co-003	4.0 (B)	4.1-3.7	0-2K
W-187-Co-004	4.0 (B)	3.8-2.9	Processing

see key on next page

Table 4.. Resistivity and Etch Pit Density
of Phase III Ingots (continued)

<u>Identification</u>	<u>TGT Resistivity (ohm-cm)</u>	<u>Actual Resistivity (ohm-cm)</u>	<u>Etch Pit Density (/cm²)</u>
W-188-W-004	4.0 (B)	4.7-3.5	0-2K
W-189-Nb-003	4.0 (B)	4.0-3.3	2-10K
W-190-Cu/Zr-001	4.0 (B)	4.4-2.9	OK-Gross Lineage
W-191-Cu/Ta-001	4.0 (B)	4.4-3.6	0-10K
W-192-Ag-001	4.0 (B)	5.6-5.2	0-2K
W-193-Sh-001	4.0 (B)	4.3-3.6	0-2K
W-194-Ti-012	4.0 (B)	3.4-2.9	0-1K
W-195-Ti/V-Mo-001	4.0 (B)	3.9-3.2	2-5K
W-196-Ti/V/Mo/Ta 001	4.0 (B)	Processing	Processing

* Low resistivity p-type ingot ($\leq$ ohm-cm)

** Use of double asterisk indicates 30 ohm-cm p-type ingot

+ This 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. Structural degradation commonly occurs at the tang end of the most heavily-doped ingots due to constitutional supercooling. (1)

Table 5. Carbon and Oxygen Concentrations

of Phase III Ingots

<u>Ingot Number</u>	<u>Carbon Concentration x 10¹⁶ atoms/cm³</u>	<u>Oxygen Concentration x 10¹⁶ atoms/cm³</u>
W-129-00-000	11.3	202
W-131-Mn-008	5.3	164
W-133-00-000	10.4	117
W-135-Fe-005	9.4	118
W-137-Ti-010	5.3	134
W-139-Mo-006	6.5	149
W-141-Mo/Cu-001	8.3	156
W*-143-Ti-002	++	++
W-145-W-001	5.8	149
W-147-N/Ni-002	14.0	157
W-149-N/Fe-003	6.6	151
W*-151-00-000 (30Ω-cm)	7.0	154
W-153-N/Ti-001	7.5	160
W-155-N/Mo-001	9.2	183
W-157-N/Ti/V-001	5.7	103
W-159-N/Cr-Mn/Ti/V-001	8.7	183
W*-161-Ti-002	6.0	138
W-163-Ni/V-001	5.0	128
W-165-Co-002	11.2	106
W-167-Nb-001	6.0	130
W*-169-Ph-004	14	96
W-171-W-002	10	86
W-173-Fe-008	Incomplete	Incomplete
W-175-W-003	10	158
W-177-N/Cr/Mn-001	8	150
W*-179-Ph-006	++	++
W-181-Cr-006	8	119
W-183-Nb-002	6	35
W-185-Cu/Ti-004	5	39
W-187-Co/-004	20	164

Table 5. Carbon and Oxygen Concentrations
of Phase III Ingots

<u>Ingot Number</u>	<u>Carbon Concentration $\times 10^{16}$ atoms/cm³</u>	<u>Oxygen Concentration $\times 10^{16}$ atoms/cm³</u>
W-189-Nb-003	13	138
W-191-Cu/Ta-001	12	110
W-193-Sn-001	9.4	200
W-195-Ti/V/Mo-001	32	110

* low resistivity ingot

** high resistivity ingot

+ Due to free carrier absorption infrared methods cannot be used for carbon and oxygen determination in these samples

resistivity silicon and further detailed examination of gettering processes by deep level transient spectroscopy (DLTS).

3.2.1 Impurity-Process Interactions in Low Resistivity Silicon

In an earlier report³ we described POCl_3 gettering of 0.2 Ω -cm silicon doped with Mo and Ti. We have completed a parallel set of experiments with HCl as the gettering medium; for purposes of comparison both sets of data are described below.

The characteristics of the ingots are:

<u>Ingot I.D.</u>	<u>Doping Concentration</u>	<u>Resistivity</u>
W143Ti002	2×10^{14} Ti cm ⁻³	0.2 Ω -cm
W144Mo001	4.0×10^{12} Ti cm ⁻³	0.2 Ω -cm
W14200000	Baseline	0.2 Ω -cm

The gettering treatments ranged from 1 hour at 950°C to a maximum of 5 hours at 1100°C. Subsequent to gettering solar cells were fabricated on the treated wafers and the devices tested by standard procedures.^{1,2}

The trend of the isochronal and isothermal data, Figures 1 and 2, respectively, parallels in general earlier results for 4 Ω -cm silicon doped with the same impurities.³ The solar cell I-V data on which these figures are based are compiled in Tables 6 through 9. Taken together the data indicate that longer times and higher temperatures promote improvements in cell efficiency. Moreover, the Mo-doped material appears to be more responsive to HCl gettering than is the Ti-doped silicon, Figure 1. A comparison of the effects of POCl_3 gettering in Mo and Ti-doped wafers proved impossible; only one useable data point, 1 hour at 950°C, was obtained when treating the Mo-doped wafers in POCl_3 . Excessive junction current was exhibited in all other cells fabricated on wafers treated for longer times and temperatures, Table 7. The large degree of scatter in the data for the low resistivity ingots is also evident from the figures, this behavior did not occur when the 4 Ω -cm material was tested.³

Figure 1 Normalized Efficiency for Isochronal Gettering

Figure 2 Normalized Efficiency for Isothermal Gettering (1100°C)

TABLE 6

POCl₃ GETTERING OF Ti-DOPED LOW RESISTIVITY SILICONIngot W143Ti002 (0.2 Ω -cm)Base W14200000 (0.2 Ω -cm)

	I _{SC} (mA)	V _{OC} (V)	FF	η (%)	$\tau_{OCD}(\mu\text{sec})$
No treatment					
Base	20.40	.598	.752	9.69	1.8
Ingot	10.90	.525	.728	4.42	1.1
Ingot/Base	.534	.878	.968	.456	.61
1 Hr @ 950°C					
Base	20.50	.598	.750	9.78	1.8
Ingot	11.60	.539	.748	4.99	1.5
Ingot/Base	.566	.901	.998	.510	.83
1 Hr @ 1000°C					
Base	20.46	.594	.708	9.09	1.2
Ingot	11.60	.540	.755	5.01	1.5
Ingot/Base	.567	.909	1.07	.551	1.2
1 Hr @ 1100°C					
Base	20.50	.596	.711	9.17	1.1
Ingot	12.96	.551	.739	5.58	1.1
Ingot/Base	.632	.924	1.04	.609	1.0
2 Hrs. @ 1100°C					
Base	20.58	.596	.774	10.18	1.5
Ingot	13.04	.540	.722	5.48	1.4
Ingot/Base	.634	.921	.933	.538	1.0
3 Hrs. @ 1100°C					
Base	20.70	.598	.758	9.93	1.6
Ingot	13.68	.556	.731	5.89	1.1
Ingot/Base	.661	.930	.964	.593	.69
5 Hrs @ 1100°C					
Base	20.35	.602	.766	9.92	1.6
Ingot	13.90	.554	.731	5.96	1.1
Ingot/Base	.683	.920	.954	.601	.69

TABLE 7
 POC₂ GETTERING OF Mo-DOPED LOW RESISTIVITY SILICON
 Ingot W144Mo001
 Base W14200000

	I _{SC} (mA)	V _{OC} (V)	FF	η(%)	τ _{OC} (μsec)
No Treatment					
Base	20.40	.595	.770	9.89	1.7
Ingot	17.46	.539	.642	6.46	.7
Ingot/Base	.856	.906	.834	.653	.41
1 Hr @ 950°C					
Base	20.50	.595	.735	9.50	1.3
Ingot	17.20	.569	.709	7.34	1.0
Ingot/Base	.839	.956	.965	.773	.77
1 Hr @ 1000°C					
Base	20.10	.597	.788	10.0	1.7
* Ingot	(15)	(.25)	(.4)	(2)	(.1)
Ingot/Base	-	-	-	-	-
1 Hr @ 1100°C					
Base	20.30	.598	.784	10.11	1.6
* Ingot	(16)	(.4)	(.5)	(3)	(.1)
Ingot/Base	-	-	-	-	-
2 Hr @ 1100°C					
Base	20.56	.600	.775	10.11	2.0
* Ingot	(16)	(.4)	(.4)	(2)	.1
Ingot/Base	-	-	-	-	-
3 Hrs @ 1100°C					
Base	20.40	.599	.769	9.94	1.6
* Ingot	(15)	(.2)	(.4)	(1)	1
Ingot/Base	-	-	-	-	-
5 Hrs. @ 1100°C					
Base	20.40	.600	.769	9.95	1.6
Ingot	No useable data.				
Ingot/Base					

* The ingot samples in these gettering cycles showed very poor junction characteristics. The averages computed are not sufficiently meaningful to calculate ratios. See TEXT.

