410
11/7/80 T.S.

Dr. 1989

DOE/JPL/954331-80/10

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

MASTER

Effects of Impurities and Processing on Silicon Solar Cells
Eighteenth Quarterly Report, January—March 1980

By

R. H. Hopkins

J. R. Davis

A. Rohatgi

R. B. Campbell

P. Rai-Choudhury

M. H. Hanes

H. C. Mollenkopf

J. R. McCormick

April 1980

Work Performed Under Contract No. NAS-7-100-954331

Westinghouse R&D Center
Pittsburgh, Pennsylvania

U.S. Department of Energy

Solar Energy

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

DISCLAIMER

"This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof."

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$6.00
Microfiche \$3.50

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

Effects of Impurities and Processing on Silicon
Solar Cells

Eighteenth Quarterly Report

April 1980

January 1980-March 1980

R. H. Hopkins, J. R. Davis, A. Rohatgi,
R. B. Campbell, and P. Rai-Choudhury, and M. H. Hanes
Westinghouse Research and Development Center
and
H. C. Mollenkopf and J. R. McCormick
Hemlock Semiconductor Corporation

Contract No. 954331

The JPL Low-Cost Silicon Solar Array Project is sponsored by the U. S. Department of Energy and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays. This work was performed for the Jet Propulsion Laboratory, California Institute of Technology by agreement between NASA and DOE.

Westinghouse R&D Center
1310 Beulah Road
Pittsburgh, Pennsylvania 15235

NEW TECHNOLOGY

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

TABLE OF CONTENTS

	Page
1. SUMMARY	1
2. INTRODUCTION	3
3. TECHNICAL PROGRESS	4
3.1 Phase IV Program.	4
3.2 Crystal Growth and Analysis	5
3.2.1 Ingot Preparation.	5
3.2.2 Ingot Evaluation	5
3.3 Polycrystalline Material and Solar Cells.	12
3.3.1 Analysis of Vanadium and Molybdenum Doped Poly Silicon Solar Cells.	12
3.3.2 Microstructural Characterization of Poly- crystalline Ingots	17
3.4 Gettering of V-doped Silicon During Device Diffusion. .	18
3.5 The Permanence of Impurity Effects in Silicon Solar Cells	25
3.5.1 Experimental Method.	26
3.5.2 Interpretation of Data	26
3.5.3 Behavior of Cells Containing Iron.	26
3.5.4 General Observations	27
4. CONCLUSIONS.	31
5. PROGRAM STATUS	32
6. REFERENCES	33
7. ACKNOWLEDGEMENTS	34

LIST OF ILLUSTRATIONS

Figure		Page
1	Photomicrograph of two regions with Schottky barrier diodes (50X). (a) Active vanadium concentration $1.8 \times 10^{14} \text{ cm}^{-3}$. (b) Active vanadium concentration $0.9 \times 10^{14} \text{ cm}^{-3}$	16
2	Optical photomicrograph from a section cut <u>normal</u> to the growth direction of Ingot W201Mo007. The eutectic-like network is composed of Mo silicide intertwined with the silicon host crystal. The second phase network extends in the growth direction and also lies parallel to twin boundaries ({111} traces) on the plane of polish. 100X magnification.	19
3	Cellular structure composed of a eutectic mixture of silicon and molybdenum silicide interspersed within the matrix of the polycrystalline Ingot W201Mo (60X Reflected Light). . .	20
4	Cr silicide inclusions caused by constitutional supercooling during the growth of Ingot W204Cr (a) Inclusions outcrop on the wafer surface, reflected light photomicrograph (b) Infrared transmission photomicrograph of the same area showing the inclusions threading through the same area of the bulk wafer, (60X)	21
5	Microstructure of Ingot W202Ti. (Lightmicroscopy, ~6X.) . .	22
6	Vanadium concentration profile in a wafer after 50 minutes diffusion in POCl_3	24

LIST OF TABLES

TABLE		Page
1	Ingot Impurity, Structure and Task.	6
2	Ingot Impurity Concentration.	7
3	Best Estimate of Impurity Concentrations.	9
4	Ingot Electrical and Defect Characteristics	10
5	Ingot Carbon and Oxygen Concentrations.	11
6	Solar Cell Data for V-doped Polycrystalline and Single Crystal Solar Cells (No AR Coating)	13
7	Concentration of $E_v + 0.42\text{eV}$ Trap at Various Locations of the Polysilicon Wafer Contaminated with $4 \times 10^{14}\text{cm}^{-3}$ Vanadium	15
8	Vanadium Concentration Profile after the Solar Cell Diffusion ($825^\circ\text{C}/50\text{ min POCl}_3$) On Ingot W009V001.	23
9	Ingots Used in Permanence Studies	28
10	Permanence Studies Data	29
11	Projected Behavior of Solar Cells	30

1. SUMMARY

The overall objective of this program is to define the effects of impurities, various thermochemical processes, and any impurity-process interactions upon the performance of terrestrial 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.

Fifteen 4 ohm-cm p-type ingots were grown during this quarter, both single crystal and polycrystal, to initiate the Phase IV effort. These ingots were evaluated through electrical measurements, spark source mass spectroscopy, and atomic absorption spectroscopy of the melt. Carbon and oxygen concentrations were measured by IR spectroscopy and found to be within normal limits.

Cells made from Mo-doped poly material exhibited very low efficiencies. This was found to be due to cellular breakdown during growth of the silicon ingot, creating separate phases at the cell boundaries which effectively short circuit the solar cells fabricated on the ingot wafers. Schottky barrier diodes made on this material exhibited high reverse current leakage so that deep level transient spectroscopy (DLTS) measurements could not be made. Metallographic examination of the material confirmed the presence of the molybdenum silicide-silicon tectic at cell boundaries. Further studies of Mo-doped polycrystalline will be performed on ingots prepared with lower Mo concentrations and/or lower growth rates.

Cells made from vanadium-contaminated polycrystalline Si also showed very low efficiency due to junction shorting effects; however, a few of the cells with lower inclusion densities could be measured. The concentration of active V deep levels measured by DLTS was close to the value projected from single crystal segregation coefficient data.

DLTS has also been used to map the vanadium concentration-depth profile in solar cells made on V-doped single crystal wafers. Analysis of these data indicate that phosphorus diffusion getters V from the material by a diffusion-controlled process.

Projections of effective life of solar cells containing some specific impurities were made. On the basis of data derived from elevated temperature stressing of solar cell material, it is concluded that cells containing Mo or Ti as impurities will not degrade appreciably during a twenty year period due to impurity aging effects. However, initial data indicate that cells containing Cr, Nb, or Ag degrade more rapidly than Mo or Ti-doped cells; and may not retain useful efficiencies over a twenty year period.

2. INTRODUCTION

This is the eighteenth quarterly report describing activities conducted under JPL Contract 954331, and is the first report on the recently initiated Phase IV effort.

In Phase III, "An Investigation of the Effects of Impurities and Processing on Silicon Solar Cells," effects of thermal processes, impurities, and impurity-process interactions were determined and documented. The development of this data base has led to a more precise definition of what constitutes an acceptable "Solar Grade" Silicon. In addition, it has provided silicon manufacturers with a rationale for selection of construction materials; moreover, it has helped ingot, sheet, or ribbon manufacturers to specify the purity of silicon feedstocks; finally, it has enabled cell manufacturers to define acceptable wafer purities for cell fabrication and to choose processes which minimize adverse impurity effects. In short, the impurity effect data provide a basis for cost-benefit analysis to producers and users of Solar Grade Silicon.

In Phase IV of this program, the approaches and techniques developed in Phase III are being extended to several new areas, as well as to developing an improved data base for aging effects and certain process-related phenomena. The Phase IV tasks include evaluation, by previously developed process techniques, of the properties of silicon produced by experimental low cost processes; extending threshold impurity concentration data to high efficiency cells; measuring the effects of interaction between impurities and grain boundaries in polycrystalline solar cells; evaluating the long term effects of impurities in solar cells; and examining the effects of processes such as ion implantation on contaminated solar cells.