TABLE 8
HCl GETTERING OF Ti DOPED LOW RESISTIVITY SILICON
Ingot W143Ti002
Base W14200000

	I _{SC} (mA)	V _{OC} (V)	FF	n(%)	τ_{OCD} (usec)
No Treatment					
Base	20.40	.598	.752	9.69	1.8
Ingot	10.90	.525	.728	4.42	1.1
Ingot/Base	0.534	.878	.968	.456	.61
1 Hr @ 1000°C					
Base	20.20	.588	.750	9.50	1.8
Ingot	14.70	.548	.679	5.80	0.9
Ingot/Base	.738	.932	.905	.610	.5
1 Hr @ 1100°C					
Base	20.20	.594	.746	9.47	1.3
Ingot	14.87	.547	.669	5.77	.9
Ingot/Base	.736	.921	.897	.609	.69
2 Hrs @ 1100°C					
Base	20.10	.592	.732	9.21	1.0
Ingot	15.62	.548	.667	6.04	.9
Ingot/Base	0.777	.926	.911	.565	.9
4 Hrs @ 1100°C					
Base	20.30	.590	.732	9.27	1.3
Ingot	16.07	.547	.671	6.26	1.0
Ingot/Base	.792	.927	.917	.675	.77

TABLE 9
HCL GETTERING OF Mo-DOPED LOW RESISTIVITY SILICON

Ingot W144Mo001
Base W14200000

	I _{SC} (mA)	V _{OC} (V)	FF	η(%)	τ _{OC} (μsec)
No Treatment					
Base	20.40	.595	.770	9.89	1.7
Ingot	17.40	.558	.675	6.96	.8
Ingot/Base	.85	.94	.88	.70	.5
1 Hr @ 1000°C					
Base	20.10	.584	.694	8.62	.9
Ingot	17.35	.533	.585	5.76	.6
Ingot/Base	.86	.92	.84	.67	.7
1 Hr @ 1100°C					
Base	19.88	.548	.606	7.00	.7
Ingot	16.70	.560	.679	6.72	.9
Ingot/Base	.84	1.02	1.2	.96	1.2
2 Hrs @ 1100°C					
Base	19.75	.579	.684	8.29	.8
Ingot	17.30	.547	.622	6.23	.5
Ingot/Base	.87	.94	.91	.75	.7
4 Hrs @ 1100°C					
Base	18.85	.561	.649	7.25	.7
Ingot	17.40	.560	.670	6.90	.8
Ingot/Base	.92	1.0	1.02	.95	1.1

Close examination of the data in Table 7 indicates that poor junction quality leads to excessive junction currents and extremely low efficiencies in almost all of the Mo-doped cells made on gettered material. Although we calculated efficiency values for each treatment cycle, no meaningful correlation with the data for the baseline ingot could be made. However, we note that in general the baseline cells subjected to the same gettering cycles exhibited excellent efficiencies, typically 10% without AR coatings. Thus, the rather poor and scattered efficiency values for the Mo-doped cells cannot be ascribed to processing problems since they were fabricated concurrently with the baseline material.

The behavior of the low resistivity material, and perhaps the Mo-doped material in particular can be rationalized on the basis of a model we described in the Sixth Quarterly Report of this program.⁴ We review that discussion here.

As the doping level in the silicon increases, the effective width of the junction region narrows and thus there is an increased probability of junction penetration and shortings by any defects or precipitates present in the device. Even if these defects penetrate only partially into the high field junction region, significant field emission currents will result which cause a depression in cell fill factor and open circuit voltages. This is what was observed in the case of the Mo ingot, Table 7. Thus a possible explanation for the behavior is that during gettering some diffusion of Mo impurities to the surface introduces defects which remain in the junction region to initiate the large excess junction current. The behavior is apparently species dependent since it was not noticed during the gettering of the Ti-doped wafers. Some further experiments are underway to clarify this point but the general trend of the data suggest that gettering is relatively ineffective for improving the cell performance of low resistivity material containing high concentrations of impurities like Mo or Ti, since device yield is adversely affected.

TABLE 10

Variation in cell efficiency and trap concentration (N_T) at the junction and at a 6-8 μm depth as a function of gettering treatment for Ingot 137 (original metallurgical Ti concentration, $2.0 \times 10^{14} \text{cm}^{-3}$)

GETTERING CONDITION	NORMALIZED CELL EFFICIENCY (η/η_B), (%)	CONCENTRATION OF $E_V+0.30\text{eV}$ TRAP (cm^{-3})	
		at the Junction	at 6-8 μm depth
None (starting wafer)		7.0×10^{13}	—
None (solar cell)	42.8	1.76×10^{13}	5.23×10^{13}
950°C/1 hr.	46.7	6.35×10^{12}	2.60×10^{13}
1000°C/1 hr.	51.0	3.94×10^{12}	2.80×10^{13}
1100°C/1 hr.	52.9	2.99×10^{12}	2.33×10^{13}
1100°C/2 hr.	55.4	2.50×10^{12}	1.50×10^{13}
1100°C/3 hr.	59.1	2.39×10^{12}	1.20×10^{13}
1100°C/5 hr.	66.2	1.49×10^{12}	6.47×10^{12}

3.2.2. Detailed Analysis of Gettering by Deep Level Spectroscopy

Deep level transient spectroscopy provides a means to measure the electrically active concentration of an impurity species in the vicinity of a p/n junction or Schottky barrier. By etching steps to successively greater depths in a silicon wafer the method can be used to map the profile or gradient of the electrically active species caused, for example, by gettering or by the diffusion used to form the solar cell itself. Previously⁵ we showed that the active Ti concentration near the cell junction decreases systematically as gettering time and temperature are extended. We also demonstrated that the standard POCl_3 diffusion step (50 minutes at 850°C) used to form our solar cells produces a Ti gradient: the Ti concentration increases nearly tenfold over a $12\text{ }\mu\text{m}$ distance going from the surface into the bulk wafer.

We have now completed additional studies of the impurity profiles formed by various gettering treatments. To accomplish this we fabricated Schottky barrier diodes on the region of the silicon wafers adjacent to the solar cell mesa. In this way the active impurity concentration corresponding to a depth about 6 to $8\text{ }\mu\text{m}$ (the mesa height) below the cell junction could be measured by DLTS and compared to the impurity concentration near the wafer surface (junction).

It is quite clear from the data, Table 10, that there is a surface to center variation in Ti concentration or a Ti-profile in each wafer. In each case the active Ti concentration at a 6-8 μm depth is higher than at the junction. There is about an order of magnitude reduction in the Ti content at a 6-8 μm depth as a result of $1100^\circ\text{C}/5\text{ hr } \text{POCl}_3$ gettering compared to that in an ungettered cell; this parallels the reduction in Ti concentration at the junction. A similar trend, Table 11, was obtained for ingot W134 which contained a lower initial Ti concentration, $3 \times 10^{13}\text{ cm}^{-3}$. This work remains to be completed.

TABLE 11

Variation in cell efficiency and trap concentration at the junction and 6-8 μm depth, as a function of POCl_3 gettering treatment for Ingot 134 (original metallurgical Ti-concentration $3 \times 10^{13} \text{cm}^{-3}$)

GETTERING CONDITION	NORMALIZED CELL EFFICIENCY (η/η_B), (%)	CONCENTRATION OF $\text{Ev}+0.30\text{eV}$ TRAP cm^{-3}	
		at the Junction	at 6-8 μm deep
None (starting wafer)		1.76×10^{13}	1.76×10^{13}
None (solar cell)	57.9	3.6×10^{12}	*
950/1 Hr	59.0	3.18×10^{12}	8.7×10^{12}
1000/1 Hr	61.5	*	6.33×10^{12}
1100/1 Hr	68.5		4.30×10^{12}
1100/2 Hr	68.8	1.65×10^{12}	*
1100/3 Hr	70.5	4.96×10^{11}	*
1100/5 Hr	76.9	*	*

* To be completed

We noted earlier⁵ that the Ti concentration was too small to detect near the junctions of cells heavily gettered by HCl. A reduction of the active Mo concentration by a factor of two compared to cells made on untreated wafers was obtained by gettering in HCl for 5 hours at 1100°C. To gain some insight into the reasons for the observed behavior we divided one of the HCl gettered (1 hour, 1100°C) cell mesas into several pieces, then etched off material to depths ranging from 5 to 54 μm below the original junction. On each piece a Schottky barrier was fabricated and the active Ti concentration was measured by DLTS. As before a profile in the Ti concentration formed during gettering, Table 12. The Ti concentration at 54 μm into the sample remains well below the active bulk value, $8 \times 10^{13} \text{ cm}^{-3}$ indicating that the gettering treatment is very effective in deactivating or extracting Ti compared to the cell diffusion step itself (see Figure 5, Reference 5). This is as expected if the process is diffusion-controlled.

In a similar series of experiments we searched for any Mo concentration profile formed during gettering. As the data in Table 13 suggest, the Mo concentration in the wafers returns to its bulk value within a short distance (6-8 μm) from the surface. Thus, even at protracted times and elevated temperatures little Mo appears to diffuse from the sample, a fact consistent with the relatively poor response of this impurity to gettering.⁵

3.2.3 Experiments in Progress

A second group of ingots are now undergoing POCl_3 and HCl gettering cycles.

The ingots in these tests include Cr and Fe dopants (rapid diffusers in silicon) and a Cu-Ti combination to explore possible synergic behavior:

W166Fe007
W181Cr006
W182Cr007
W185CuTi004

TABLE 13

Variation in trap center density as a function of HCl
gettering treatment for Mo-doped silicon (Ingot W-139-Mo)

INGOT W139 MO

<u>Gettering Condition</u>	<u>$N_T(\text{cm}^{-3})$ at the junction</u>	<u>$N_T(\text{cm}^{-3})$ at 6-8 μm depth</u>
None	4.4×10^{12}	4.4×10^{12}
1000°C/1 hr.	1.9×10^{12}	5.0×10^{12}
1100°C/1 hr.	2.3×10^{12}	3.9×10^{12}
1100°C/5 hr.	2.2×10^{12}	4.6×10^{12}

W166Fe007 is a replacement for an earlier iron ingot that showed structural degradation after crystal growth. W180Ti001 has a resistivity of 0.5 Ωcm which is intermediate to the Ti ingots previously studied (4 Ωcm and 0.2 Ωcm). A summary of all gettering results will be presented in a forthcoming report.