3. TECHNICAL PROGRESS

3.1 Phase IV Program

The Phase IV effort of this program has been initiated under a modification to the present contract. While the details of the program cannot be completely specified until the contract for Phase IV is signed, five major areas have been defined for study.

- An assessment will be made of the properties of experimental silicon materials being developed as part of the LSA project. The evaluation may include chemical analyses of melts and ingots made from the silicon, ingot microstructure, bulk recombination lifetime, resistivity, solar cell I-V measurement and modeling of cell performance to identify potentially harmful impurity effects.
- The effects of impurities on the performance of high efficiency silicon solar cells will be studied to define threshold impurity concentrations in such devices. New device models or modifications to existing models will be made to project the performance of contaminated high efficiency cells.
- The effects on materials properties and solar cell performance caused by impurities introduced into polycrystalline silicon will be evaluated. It is expected that a variety of techniques such as mass spectroscopy, microstructural analysis, deep level spectroscopy, and electron beam induced current analysis will be coupled with solar cell performance data to identify the overall and localized effects of impurities in polycrystalline devices.
- An extension of our studies of the long term effects of impurities on silicon material properties and solar cell performance will be made to broaden the current data base. The studies are expected to include (1) accelerated (high temperature) aging of impurities

introduced by crystal growth and diffusion and (2) low temperature aging of impurity-doped cells under the presence of electrical bias. Appropriate models formulated as part of the study will be used as a basis for projecting long term impurity effects in silicon solar cells.

- Processing studies will be expanded to examine the combined effects of impurities and high temperature processing treatments on the silicon material properties and solar cell performance of polycrystalline silicon and ion-implanted silicon. The high temperature treatments may include annealing, HCl gettering, and ion-implant damage gettering, alone or in combination.

3.2 Crystal Growth and Analysis

3.2.1 Ingot Preparation

Ingot preparation focused mainly on polycrystalline and monocrystalline silicon ingot growth in support of the permanence, high efficiency and polycrystalline tasks of the Phase IV effort. Fifteen 4 ohm-cm p-type silicon ingots were produced. Each ingot's intentionally added impurity concentration, associated crystalline structure and task designation are indicated in Table 1. As with the earlier phases of the program, each of the ingots was prepared by the Czochralski crystal growth method. Details of the crystal growth equipment and conditions can be found in earlier reports.^(1,2)

3.2.2 Ingot Evaluation

All ingots, target impurity concentration, impurity concentrations based on atomic absorption melt analysis (calculated concentrations), and impurity concentrations measured by spark source mass spectrometry^(2,3) are listed in Table 2.

The calculated ingot concentration data obtained from atomic absorption analysis of the ingot melt after crystal growth agrees within experimental error with the target values, while the spark source mass spectrometer ingot sample analysis shows a large discrepancy between the target and measured values for the polycrystalline ingots. This

TABLE 1. INGOT IMPURITY, STRUCTURE AND TASK

<u>Impurity</u>	<u>Structure</u>	<u>Task</u>
NA*	Single	Baseline
NA	"	"
V	Poly	Poly
Mo	"	"
Ti	"	"
V	"	"
Cr	"	"
Fe	"	"
V	Single	High Efficiency
Mo	"	"
Cr	"	"
Ti	"	Permanence
Ti	"	"
Cu	"	Processing
Cu	"	Processing

* NA denotes no intentionally added metallic impurities

TABLE 2. INGOT IMPURITY CONCENTRATION

<u>Ingot Identification</u>	<u>Target Concentration (10^{15} atoms/cm³)</u>	<u>Calculated Concentration (10^{15} atoms/cm³)</u>	<u>Mass Spec. Analysis (10^{15} atoms/cm³)</u>
W-198-00-000	None	N/A	None
W-199-00-000	None	N/A	None
W-200-V-004-Poly	0.4	0.38	18.5*
W-201-Mo-007-Poly	0.005	0.003	77*
W-202-Ti-013-Poly	0.02	0.018	<0.25
W-203-V-005-Poly	0.04	0.053	<0.15
W-204-Cr-008-Poly	1.0	0.82	1322*
W-205-Fe-009-Poly	0.02	Processing	Processing
W-206-V-006	0.02	0.026	<0.15
W-207-Mo-008	0.002	0.002	<0.5
W-208-Cr-009	0.2	0.19	0.6
W-209-Ti-014	0.02	Processing	<0.25
W-210-Ti-015	0.08	Processing	<0.25
W-211-Cu-007	1.0	Processing	2.6
W-212-Cu-008	10	Processing	Processing

* Indicative of grain boundary effects in doped polycrystalline silicon

discrepancy between the target and spark source data is indicative of the spark source discharge striking local regions in the polycrystalline samples where the concentration of the intentionally-added impurity is higher with respect to the bulk silicon due to impurity segregation effects. The apparent discrepancy is largest for poly-ingots W-200, W-201 and W-204 where sub-millimeter size grain structure due to constitutional supercooling is predominant. This should be contrasted with poly ingots W-202 and W-203 (mm-sized grains) where better agreement exists between target and spark source evaluations. (See Section 3.3)

A best estimate⁽³⁾ of the impurity concentrations in all ingots prepared in Phase IV are tabulated in Table 3. The values for the poly ingots are essentially the same as the calculated values because of the influence of the grain boundaries on the spark source mass spectrometer evaluations. Insufficient data analysis of W-208-Cr at the present time and the fact that spark source analysis tests localized sample areas explains why the best estimate was derived from atomic absorption analysis of a large dissolved chromium-doped silicon sample.

The resistivity and etch pit data for ingots W-198 through W-212 are listed in Table 4. The values for each ingot fall close to the norms established in earlier phases⁽³⁾ of this program. Etch pit analysis is not applicable to the polycrystalline samples.

The carbon and oxygen concentrations of each odd numbered ingot continue to be measured by infrared absorption at room temperature. The amplitude 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 to 5×10^{17} atoms/cm³ for carbon and 5 to 150×10^{16} atoms/cm³ for oxygen. As usual, no significant deviations from these values were observed this quarter, as indicated in Table 5.

TABLE 3. BEST ESTIMATE OF IMPURITY CONCENTRATIONS

<u>Ingot Identification</u>	<u>Best Estimate of Impurity Conc. (10^{15} atoms/cm³)</u>
W-198-00-000	NA
W-199-00-000	NA
W-200-V-004-Poly	0.38
W-201-Mo-007-Poly	0.003
W-202-Ti-013-Poly	0.018
W-203-V-005-Poly	0.05
W-204-Cr-008-Poly	0.82
W-205-Fe-009-Poly	Incomplete
W-206-V-006	0.026
W-207-Mo-008	0.002
W-208-Cr-009	0.19
W-209-Ti-014	Processing
W-210-Ti-015	Processing
W-211-Cu-007	Processing
W-212-Cu-008	Processing

TABLE 4. INGOT ELECTRICAL AND DEFECT CHARACTERISTICS

<u>Ingot Identification</u>	<u>TGT Resistivity (ohm-cm)</u>	<u>Actual Resistivity (ohm-cm)</u>	<u>Etch Pit Density (/cm²)</u>
W-198-00-000	4.0	4.1-3.9	0-3K
W-199-00-000	4.0	3.7-3.5	1-5K
W-200-V-004/Poly	4.0	3.6-2.3	NA
W-201-Mo-007/Poly	4.0	3.8-2.3	NA
W-202-Ti-013/Poly	4.0	5.3-3.9	NA
W-203-V-005/Poly	4.0	4.4-3.8	NA
W-204-Cr-008/Poly	4.0	4.7-4.3	NA
W-205-Fe-009/Poly	4.0	Incomplete	Incomplete
W-206-V-006	4.0	3.7-3.6	0-5K
W-207-Mo-008	4.0	3.8-3.5	0-15K
W-208-Cr-009	4.0	3.7-3.5	0-15K
W-209-Ti-014	4.0	4.0-3.3	0-10K
W-210-Ti-015	4.0	4.0-3.5	0-5K
W-211-Cu-007	4.0	Processing	Processing
W-212-Cu-008	4.0	Processing	Processing