3.3 The Permanence of Impurity Effects in Silicon Solar Cells

Solar arrays are expected to exhibit an operating lifetime of 20 years. In addition to the mechanical failures such as hail, wind and water penetration any changes in the solar cell characteristics themselves over a period of time must be determined. Since the cells may be fabricated from silicon which contains various impurities, they may be susceptible to aging effects unobserved in cells fabricated from semiconductor grade silicon.

To estimate the stability of the cell characteristics under long term operation, a series of high temperature heat treatments are being carried out on wafers containing impurities. The cell parameters are measured after the treatments and then compared to the original properties of the devices. To establish a baseline, semiconductor grade wafers are treated in the same way and at the same time. Extrapolation of the high temperature data to lower temperatures and longer times via a model of the degradation process then provides a means to estimate the useful lifetime under normal operating conditions.

Thus far data has been gathered mainly for Ti ($1 \times 10^{14} \text{Ti/cm}^3$) and Mo-doped ($4 \times 10^{12} \text{Mo/cm}^3$) ingots. Both of these elements apparently diffuse slowly under thermal activation in silicon.⁵ If cell degradation is by a diffusion controlled mechanism, little change in cell characteristics might be expected in these cases. When the data are plotted in an Arrhenius form, the time to failure for the Mo doped ingot at 200°C is greater than 10^5 hours (20 years = 1.75×10^5 hours).⁵ Data for the Ti-doped material also shows little change with heat treatment indicating an operating lifetime for the Ti-doped devices greater by several orders of magnitude than those for the Mo-doped devices.

We are in the process of completing aging experiments on wafers doped with Cr, an impurity expected to diffuse much more rapidly in silicon than do Mo or Ti. Treatments have been carried out so far at 500, 600 and 800°C on ingot W072Cr005(4×10^{14} Cr cm⁻³).

The experimental data plotted in Figure 3 suggest that degradation of the Cr-doped devices does proceed more rapidly than in the cases of Ti and Mo. In the figure "time to failure" is defined as the time at any given temperature required to degrade the efficiency of the impurity-doped devices to 90% of the value for the unaged material. If the data are extrapolated as suggested in Figure 3 a time to failure between 100 and 1000 hours at 200°C would be projected. The three data points, however, do not fit a good straight line suggesting that for Cr a different degradation mechanism may prevail at high than at low temperatures. To test this conjecture additional aging experiments will be performed.

3.4 Investigations of Anisotropic Impurity Distributions in Silicon

Previously we showed that Ti and Mn, impurities which diminish cell performance by reducing bulk lifetime,¹ caused no excess performance degradation on large diameter wafers that could be ascribed to non-uniform impurity distribution.³ We have now evaluated two more 3-inch diameter Czochralski ingots doped, respectively, with 2.4×10^{16} Cu and 5.1×10^{14} Fe. Cu is expected to degrade cell performance primarily by junction mechanisms while Fe affects the junction as well as bulk lifetime.^{1,2} We have also examined 3 to 4 cm wide silicon web crystals doped with Ti and V at target levels of about 10^{13} cm⁻³. In both cases the potential variation in material properties due to impurities was mapped via a grid of 1cm² test cells and smaller diodes distributed across the surface of the Czochralski or web wafers.

3.4.1 Anisotropy Effects in Large Diameter CZ Ingots

Two three inch diameter ingots, W173Fe and W172-Cu were tested as follows. Each experimental run consisted of 7 wafers, 2 from the seed end, 3 from center and 2 from tang end of the ingot. One wafer from each end was divided into quarters to provide as many 1cm²

Figure 3 Time to failure ($n/n_B = 0.9$) as a function of aging temperature for Cr-doped silicon solar cells. Ingot W072Cr005.

miniature cells as possible fabricated by the standard process.^{1,2} Thirty mil diameter mesa diodes were made on one wafer from the center of each ingot after the solar cell diffusion. The OCD lifetime was measured on these small mesa diodes to map any bulk lifetime anisotropy. On the remaining wafer from each end, 12 1cm^2 cells were fabricated. Cell efficiency and OCD lifetime were measured on each miniature cell to gauge any anisotropy in ingot characteristics.

3.4.1.1 Cu-Doping

The cell data for ingot W-172-Cu are listed in Table 14 and illustrated in Figure 4. Overall the results indicate that the average miniature cell efficiency, from seed to tang and over the entire 3" diameter of the wafers, is about 90% of the baseline with a standard deviation of 15.6%. $1\text{cm} \times 1\text{cm}$ cells made on 1" diameter ingot 017-Cu doped with $1.7 \times 10^{16} \text{ cm}^{-3}$ Cu showed an average efficiency of 91.2% of the baseline with a standard deviation of 5.3%. Thus the average efficiency of the Cu-contaminated ingot is essentially independent of the ingot-diameter; however, the standard deviation of the cell data is almost 3 times larger in 3" diameter ingot as compared to cells made on the smaller ingot.

A closer examination of the cell data reveals that there are a few miniature cells in the efficiency range of 6 to 9%; most of these cells have high "N" factors (greater than 2) which is indicative of higher junction leakage or shunting. This is expected because our previous studies showed that Cu tends to precipitate at various locations within the bulk wafer. If the precipitates form in the depletion region of the device they will cause excess leakage current. The probability of such an occurrence increases with the size of the wafer which may account for the increased scatter in the large ingot cell data. The OCD lifetime data from the 30 mil mesa diodes, Figure 4, show about a $\pm 50\%$ variation across the lifetime map. This scatter can also be influenced by the junction leakage current. I_{SC} , a parameter which is a much better indication of the wafer bulk lifetime, shows a standard deviation of only 10%.

Seed : (%) Efficiency

Center : (%) Efficiency

Tang : (%) Efficiency

Center - OCD Lifetime (μsec)

Fig. 4 – Solar cell efficiency and lifetime data distribution across and along a 3 inch diameter CZ ingot. Nominal doping $2.4 \times 10^{16} \text{ cm}^{-3} \text{ Cu}$

TABLE 14

SOLAR CELL DATA FOR A 3 INCH CU-DOPED CZOCHRALSKI INGOT

90713 W172CU006 (24F15) THREE INCH MATERIAL W132 CO. 000
 SOL14 8 /27/79 AM1: PO=91.6CMW/CM² NO AP COATING

ID	ISC	VOC	IP	LOG(10)	N	F	FF	FFF	OCF	VFPA	FCFF
2F*	21.90	.562	20.03	-7.170	1.70	-.51	.754	9.81	2.00	.00	.00
11F.*	22.90	.559	20.33	-5.642	2.33	-1.32	.720	9.74	2.00	.00	.00
12F	22.90	.560	20.51	-6.423	1.96	.20	.705	9.57	2.12	.00	.00
13F	22.90	.560	20.99	-7.363	1.63	-.29	.754	10.22	4.42	.00	.00
14F	22.60	.559	20.76	-7.572	1.58	-.18	.756	10.10	4.23	.00	.00
21F	22.70	.554	20.35	-6.146	2.06	-.74	.725	9.64	2.51	.00	.00
22F	22.90	.557	20.99	-7.411	1.61	-.18	.751	10.14	4.29	.00	.00
23F*	20.30	.548	16.10	-3.289	5.69	-7.83	.638	7.51	2.09	.00	.00
24F	22.60	.555	20.55	-6.881	1.77	-.43	.743	9.85	2.90	.00	.00
21F.*	23.50	.553	20.66	-5.349	2.48	-1.30	.705	9.69	.13	.00	.00
22F.*	23.10	.550	20.34	-5.684	2.27	-.28	.689	9.25	2.34	.00	.00
33F	23.30	.557	21.28	-7.093	1.70	-.43	.751	10.20	1.30	.00	.00
34F	23.20	.557	21.31	-7.541	1.58	-.16	.755	10.31	2.21	.00	.00
>THIS IS THE SEED WAFFER											
1F	20.70	.556	18.77	-6.704	1.85	-.70	.742	9.03	2.86	.00	.00
2F.*	20.80	.543	15.31	-2.707	8.52	*****	.586	7.00	1.04	.00	.00
3F	21.50	.554	18.96	-5.386	2.49	-1.75	.715	9.00	2.00	.00	.00
4F.*	19.80	.511	13.81	-3.693	4.28	4.40	.433	2.63	.00	.00	.00
5F	22.40	.539	18.80	-4.356	3.33	-1.87	.648	8.27	1.20	.00	.00
6F	21.20	.525	16.89	-3.842	4.04	-1.59	.584	6.87	.52	.00	.00
7F	22.60	.556	20.56	-6.837	1.79	-.58	.746	9.92	2.00	.00	.00
8F	23.40	.560	21.54	-7.722	1.54	-.09	.758	10.50	2.51	.00	.00
9F	22.30	.560	20.47	-7.369	1.64	-.57	.763	10.07	2.64	.00	.00
10F	22.50	.556	20.28	-6.264	2.01	-1.03	.739	9.77	2.86	.00	.00
11F	22.50	.559	20.60	-7.131	1.70	-.71	.760	10.11	2.90	.00	.00
13F.*	16.30	.379	11.81	-17.086	.41	14.25	.376	2.46	2.90	.00	.00
14F	22.90	.558	21.34	-8.805	1.30	.13	.775	10.48	2.90	.00	.00
15F	22.30	.556	20.07	-6.179	2.05	-1.17	.739	9.69	2.25	.00	.00
16F	22.90	.558	21.05	-7.664	1.55	-.05	.754	10.19	2.90	.00	.00
17F	22.90	.558	21.15	-7.947	1.48	-.13	.764	10.33	2.64	.00	.00
18F	22.40	.560	21.19	-8.497	1.36	-.00	.773	10.44	2.64	.00	.00
19F	22.40	.560	20.09	-6.059	2.12	-1.14	.733	9.72	2.64	.00	.00
20F	22.80	.560	21.19	-8.497	1.36	-.00	.773	10.44	2.64	.00	.00
21F	22.40	.558	20.69	-7.497	1.49	-.26	.768	10.15	2.90	.00	.00
22F	22.50	.556	20.68	-7.485	1.59	-.43	.762	10.08	2.90	.00	.00

TABLE 14 (Continued)

>THIS IS THE CENTER WAFER

10	21.70	.541	18.46	-4.653	3.02	-1.51	.659	8.19	1.04	.00	.00
20	22.60	.553	20.46	-6.635	1.95	-.51	.736	9.73	1.04	.00	.00
30	24.00	.552	21.04	-5.256	2.54	-1.32	.701	9.85	2.30	.00	.00
40.*	26.80	.538	20.74	-3.262	5.29	-3.32	.579	8.83	2.30	.00	.00
50.*	28.20	.552	21.64	-2.916	6.66	-6.28	.605	9.96	2.21	.00	.00
60	21.90	.554	20.16	-7.694	1.53	-.22	.760	9.75	3.12	.00	.00

>THIS IS THE TANG WAFER

11	20.80	.550	18.67	-6.480	1.91	-.01	.713	9.62	2.34	.00	.00
21	22.50	.547	18.93	-4.364	2.36	-2.06	.654	8.51	1.43	.00	.00
31	21.30	.549	19.05	-6.286	1.99	-.12	.709	8.77	2.47	.00	.00
41	20.30	.556	18.43	-6.681	1.86	-1.00	.749	8.95	3.00	.00	.00
51	23.50	.556	20.64	-5.273	2.55	-1.51	.707	9.77	3.25	.00	.00
61	21.60	.558	19.95	-7.906	1.49	-.25	.767	9.77	3.64	.00	.00
71	21.90	.556	20.24	-7.955	1.48	-.29	.769	9.91	.33	.00	.00
91	21.90	.556	19.65	-6.173	2.06	-.84	.727	9.37	3.25	.00	.00
101	21.90	.554	20.16	-7.691	1.55	-.21	.760	9.82	3.25	.00	.00
111	21.60	.555	19.90	-7.730	1.53	-.32	.764	9.69	3.00	.00	.00
121	22.30	.555	20.37	-7.148	1.69	-.38	.750	9.81	3.51	.00	.00
131	21.50	.556	19.67	-7.171	1.69	-.59	.756	9.56	3.51	.00	.00
141.*	17.20	.433	11.11	-12.063	.78	19.11	.334	2.93	.00	.00	.00

>THIS IS WAFER A

THIS IS WAFER A

~~WAFER B~~

1	12.50	.527	10.81	-5.320	2.58	-1.58	.673	4.69	1.30	.00	.00
2	20.80	.537	18.42	-5.699	2.23	-1.02	.709	8.38	2.22	.00	.00
4.*	18.60	.542	15.81	-4.441	3.34	-3.62	.681	7.26	1.60	.00	.00
5	20.90	.544	18.72	-6.045	2.08	-1.16	.730	8.74	2.03	.00	.00
6	20.10	.522	17.37	-5.039	2.61	-1.29	.677	7.51	1.00	.00	.00
8	16.80	.522	13.97	-4.373	3.40	-2.29	.634	5.96	1.17	.00	.00
9	21.80	.548	19.74	-6.565	1.87	-.77	.741	9.37	2.60	.00	.00
10	20.60	.547	18.34	-5.824	2.21	-1.25	.721	8.59	2.34	.00	.00
12.*	13.70	.515	11.06	-4.089	3.86	-3.20	.604	4.51	.78	.00	.00

>THIS IS WAFER B

1	22.40	.557	20.76	-8.364	1.39	.13	.766	10.10	2.51	.00	.00
2	22.40	.553	20.62	-7.777	1.51	-.03	.756	9.91	2.25	.00	.00
3	22.40	.554	20.20	-6.596	1.87	-.13	.722	9.49	2.86	.00	.00
4	22.50	.552	20.44	-6.831	1.78	-.43	.741	9.73	3.00	.00	.00
5	22.40	.551	20.22	-6.417	1.93	-.81	.738	9.63	3.00	.00	.00
6	11.70	.536	10.24	-5.483	2.52	-2.84	.700	4.64	1.25	.00	.00
7	22.30	.552	20.21	-6.686	1.83	-.51	.738	9.61	2.86	.00	.00
8	21.60	.553	19.84	-7.495	1.58	-.36	.759	9.59	3.51	.00	.00
9	22.30	.549	19.79	-5.627	2.31	-1.36	.719	9.31	2.24	.00	.00
10	20.80	.539	18.48	-5.721	2.23	-1.36	.720	8.52	1.82	.00	.00
11	21.50	.552	19.67	-7.187	1.67	-.55	.755	9.49	3.25	.00	.00
12	21.40	.552	19.56	-7.234	1.66	-.33	.750	9.37	3.25	.00	.00

TABLE 14 (Continued)

>THIS IS WAFER C

1	20.70	.550	18.67	-6.548	1.89	-.41	.727	8.76	2.60	.00	.00
2	20.00	.543	17.24	-4.964	2.78	-1.49	.676	7.76	1.92	.00	.00
4	22.30	.547	19.51	-5.305	2.50	-1.12	.694	8.95	2.21	.00	.00
5	22.60	.552	20.55	-6.945	1.74	-.27	.740	9.76	3.00	.00	.00
6	21.90	.549	19.64	-6.260	1.99	-.46	.719	9.15	2.00	.00	.00
8	21.70	.539	18.84	-5.047	2.66	-1.48	.687	8.50	1.56	.00	.00
9	22.10	.546	19.57	-5.678	2.27	-.94	.708	9.00	2.30	.00	.00
10	17.60	.537	14.71	-4.416	3.37	-2.31	.642	6.42	1.60	.00	.00
11	18.30	.530	15.52	-4.732	2.96	-1.40	.651	6.68	1.82	.00	.00
12	18.80	.540	16.24	-5.098	2.67	-1.21	.674	7.23	1.43	.00	.00

AVERAGE: 90713 BASELINE W133 00 000

	22.89	.557	20.94	-7.054	1.74	-.28	.742	10.02	3.38	.00	.00
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STD	.24	.002	.33	.498	.17	.25	.017	.28	1.05	*	*
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90713 W17200006 (24F15) THREE INCH MATERIAL

	21.39	.550	19.17	-6.429	2.08	-.83	.725	9.05	2.67	.00	.00
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STD	2.12	.009	2.19	1.204	.60	.67	.041	1.28	.92	*	*
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PERCENT OF BASELINE

	93.5	98.6	92.0	108.9	120	*****	97.6	90.3	78.9	*****	*****
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STD	10.4	2.0	12.1	24.7	49	742.5	7.9	15.6	60.6	*****	*****
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3.4.1.2 Fe-Doping

The effect of Fe-doping on the properties of the 3" diameter ingots is summarized in Table 15 and Figure 5. The average efficiency of the miniature cells was 77.6% of the baseline with a standard deviation of 11.4%. One cm² cells made on ingot 016-Fe doped with about 8.5×10^{14} Fe were 86.4% of the baseline with a standard deviation of 7.5%. Since 3" diameter ingot-173 had somewhat less Fe (5.1×10^{14} cm⁻³), it appears that the average efficiency of Fe-contaminated solar cells decreases with the increase in the ingot diameter on which the cells are made (subject to the accuracy of the values for the metallurgical Fe concentration). This contrasts with the behavior of Mn, Ti and Cu.

The average short current of the miniature cells on 3" diameter wafers is 87.9% of the baseline, while the average value for cells on the 1" diameter wafers (which contains more Fe) is 89.7% of the baseline. This implies that the bulk lifetime is lower, or the electrically active Fe concentration is higher, in the 3" diameter ingot. A closer look at the cell data Table 15 indicates that there are many cells tabulated which have low "N" factors, i.e. exhibit little effect of iron on the junction. For these low N-factor devices cell efficiencies are close to 90% of the baseline value as would be expected on the basis of the Fe content of the ingot. The cells made on the 1" diameter ingot had very reasonable N factor values, averaging about 1.25. This suggests that most of the additional degradation seen in the 3" diameter ingot can be ascribed to an N-factor increase caused by excess Fe precipitated near the device junctions. From Figure 5 it is evident that there are no preferred sites on the 3 inch diameter wafer for which this effect is significantly above average. Device performance is distributed in a random fashion. The OCD lifetime map on the 30 mil mesa diodes also shows no striking anisotropy and/or preferred high lifetime regions.