TABLE 5. INGOT CARBON AND OXYGEN CONCENTRATIONS

<u>Ingot Identificaion</u>	<u>Carbon Concentration (10^{16} atoms/cm³)</u>	<u>Oxygen Concentration (10^{16} atoms/cm³)</u>
W-201-Mo-007/P	7.0	120
W-203-V-005/P	12	116
W-205-Fe-009/P	8.0	66
W-207-Mo-008	5.4	84
W-209-Ti-014	6.4	120
W-211-Cu-007	6.0	111

3.3 Polycrystalline Material and Solar Cells

3.3.1 Analysis of Vanadium and Molybdenum Doped Poly Silicon Solar Cells

One vanadium doped poly ingot, W-200-V, containing $4 \times 10^{14} \text{ cm}^{-3}$ V, and one Mo doped poly ingot, W-201-Mo, containing $4 \times 10^{12} \text{ cm}^{-3}$ Mo, were grown. Wafers cut from the ingots were etched down to 10 mils thickness and n^+p solar cells were fabricated on them by our standard diffusion process ($825^\circ\text{C}/50 \text{ min}$, POCl_3). Each experimental run consisted of 10 wafers from the center, 5 wafers from the seed end and 5 uncontaminated baseline wafers. The uncontaminated baseline material gave very good cells, (Table 6) with efficiencies about 10% (without AR coating); however, no electrical output could be obtained from the Mo-doped cells. A detailed dark I-V analysis revealed that this was a consequence of the extremely low shunt resistance of the cells — on the order of 0.1Ω . As we show in the following section, this result was a consequence of inclusion formation in the ingot, which produced large localized metal concentrations. Such large concentrations particularly along grain boundaries can lead to a short.

In the case of the V-doped ingot, 13 out of 15 cells also showed low shunt resistance of the order of 2Ω . Thus some electrical output could be measured in these cases. This is consistent with the crystal structure analysis which showed a partial crystal breakdown in this ingot.

Unlike the other 13 cells, wafers 7C and 7D were not dominated by the shunt resistance; therefore, the solar cell efficiencies could be measured and these data are listed in Table 6. Table 6 also shows the average solar cell performance of the single crystal Ingot V-009, which contained a vanadium concentration approximately equivalent to that of the polycrystalline ingot.

Some useful comparisons can be made from the very limited data on Ingot V-200. Sample 7C had a very good shunt resistance $K\Omega$, a low series resistance 0.7Ω , short circuit current of 13.3mA, and an efficiency of 4.67%. This cell efficiency is similar to the 3.9%

TABLE 6 SOLAR CELL DATA FOR V-DOPED POLYCRYSTALLINE AND SINGLE CRYSTAL SOLAR CELLS (No AR Coating)

ID	I_{SC}(mA)	V_{OC}(V)	I_P(mA)	FF	EFF (%)
BASELINE	22.30	0.565	20.85	0.778	10.28
W200V-7C (poly)	13.30	0.468	12.02	0.719	4.67
W200V-8C (poly)	12.50	0.443	9.03	0.519	3.03
W009V (single)	10.21	0.467	9.48	0.769	3.88

efficiency obtain on single crystal Ingot V-09. Slightly higher I_{sc} in the poly cell suggests better bulk lifetime in this cell or some segregation of V to the grain boundaries. More data, e.g. from deep-level spectroscopy, will be necessary to substantiate this conclusion. Sample 8C has an efficiency because it showed considerable junction leakage, consistent with the large n factor obtained on the cell. This can result from the presence of grain boundaries and/or impurity precipitates in the depletion region. These results are very similar to those for Ti-doped poly cells, in which case we concluded that although there is somewhat less active Ti in the bulk of the poly cell, overall efficiencies on single crystal and poly crystal cells were not very different due to the damaging influence of grain boundaries (3A). Another V-doped poly ingot with a lower V concentration has been grown to obtain data free from the crystal breakdown effects.