Both Cu and Fe are rapidly diffusing species in silicon and have a tendency to precipitate.^{1,2} These impurities both degrade solar cell performance due to excess junction leakage, an effect which appears

TABLE 15

SOLAR CELL DATA FOR AN Fe-DOPED 3 IN. DIAMETER CZ CRYSTAL

90712 W173FE008 (5.1F14) THREE INCH MATERIAL 5132 00 000
 SOL14 8 /20/79 AM11 PO=91.60MW/CM² NO AF COATING

ID	ISC	VOC	IF	LOG(10)	N	F	FF	FFF	QW	WAVE	TEMP
2E*	21.90	.560	19.61	-5.982	2.16	-1.23	.731	9.48	.00	.00	.00
11F.*	22.00	.555	19.56	-5.944	2.16	-.49	.706	9.16	4.99	.00	.00
12F	22.50	.555	20.39	-6.676	1.84	-.52	.736	9.75	4.16	.00	.00
21F	22.40	.555	20.22	-6.628	1.86	-.16	.724	9.52	4.22	.00	.00
22F	22.40	.555	20.16	-6.410	1.95	-.46	.726	9.54	4.55	.00	.00
3F*	26.10	.550	20.40	-3.179	5.72	-5.11	.608	9.23	1.82	.00	.00
>THIS IS THE SEED WAFER											
11S	21.40	.548	19.39	-6.958	1.73	.16	.725	8.99	2.86	.00	.00
12S	21.30	.546	19.03	-5.979	2.12	-1.00	.723	8.89	2.34	.00	.00
21S	21.00	.546	18.93	-6.451	1.91	-.61	.731	8.86	2.60	.00	.00
22S	20.70	.544	18.31	-5.520	2.37	-1.63	.717	8.54	2.47	.00	.00
23S	20.80	.543	18.55	-5.869	2.17	-1.22	.723	8.64	2.73	.00	.00
24S	21.00	.543	18.94	-6.465	1.89	-.65	.732	8.93	3.00	.00	.00
25S	20.30	.541	18.33	-6.642	1.83	-.34	.729	8.46	2.47	.00	.00
31S	21.70	.545	19.54	-6.457	1.90	-.42	.726	9.08	2.21	.00	.00
32S	21.50	.546	19.51	-6.870	1.75	-.27	.736	9.13	2.34	.00	.00
33S	21.40	.544	19.34	-6.647	1.83	-.36	.731	9.00	2.34	.00	.00
41S.*	21.60	.544	16.61	-5.735	2.23	8.00	.461	5.73	1.60	.00	.00
42S	21.70	.538	19.39	-6.162	2.00	-.38	.713	8.80	2.21	.00	.00
>THIS IS THE TANG WAFER											
11T	17.60	.507	14.36	-4.058	3.67	-2.69	.618	5.83	.39	.00	.00
12T	19.00	.520	16.56	-5.415	2.35	-.62	.678	7.09	.65	.00	.00
13T	17.60	.507	15.36	-5.478	2.27	-.68	.681	6.42	.52	.00	.00
14T	18.10	.511	15.83	-5.501	2.27	-.76	.685	6.70	.52	.00	.00
21T	19.50	.522	16.63	-4.807	2.82	-1.26	.658	7.08	.65	.00	.00
22T.*	18.00	.503	14.50	-3.793	4.09	-3.86	.616	5.90	.39	.00	.00
23T	17.90	.504	15.20	-4.722	3.83	-1.64	.657	6.27	.52	.00	.00
24T	18.80	.514	16.49	-5.579	2.23	-.64	.688	7.03	.65	.00	.00
25T.*	17.60	.500	13.81	-3.388	5.08	-6.66	.611	5.68	.39	.00	.00
31T	19.00	.517	16.13	-4.620	2.98	-2.02	.662	6.88	.52	.00	.00
32T	19.00	.517	16.70	-5.683	2.18	-.45	.688	7.15	.65	.00	.00
33T	18.60	.512	15.53	-4.348	3.27	-2.26	.643	6.47	.52	.00	.00
41T	19.00	.516	16.37	-5.203	2.48	-.35	.659	6.83	.65	.00	.00
42T	18.10	.508	15.59	-5.219	2.44	-.34	.658	6.39	.52	.00	.00
43T	19.20	.518	16.99	-5.838	2.10	-.60	.701	7.37	.65	.00	.00
44T.*	17.40	.498	13.99	-3.765	4.14	-4.26	.617	5.66	.39	.00	.00

TABLE 15(Continued)

>THIS IS THE CENTER WAFER

11C	19.30	.521	16.84	-5.359	2.39	-.97	.686	7.29	.65	.00	.00
12C	19.90	.526	17.33	-5.269	2.46	-1.08	.685	7.58	.78	.00	.00
13C.*	18.00	.511	14.70	-3.828	4.09	-4.84	.642	6.25	.50	.00	.00
21C	19.80	.526	17.20	-5.301	2.44	-.66	.675	7.43	.72	.00	.00
22C	18.50	.516	16.31	-5.722	2.16	-.71	.697	7.03	1.43	.00	.00
23C	20.40	.527	18.16	-6.073	2.01	-.33	.705	8.02	.91	.00	.00
24C	18.90	.514	16.35	-5.224	2.45	-.68	.669	6.87	.65	.00	.00
25C	19.10	.514	16.63	-5.297	2.40	-1.04	.684	7.10	.65	.00	.00
31C	19.50	.517	17.18	-5.621	2.21	-.88	.698	7.45	.65	.00	.00
32C	19.90	.525	17.00	-4.853	2.78	-1.14	.659	7.28	.91	.00	.00
33C	20.10	.529	17.75	-5.605	2.26	-1.17	.707	7.95	-.91	.00	.00
41C	19.00	.519	16.74	-5.714	2.17	-.59	.694	7.24	.65	.00	.00
42C	19.20	.519	17.04	-5.989	2.03	-.37	.701	7.39	.65	.00	.00
43C.*	18.70	.517	13.78	-2.925	7.06	-8.77	.560	5.72	8.06	.00	.00
44C	18.90	.514	16.60	-5.556	2.24	-.87	.693	7.12	8.06	.00	.00

>THIS IS WAFER A

1	20.90	.541	18.44	-5.667	2.27	-.74	.600	8.37	1.00	.00	.00
2	21.00	.535	18.71	-5.968	2.08	-.74	.714	8.40	1.57	.00	.00
3.*	21.10	.537	16.24	-3.380	5.24	-3.62	.567	6.80	1.56	.00	.00
4	20.80	.540	18.71	-6.420	1.90	-.46	.724	8.60	2.21	.00	.00
5	20.70	.536	18.60	-6.334	1.92	-.61	.726	8.51	1.82	.00	.00
6	20.50	.536	18.33	-6.190	1.99	-.49	.715	8.31	1.60	.00	.00
7	20.30	.537	18.32	-6.468	1.88	-.90	.736	8.48	1.82	.00	.00
8	20.30	.538	18.40	-6.691	1.80	-.71	.742	8.57	2.00	.00	.00

>THIS IS WAFER B

1	20.50	.526	16.70	-4.373	3.27	.28	.585	6.68	.91	.00	.00
2.*	19.00	.510	13.39	-4.579	2.98	8.60	.415	4.25	.91	.00	.00
3.*	20.70	.528	15.79	-3.510	4.81	-1.72	.542	6.20	.91	.00	.00
4	20.30	.527	17.96	-5.713	2.19	-.89	.705	7.98	1.07	.00	.00
5	19.20	.523	16.89	-5.535	2.29	-1.11	.699	7.43	.82	.00	.00
6	19.20	.519	16.77	-5.842	2.10	.86	.659	6.95	.78	.00	.00
7	19.90	.520	17.42	-5.384	2.36	-1.17	.695	7.60	.75	.00	.00
8	18.90	.519	16.44	-5.097	2.57	-1.91	.694	7.20	.75	.00	.00
9	18.00	.507	15.18	-4.766	2.80	-.69	.636	6.14	5.00	.00	.00
10	18.20	.509	15.73	-5.177	2.47	-.93	.671	6.57	5.00	.00	.00

>THIS IS WAFER C - METALIZATION LOOKS BAD -

1.*	15.50	.498	10.13	-3.665	4.47	7.69	.390	3.18	.20	.00	.00
2.*	14.00	.502	10.23	-5.488	2.31	12.74	.426	3.17	.20	.00	.00
3.*	20.00	.516	15.00	-3.484	4.81	-1.10	.522	5.70	.50	.00	.00
4	20.20	.516	15.99	-4.044	3.67	.13	.559	6.16	.45	.00	.00
5	19.70	.507	16.29	-4.641	2.88	.55	.598	6.31	.39	.00	.00
6.*	19.20	.504	13.82	-3.559	4.55	1.78	.469	4.80	.10	.00	.00
7.*	17.00	.459	10.56	-2.776	7.32	-1.80	.397	3.27	.10	.00	.00
8	20.20	.491	15.87	-3.825	3.84	-.93	.563	5.91	.10	.00	.00
9	20.30	.515	16.41	-4.362	3.22	.72	.573	6.33	.65	.00	.00
10	19.30	.512	15.05	-3.800	4.09	-.86	.554	5.79	.65	.00	.00
11	18.00	.488	13.88	-4.162	3.37	2.29	.517	4.80	.42	.00	.00
12.*	17.30	.507	11.54	-3.275	5.55	2.55	.420	3.89	.38	.00	.00

TABLE 15 (Continued)

AVERAGES: 90712 BASELINE W133 00 000												
	22.43	.555	20.26	-6.571	1.88	-.38	.729	9.60	4.23	.00	.00	
STD	.05	.000	.10	.116	.05	.16	.006	.10	.16	*	*	
90712 W173FE008 (5.1E14) THREE INCH MATERIAL												
	19.72	.524	17.16	-5.495	2.42	-.69	.679	7.45	1.55	.00	.00	
STD	1.09	.014	1.36	.777	.54	.74	.051	1.01	1.60	*	*	
PERCENT OF BASELINE												
	87.9	94.3	84.7	116.4	128	17.6	93.1	77.6	35.7	*****	*****	
STDZ	5.1	2.5	7.2	13.5	33	353.4	7.8	11.4	39.6	*****	*****

Seed - (%) Efficiency

Center - (%) Efficiency

Tang - (%) Efficiency

Center - OCD Lifetime (μsec)

Fig. 5 - Miniature cell efficiency and OCD lifetime map on a 3 inch diameter Fe-doped ingot. Nominal doping $5.1 \times 10^{14} \text{ cm}^{-3} \text{ Fe}$

randomly distributed across a wafer. Likewise, they result in greater scatter in the efficiency data. In contrast the impurities like Ti and Mn degrade the cell performance primarily by lowering the bulk lifetime and therefore exhibit much tighter cell parameter distributions. Going from 1" to 3" diameter the anisotropy or the scatter is not greatly increased for impurities like Ti and Mn, however scatter for Fe and Cu is appreciably increased due to the increased likelihood of encountering a junction-degrading precipitate.

3.4.2 Anisotropy Effects in Silicon Web Crystals

Silicon web crystals 2.5 to 4 cm wide were grown from melts doped respectively with $1.77 \times 10^{18} \text{ cm}^{-3}$ Ti and $1.5 \times 10^{18} \text{ cm}^{-3}$ V. One cm^2 size test cells were distributed across the width of each crystal at positions corresponding to the start, midpoint, and end of growth in each case. No back surface field or AR coatings were employed. Schottky barrier diodes were also fabricated on pieces of as grown material from each of the crystals so that an estimate of the amount of electrically active impurity could be made. The nominal web resistivity was $8.3 \Omega\text{-cm}$, chosen somewhat higher than for the CZ crystals to improve the sensitivity of the DLTS measurements.

In general at any position along the length of a web we saw no statistically significant edge to edge variation in cell performance either for V or Ti. We conclude that for crystals up to 4cm wide lateral impurity variations are small or absent.

For the Ti-doped web the average uncoated cell efficiencies for the start, middle, and end portions were 7.3, 7.14 and 6.5% with an overall average of about 7% absolute. Previously we measured the uncoated efficiency of uncontaminated web cells made without backsurface fields to be about 9%.² Thus the average normalized efficiency of the Ti-doped web is about 0.78. The DLTS data revealed that the same Ti-induced $E_V + 0.3\text{eV}$ level observed in CZ material was also present in the web crystal. The average electrically-active concentration for this level in web was $2.9 \times 10^{12} \text{ Ti cm}^{-3}$. Assuming the same proportion of the metallurgically-added Ti is active in web as in CZ material, about 0.4, (see section 3.5) then we calculate the actual Ti content of the web to be

about $7.3 \times 10^{12} \text{ Ti cm}^{-3}$. The impurity-performance model^{2,5} predicts that the normalized cell efficiency for this Ti concentration should be about 0.8 in fair agreement with the experimental value of 0.78.

We can obtain an approximate value for the Ti segregation coefficient for web growth by dividing the estimated metallurgical Ti concentration $7.3 \times 10^{12} \text{ cm}^{-3}$ by the melt doping concentration, $1.77 \times 10^{18} \text{ cm}^{-3}$. The value obtained, $k_{\text{Ti}}^{\text{web}} = 4 \times 10^{-6}$ is about a factor of two greater than the value for Czochralski growth (Appendix 8.1). This is consistent with model predictions for solute partitioning during web growth.⁶ The fact that Ti segregates during growth is also reflected in the reduction in solar cell efficiency as the Ti concentration increases along the crystal length.

It was not possible to gather clear cut evidence on cell performance variation along the length of the V-doped web crystals; several of the cells showed large resistive effects. The average uncoated cell efficiency for all the cells was 7.3%, corresponding to a normalized efficiency of 0.81 with respect to uncontaminated web cells. Again the DLTS data reveal the same $E_V + 0.42 \text{ eV}$ level present in the web as we detected earlier in the V-doped CZ material. The average concentration of this trap level in the web was $7.7 \times 10^{11} \text{ cm}^{-3}$. Only about 0.3 of the metallurgical V becomes electrically active in the CZ crystals. If we assume this to be true for web as well, then we estimate the metallurgical concentration of V in web at about $3.6 \times 10^{13} \text{ cm}^{-3}$. The model projection predicts a normalized cell efficiency of 0.75 compared to the measured value of 0.81, a fair agreement.

From the melt doping concentration, $1.5 \times 10^{18} \text{ V cm}^{-3}$, and the estimated metallurgical concentration of V in the web, $3.6 \times 10^{13} \text{ cm}^{-3}$ we calculate $k_V^{\text{web}} = 2.4 \times 10^{-5}$. This value is also larger than that measured for V segregation during Czochralski growth, $k_V^{\text{CZ}} = 4 \times 10^{-6}$.

In both cases the impurity model predicts higher cell performance than that measured for the impurity doped webs. The cell data for the web reported here are normalized against baseline web cell with 4 $\Omega \text{ cm}$ resistivity. If the cell data were normalized against baseline web cells made on 8 $\Omega \text{ cm}$ material this would tend to raise the normalized efficiency making agreement with the model projection somewhat better. A second possible source

Figure 6 Variation in electrically active impurity concentration with metallurgical concentration for as grown silicon ingots.

of error is the application to web of the proportionality constants relating trap concentration and metallurgical concentration which were derived from CZ data, section 3.5. We intend to clarify these points in future experiments.

3.5 The Electrical Activity of Impurities in As-Grown Silicon Ingots

3.5.1 Active Impurity Concentrations

A central assumption of the impurity effects model which connects cell performance to silicon impurity concentration^{1,2} is that the electrically active impurity concentration (N_T) is a fixed fraction of the metallurgical concentration (N_M) added during crystal growth. The excellent agreement of the model predictions with theory has tended to substantiate this hypothesis. DLTS measurements provide a means to test the assumption directly.

We carried out these tests by fabricating Ti-Au Schottky barrier diodes directly on as-grown wafers from ingots doped with Ti, V, Cr or Mo. Use of Schottky diodes eliminates the need for high temperature processing which may perturb the electrical state of the impurity. For each impurity we selected wafers from ingots representing several concentrations.

It is evident from Figure 6 that a relationship between N_T and N_M in fact exists. Note that the slope of the plot is 45° for all four impurities implying that the relationship is actually linear or

$$N_T = k N_M$$

where $k \leq 1$ ^{*}. The proportionality constant $k = 1$ for Mo, 0.4 for Ti, 0.25 for Cr and 0.3 for V. Thus for the same metallurgical impurity concentration in the ingot the electrically active concentration depends on the particular impurity species. Notice in the case of Mo we found only

^{*} Here N_T is the concentration of the dominant majority² carrier trap which may or may not be the trap controlling the lifetime. In case of Ti it is $E_V+0.30\text{eV}$, for V it is $E_V+0.42\text{eV}$ and for Cr it is the $E_V+0.31\text{eV}$ trap.

one deep level and its activity is 100% which give us confidence in our measurement techniques. Since lifetime $\tau = 1/\sigma N_T V_{th}$, it is the product of capture cross section and active impurity concentration which determines the bulk lifetime. From our model curves we know that for a given metallurgical concentration the degradation in cell performance diminishes in the order Mo, Ti, V and Cr. The electrical activity also decreases in the same order. Experiments are being conducted to determine the capture cross sections which may provide a means to determine which level is controlling lifetime.

3.5.2 Capture Cross-Section Determination by DLTS

The need for determining capture cross sections is suggested from the above discussion. This data also strengthens our impurity model and gives a clearer insight into the general behavior of impurities in silicon. We have recently begun experiments to determine the capture cross section of the recombination centers introduced in silicon by various impurities. The cross section is determined by measuring the capture rate. This may be accomplished by determining the change in the peak heights of the DLTS signal as the carrier injecting pulse duration is varied. The peak height, or the density of filled trap $N(t)$ is related to the pulse width t , according to the following expression:

$$N(t) = N_{TT} [1 - \exp(-t \cdot c)] \quad (1)$$

where N_{TT} is the total concentration of the traps and C is the capture rate. Equation (1) can be rewritten as

$$\frac{N_{TT} - N(t)}{N_{TT}} = \exp(-t \cdot c) \quad (2)$$

Thus the capture rate can be obtained from the slope of an Arrhenius-type plot of $N_{TT} - N(t)/N_{TT}$ vs. the pulse width.

The capture rate is related to the capture cross section according to the following expression

$$C = \langle V_{th} \rangle N \sigma \quad (3)$$

where $\langle V_{th} \rangle$ is the mean velocity of the carriers at the DLTS peak temperature $= \sqrt{3KT/m^*}$, N is the doping density and σ is the capture cross section.

Figures 7 and 8 show the change in the DLTS peak height as a function of the pulse width for the $E_V + 0.3$ eV trap induced by Ti in silicon and $E_V + 0.42$ eV trap introduced by V, respectively. Figure 9 shows the plot of $\log (N_{TT} - N(t)/N_{TT})$ vs. pulse width for the Ti-induced $E_V + 0.30$ eV trap and V-induced $E_V + 0.42$ eV trap. The capture cross section deduced from the capture rates were $5.3 \times 10^{-18} \text{ cm}^2$ at 190°K for Ti and $9.1 \times 10^{-19} \text{ cm}^2$ at 256°K for V trap.

The work in progress is to determine the capture cross sections for other levels introduced by Ti and V, and for levels introduced by several other impurities which degrade solar cell performance. This data is to better interpret and predict impurity effects in solar grades of silicon.