We fabricated 30 mil diameter Ti-Au Schottky barrier diodes on the Mo and V-contaminated poly wafers to assess the active impurity concentration by DLTS measurements. The Schottky barrier diodes on the Mo-doped wafer were very leaky; therefore, DLTS measurements could not be performed. However, the Schottky barrier diodes on V-doped cells were sufficiently good that DLTS data were acquired on 8 diodes located on different regions of the wafer, Table 7. On all the diodes, a dominant deep level at $E_V + 0.42\text{eV}$ was observed and its concentration was used to designate the active vanadium concentrations in Table 7. The same deep level was observed in the V-doped single crystal Ingot W009 and its concentration was $1 \times 10^{14} \text{ cm}^{-3}$. The data in Table 7 show that in the poly wafer the active V concentration is in the range $0.9\text{--}1.8 \times 10^{14} \text{ cm}^{-3}$ indicating that behavior of V impurity is not very different in poly and single crystal silicon. A variation of a factor of 2 suggests that there may be a small amount of segregation of V at the grain boundaries. Figure 1 shows the photograph of the two Schottky barrier diodes which gave minimum and maximum active V concentrations. From these pictures it is difficult to relate the variation in V concentration to the microstructural features. Further work on this point will be carried out on the V-doped poly ingot free from inclusions.

TABLE 7 CONCENTRATION OF $E_v + 0.42\text{eV}$ TRAP AT VARIOUS LOCATIONS OF
THE POLYSILICON WAFER CONTAMINATED WITH $4 \times 10^{14}\text{cm}^{-3}$ VANADIUM

Schottky Barrier Diode No.	Concentration of $E_v + 0.42\text{eV}$ Trap (cm^{-3})
1	1.8×10^{14}
2	1.6×10^{14}
3	0.93×10^{14}
4	1.3×10^{14}
5	0.9×10^{14}
6	1.3×10^{14}
7	1.3×10^{14}
8	1.3×10^{14}

Figure 1 Photomicrograph of two regions with Schottky barrier diodes (50X). (a) Active vanadium concentration $1.8 \times 10^{14} \text{cm}^{-3}$. (b) Active vanadium concentration $0.9 \times 10^{14} \text{cm}^{-3}$.

3.3.2 Microstructural Characterization of Polycrystalline Ingots

When we found the large shunting effects indicated by the solar cell data for ingots W200Mo and W201V, we carried out a detailed microstructural evaluation of wafers from the ingots in order to identify the source of the problem.. Both conventional reflected light and transmission infrared microscopy were performed on chemically polished slices from each of the polycrystalline ingots so far grown.

In each of the most heavily doped polycrystalline ingots W200Mo, W201V, and W204Cr, there was clear evidence of cellular structure formed by constitutional supercooling. The most classic example is depicted in Figures 2 and 3 from ingot W200Mo in which a eutectic mixture of silicon and Mo silicide is dispersed at "cell" boundaries within the silicon crystal matrix. The two-phase mixture at the cell boundaries is clearly visible in Figure 3.

The form of the second phase in ingots W201V and W204Cr is more dispersed, for example, in a comparison of Figures 4(a) and 4(b) which are, respectively, a reflected light and an IR transmission photograph of the same area of Ingot W204Cr. The second phase particles are elongated in the growth direction and also tend to aggregate along preferential directions in the ingot.

Because the second phase particles outcrop on the surface of the wafers, the inclusions can short the cell junction as well as affecting the transverse resistivity of devices made on the wafers. Shunting is a manifestation of this behavior. The inclusions also produce the excessively high and variable measurements of impurity concentration exhibited by the mass spectrometer, Table 2. We successfully grew single crystal ingots at impurity concentrations where structural breakdown occurs in the polycrystalline material. Grain boundaries, known to be a preferred location for the onset of interface instability, apparently trigger structural breakdown in the polycrystalline ingots at a lower impurity threshold (C_{ℓ}^*) than in the single crystal ingots. We expect to regrow these ingots, either reducing the impurity content or the growth rate, to eliminate constitutional supercooling.