3.5.3 Impurity Levels in Silicon

Energy level data provide a means to identify unknown contaminants in silicon. Earlier we reported the deep levels in silicon due to various impurities.² Those levels were obtained using the p-n junction of the cell itself. The minority carrier trap is particularly difficult to detect and to determine accurately this way. Therefore, we have now used impurity-doped p and n silicon to examine the hole or electron traps. In order to avoid high-temperature processing effects we have used the Schottky carrier diodes fabricated on wafers cut from the ingot. 30 mil diameter Ti-Au Schottky diodes were used for p-type ingots while Al Schottky barriers were employed for the n-type material. Another advantage of performing the measurement on the as-grown ingot is

Figure 7 DLTS Signal as a Function of Pulse Width for $E_V+0.30\text{eV}$ Trap Induced by Ti in Silicon

Figure 8 DLTS Signal as a Function of Pulse Width for the $E_V+0.42\text{eV}$ Trap Induced by V in Silicon

Figure 9 Capture Cross Section of Ti and V Induced Levels in Si

that there is no impurity profile introduced by the POCl_3 diffusion. Thus the impurity content undergoes no reduction due to gettering which may make it undetectable.

Table 16 shows the deep levels obtained by the Schottky barrier method. These data are much more reliable and accurate than reported in previously² because the peaks observed were large and much more distinct. The data for W, Nb and are being confirmed since the observed active concentration was very small and the data was not as good as for the other impurities.

3.6 Model Extension — Impurity Effect Comparisons

It would be useful to have a way of examining the relative impact of impurities on cells made from different materials, (for example like polysilicon,) different resistivities or doping types. By such a comparison it would be possible to determine the sensitivity of cell performance to the concentration of one selected impurity out of several present in the silicon. We could thus assess the benefit of specific silicon purification processes.

A convenient parameter to use for comparisons is N_{ox} , the threshold concentration for the impurity of interest. In the model analysis,^{1,2} N_{ox} was determined for each of the impurities in 4 ohm-cm p-base cells and for nearly all in 1.5 ohm-cm n-base devices. It will be recalled that when a single metal contaminant reaches its threshold concentration the cell short-circuit current will be reduced to $\sim 97\%$ of the baseline value.

The threshold N_{ox} was defined from the basic model equation describing the effect of impurity concentration on short-circuit current.

$$\left(\frac{I_n}{I_n} - 1 \right)^2 = C_1 + C_{2x} N_x \quad (4)$$

which can be rewritten as:

TABLE 16 DEEP LEVELS IN AS GROWN SILICON INGOTS

DLTS MEASURED TRAP ENERGY LEVELS FOR IMPURITIES IN SILICON

Mo	$E_v + 0.30$
Ti	$E_v + 0.30$ $E_c - 0.26$
V	$E_v + .42$ $E_c - .225$ $E_c - .46$
Mn	$E_v + 0.40$
Fe	$E_v + 0.40$
Cr	$E_v + .22$ $E_v + .31$ $E_c - .25$
Ta	$E_v + .285$ $E_v + .44$
Al	$E_v + .43$ $E_v + .47$
Cu	—
Nb	$E_v + .12$
Ni	—

$$\left(\frac{I_{n\infty}}{I_n} - 1\right)^2 = C_{2x} \left(\frac{C_1}{C_{2x}} + N_x\right) \quad (5)$$

or defining $N_{ox} = C_1/C_{2x}$

$$\left(\frac{I_{n\infty}}{I_n} - 1\right)^2 = C_{2x} \left(N_{ox} + N_x\right) \quad (6)$$

The two species of cells to be compared are designated α and β where α denotes the base for the comparison, e.g., 4 ohm-cm p-type devices. We can calculate the threshold concentration for impurity x in the β devices from measured values of the short-circuit current in samples containing x, and the short-circuit current in β -cells containing no impurities:

For β -cells containing impurity x at a concentration $N_{x\beta}$ we have:

$$\left(\frac{I_{n\infty\alpha}}{I_{n\beta}} - 1\right)^2 = C_{2x\beta} \left(N_{ox\beta} + N_{x\beta}\right) \quad (7)$$

where all currents are normalized with respect to the I_{sc} obtained in α baseline cells. For β -cells without impurities:

$$\left(\frac{I_{n\infty\alpha}}{I_{n\beta}} - 1\right)^2 = C_{2x\beta} N_{ox\beta} \quad (8)$$

Equations (7) and (8) can be solved for $N_{ox\beta}$ without knowing the value of $C_{2x\beta}$ yielding the experimental threshold:

$$N_{ox\beta} = \frac{N_{x\beta}}{\left[\frac{\frac{In_{\infty\alpha}}{In_{\beta}} - 1}{\frac{In_{\infty\alpha}}{In_{\beta}} - 1} \right]^2 - 1} \quad (9)$$

To obtain an expected value for the degradation threshold based on the α -cell data combined with impurity-free β -cell data, we assumed that the electronic properties of the silicon are affected identically by the impurities in the α and β cases.

In the model derivation the impurity constant C_{2x} was shown to be:

$$C_{2x} = \frac{L_{\lambda}^2 \sigma_x v_{th} a_x}{D} \quad (10)$$

where L_{λ} is a model constant, 1.92×10^{-3} cm; σ_x is the effective minority carrier recombination cross-section for impurity x ; v_{th} is the thermal velocity, $\sim 10^7$ cm/s; a_x is the ratio of the density of electrically-active centers to the metallurgical density of the impurity; and D is the minority carrier diffusion constant. Thus assuming $\sigma_{x\beta} = \sigma_{x\alpha}$ and $a_{x\beta} = a_{x\alpha}$ we have:

$$C_{2x\beta} = C_{2x\alpha} \frac{D_{\alpha}}{D_{\beta}} \quad (11)$$

and we can obtain from Eq. (8) the predicted value of $N_{ox\beta}$.

$$N_{ox\beta} = \frac{D_{\beta}}{D_{\alpha}} \frac{1}{C_{2x\alpha}} \left[\frac{In_{\infty\alpha}}{In_{o\beta}} - 1 \right]^2 \quad (12)$$

Data resulting from comparing values obtained using Eq. (12) to those from Eq. (9) are shown in Figure 10 for the devices described in Table 17.

Quantities given in parentheses are present in the baseline samples in which $I_{no\alpha}$ and $I_{no\beta}$ are measured. These data show that for most of cases considered the impurity degradation effects can be projected from the behavior in the 4 ohm-cm p-base devices. The data for ingot 148, as expected, has a higher measured threshold since manganese produces less effective recombination centers in n-base than in p-base silicon.

It can also be seen that the presence of copper increases the threshold slightly for titanium and vanadium. (Data for ingot 100 is anomalous, it is thought that the titanium concentration is actually higher by a factor of three than the value quoted). Titanium in polycrystalline cells (102) acts almost identically as in single crystal devices, a result which has been corroborated by DLTS measurements.

The high and low-resistivity data agree with the projection, with low-resistivity devices slightly less affected.

Ingots 168 and 169 are heavily compensated with phosphorous and showed considerable variation in resistivity because of the difference in segregation between boron and phosphorous. As a consequence, the cell data had considerable scatter. It is apparent that the tolerance for phosphorous is sufficiently high that problems will be experienced in controlling resistivity before cell degradation due to compensation effects occurs.

Figure 10 Comparison of measured impurity degradation thresholds with those projected from single impurity data in 4 Ω -cm silicon solar cells.

Table 17
Impurity Concentrations for Multiply Doped Ingots
(10^{15} atoms cm^{-3})

Ingot No.	Ti	Cu	V	Cr	Fe	Zr	Ni	Mn
027		1.7						1.3
030		1.7		1.0				
031				1.0				1.3
037	0.22					<0.0007		
041		1.7		0.8			2.1	
043	0.033				0.56			
045	0.039			0.65	0.43			
046			0.07		0.57			
047		1.7				<0.00021	1.0	
050	0.0002		0.0004					
051	0.20	1.7						
061	0.011			1.0				
067	0.0033			0.4				0.5
073	0.0024		0.004	0.4			2.0	0.4
074	0.00033		0.0006	0.08			0.5	0.08
091				0.5				0.3
100	0.033	1.0						
111		2.5	.3					
126	Al, 1.0; B 3.5; Cr .02; Cu .80; Fe .02, Mn .02; Mo .00015; Ni .80; P .9; Ti .0004; V .0004; Zr .0004							
75	.056		.1					
104	.14	2.0						
162	.2						1.21	
185	.15	1.2						

4. CONCLUSIONS

Low resistivity ($0.2 \Omega\text{cm}$) silicon contaminated with Mo or Ti generally responds to HCl or POCl_3 much like higher resistivity material: higher gettering temperatures and longer treatment times improve cell performance. However, the devices made on gettered low resistivity material show very high scatter in performance; many cells exhibit low fill factors and open circuit voltages due to excessive junction leakage. This effect particularly evident for Mo, compromises any advantages of the gettering process. Apparently precipitates, or metal-dopant complexes, form near the high field junction region of the devices during gettering. This causes excessive field emission and shunting in the low resistivity cells.

The performance improvement due to gettering of Ti-(and to a lesser extent Mo) doped cells is due to metal out-diffusion into the phosphorus rich surface region of a wafer. DLTS data show that extended Ti profiles form during out diffusion at 1100°C . However, only abrupt profiles form for Mo, thus explaining the rather small response of the Mo-doped devices to gettering.

We have verified a central assumption of the impurity-cell performance model, that a fixed fraction of the metallurgically added impurity remains electrically-active in the as-grown ingot. We established via DLTS measurements that the electrically-active Ti, Cr, Mo, and V contents are directly proportional to the amounts of metal added to the silicon ingots. The active function is species dependent for Mo nearly all the impurity added is active; for V only about 30% is active.

By means of miniature solar cells and diodes we mapped the cell performance and lifetime across wafers cut from large diameter CZ crystals and wide silicon webs (ribbon single crystals). We found no

added performance reduction which could be ascribed to non-uniform Cu or Fe distributions across the CZ ingots or to variations in Ti or V across the width of the webs. The values of the segregation coefficients for Ti and V on web derived from DLTS data, 4×10^{-6} and 2.4×10^{-5} , respectively, are in general agreement with a theoretical model for solute partitioning during web growth.

The aging characteristics of Cr-doped solar cells differs from earlier data on Ti and V-doped devices. The performance of the Cr-doped devices appears to depreciate faster, and preliminary data suggest that more than one degradation mechanism may obtain depending on the temperature used to accelerate the aging process. Further experiments are planned to clarify this result.

The effective segregation coefficients of three additional contaminants, Ag, Pd and Sn have been determined. The values for the three metals (common contact materials for silicon devices) are $k_{\text{Ag}} = 1.7 \times 10^{-5}$, $k_{\text{Pd}} = 5 \times 10^{-5}$ and $k_{\text{Sn}} = 2.3 \times 10^{-2}$.

*Model projections from single-impurity data on 4 Ω -cm p-base solar cells can be used to describe the behavior of impurity effects in polysilicon, in low-resistivity silicon, and in n-type silicon.

5. PROGRAM STATUS

The program is on schedule as indicated by the current milestone chart, Figure 11.

5.1 Present Status

During the past report period we:

- Completed the Czochralski growth of all remaining silicon ingots for the Phase III program.
- Completed resistivity, etch pit density and carbon/oxygen analyses of 95% of the Phase III ingots.
- Determined the segregation coefficients for Ag, Pd, and Sn appropriate to Czochralski crystal growth.
- Completed HCl gettering of low resistivity silicon ingots doped with Ti and Mo, respectively.
- Performed a detailed assessment of impurity profiles formed during POCl_3 gettering of Mo and Ti at 1100°C .
- Established a correlation between the metallurgical impurity concentration and the electrically active impurity content of as grown ingots.
- Measured the capture cross sections for a variety of important recombination centers formed when impurities are introduced into the silicon lattice.
- Assessed the distribution of impurities radially and longitudinally in large diameter CZ crystals doped with Fe or Co and silicon web crystals doped with Ti and V.
- Made a preliminary assessment of the long time performance of solar cells doped with Cr.

5.2 Future Activity

During the next quarter all tasks of the Phase III program will be completed.

Figure 11

PROGRAM PLAN (SCHEDULE)
(PHASE III)

6. REFERENCES

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8. APPENDICES

Appendix 8.1 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	4.5×10^{-8}
Ni	3.2×10^{-5}
Ph	0.35
Ta	2.1×10^{-8}
Ti	2.0×10^{-6}
V	4×10^{-6}
Zn	10^{-5}
Zr	$< 1.6 \times 10^{-8}$
Co	1.0×10^{-5}
W	1.7×10^{-8}
Pd	5×10^{-5}
Ag	1.7×10^{-5}
Sn	0.032

Appendix 8.2 Ingot Impurity Concentration

<u>Ingot Identification</u>	<u>Target Concentration $\times 10^{15}$ atoms/cm³</u>	<u>Calculated Concentration $\times 10^{15}$ atoms/cm³</u>	<u>Mass Spec. Analysis $\times 10^{15}$ atoms/cm³</u>
W-129-00-000 (7.6 cm.)	NA	NA	NA
W-130-00-000 (7.6 cm.)	NA	NA	NA
W-131-Mn-008 (7.6 cm.)	0.6	0.55	0.55
W-132-Ta-003	0.000037	0.00017	<0.5
W-133-00-000	NA	NA	NA
W-134-Ti-009	0.05	0.03	<0.25
W-135-Fe-005	1.0	0.78	<1.5
W-136-Fe-006	0.3	0.24	<1.5
W-137-Ti-010	0.21	0.21	<0.25
W-138-Mo-005	0.001	0.0008	<0.5
W-139-Mo-006	0.0042	0.0054	<0.5
W-140-Ti-011 (7.6 cm.)	0.18	0.18	<0.25
W-141-Mo/Cu-001	0.004/4.42	0.003/3.68	<0.5/4.00
*W-142-00-000	NA	NA	NA
*W-143-Ti-002	0.20	0.17	<0.25
*W-144-Mo-001	0.0042	0.0044	<0.5
W-145-W-001	0.00085	0.00072	<0.15
W-146-Co-001	1.5	1.1	0.55
W-147-N/Ni-002	0.4	0.33	<1.5
W-148-N/Mn-002	0.60	0.76	0.55
W-149-N/Fe-003	0.60	0.58	<1.5
W-150-N/V-003	0.03	0.03	<0.15
**W-151-00-000	NA	NA	NA
**W-152-Ti-001	0.2	0.22	<0.25
W-153-N/Ti-003	0.01	0.017	<0.25
W-154-N/Cr-003	0.55	0.71	0.35
W-155-N/Mo-001	0.001	0.001	<0.50
W-156-N/Mo-002	0.004	0.003	<0.50
W-157-N/Ti/V-001	Ti: 0.10	0.08	<0.25
	V: 0.10	0.12	<0.15

Appendix 8.2 Ingot Impurity Concentration (cont.)

Ingot Identification	Target Concentration $\times 10^{15}$ atoms/cm ³	Calculated Concentration $\times 10^{15}$ atoms/cm ³	Mass Spec. Analysis $\times 10^{15}$ atoms/cm ³
W-158-N-Ti/V/Cr-001	Ti: 0.05	0.05	<0.25
	V: 0.05	0.05	<0.15
	Cr: 0.60	0.55	0.33
W-159-N/Cr/Mn/Ti/V-001	Cr: 0.4	0.35	0.20
	Mn: 0.4	0.32	0.25
	Ti: 0.02	0.02	<0.25
	V: 0.02	0.02	<0.15
* W-160-Ti-001	0.2	0.17	<0.25
** W-161-Ti-002	0.02	0.03	<0.25
W-162-Ni/Ti-001	Ni: 1.0	1.21	<1.5
	Ti: 0.2	0.16	<0.25
W-163-Ni/V-001	Ni: 1.0	1.01	<1.5
	V: 0.4	0.44	0.15
W-164-Ni/Mo-001	Ni: 1.0	1.23	<1.5
	Mo: 0.004	0.004	<0.5
W-165-Co-002	Co: 0.30	0.29	<0.55
W-166-Fe-007	Fe: 0.9	1.06	<1.5
W-167-Nb-001	0.01++	0.004	<0.15
* W-168-Ph-002	31	NA	(105)+
* W-169-Ph-004	40	NA	(141)+
W-170-Ph-005	56	NA	(150)+
W-171-W-002	0.0015	Incomplete	<0.15
W-172-Cu-006 (7.6 cm)	10	32	24
W-173-Fe-008 (7.6 cm)	0.64	0.51	<1.5
W-174-Ta-004	0.00084	0.00093	<0.50
W-175-W-003	0.00027	0.00029	<0.15
W-176-00-000	NA	NA	NA
W-177-N/Cr/Mn-001	Cr: 1.0	1.20	1.0
	Mn: 1.3	1.26	2.7
W-178-N/Mn/Ti-001	Mn: 1.0	0.86	2.8
	Ti: 0.1	0.08	<0.25
* W-179-Ph-006	21	NA	(73)+
* W-180-Ti-001	0.2	0.13	<0.25
W-181-Cr-006	1.0	1.04	1.0

Appendix 8.2 Ingot Impurity Concentration (cont.)

Ingot Identification	Target Concentration $\times 10^{15}$ atoms/cm ³	Calculated Concentration $\times 10^{15}$ atoms/cm ³	Mass Spec. Analysis $\times 10^{15}$ atoms/cm
W-182-Cr-007	0.25	0.37	0.65
W-183-Nb-002	0.002++	0.0024	<0.15
W-184-Pd-001	6.5	6.4	6.5
W-185-Cu/Ti-004	Cu: 1.7	1.2	<0.80
	Ti: 0.2	0.15	<0.25
W-186-Co-003	0.027	0.027	<0.55
W-187-Co-004	0.135	0.14	<0.55
W-188-W-004	0.00014	0.0002	<0.15
W-189-Nb-003	0.0005++	0.0003	<0.15
W-190-Cu/Zr-001	Cu: 2.0	1.38	2.7
	Zr: 0.0014	0.0012	<0.6
W-191-Cu/Ta-001	Cu: 2.0	0.78	2.7
	Ta: 0.00084	0.00068	<0.5
W-192-Ag-001	2.25	1.91	2.25
W-193-Sn-001	5635	4057	5635
W-194-Ti-012	0.002	0.003	<0.25
W-195-Ti/V/Mo-001	Ti: 0.003	Processing	Processing
	V: 0.003		
	Mo: 0.0006		
W-196-Ti/V/Mo/Ta	Ti: 0.003	Processing	Processing
	V: 0.003		
	Mo: 0.0006		
	Ta: 0.0003		

* Low resistivity p-type ingot ($\leq 1 \Omega\text{-cm}$).

** $30 \Omega\text{-cm}$ p-type ingot.

+ Value based on resistivity measurement.

++ Assumed K value near 1×10^{-7} .