We note that Ingots W202Ti and W203V grown from melts with considerably lower initial impurity concentrations produced polycrystalline structure with no inclusions, Figure 5. Grain size of about 1 to 2mm predominated.

3.4 Gettering of V-doped Silicon During Device Diffusion

By etching steps on the surface of a V-doped solar cell we were able to measure the V-concentration profile to a depth of 50 μ m from the junction into the bulk. DLTS was used to obtain the concentration values; the diffusion was carried out in POCl₃ for 50 min at 825°C. The experimental data, compiled in Table 8 and plotted in Figure 6 are generally consistent with the previous results for Ti-doped cells.

The electrically-active V concentration is very small, $<10^{13} \text{ cm}^{-3}$ at the junction, then rises abruptly within a depth of 25 μ m to reach the bulk value of about 10^{14} cm^{-3} . The shape of the profile is similar to that for Ti.

The gettering behavior we observed is consistent with a model in which impurity diffusion is deemed the dominant process. Mathematically, we can examine the diffusion process by assuming that, at the phosphorus (or HCl) rich surface region of the wafer, the metallic impurity is forced to a fixed concentration. Before the gettering process we assume the wafer has a uniform initial impurity concentration throughout its thickness. The one-dimensional diffusion equation is given by:

$$\frac{\partial N(x,t)}{\partial t} = D \frac{\partial^2 N(x,t)}{\partial x^2} \quad (1)$$

where $N(x,t)$ is the impurity concentration as a function of distance from the center of the wafer and the time of the gettering process. D is the diffusion constant for the impurity in silicon. The general solution of Eq. 1 can be expressed as:

$$N(x,t) = (A \sin \alpha x + B \cos \alpha x) \exp (-\alpha^2 Dt) \quad (2)$$

Figure 2 Optical photomicrograph from a section cut normal to the growth direction of Ingot W201Mo007. The eutectic-like network is composed of Mo silicide intertwined with the silicon host crystal. The second phase network extends in the growth direction and also lies parallel to twin boundaries ($\{111\}$ traces) on the plane of polish. 100X magnification.

Figure 3 Cellular structure composed of a eutectic mixture of silicon and molybdenum silicide interspersed within the matrix of the polycrystalline Ingot W201Mo (60X Reflected Light).

(a)

(b)

Figure 4 Cr silicide inclusions caused by constitutional supercooling during the growth of Ingot W204Cr (a) Inclusions outcrop on the wafer surface, a reflected light photomicrograph (b) Infrared transmission photomicrograph of the same area showing the inclusions threading through the same area of the bulk wafer, (60X).

Figure 5 Microstructure of Ingot W202Ti. (Light microscopy, ~6X.)

TABLE 8 VANADIUM CONCENTRATION PROFILE AFTER THE SOLAR CELL DIFFUSION
(825°C/50 min POCl_3) ON INGOT W009V001

Distance from the n+p interface (μm)	Concentration of the $E_V+0.42\text{eV}$ trap (cm^{-3})
0	$\left\{ \begin{array}{l} 2.9 \times 10^{12} \\ 1.40 \times 10^{13} \end{array} \right.$
2	3.4×10^{13}
6	2.12×10^{13}
7.5	4.1×10^{13}
10	4.3×10^{13}
12.5	4.83×10^{13}
20	7.66×10^{13}
25	7.96×10^{13}
30	9.0×10^{13}
50	1.05×10^{14}

NOTE: V concentration in the wafer prior to any heat treatment was $1 \times 10^{14} \text{cm}^{-3}$.

Figure 6 Vanadium concentration profile in a wafer after 50 minutes diffusion in POCl_3 .

It was previously shown⁽⁴⁾ that, with the appropriate boundary conditions, two solutions for this equation can be derived. Both solutions are in an infinite series form; the solution chosen for computation is that form which converges more rapidly for specific values of D and t .

Phosphorus gettering of vanadium was examined experimentally using DLTS measurement on step-etched surfaces to obtain the concentration profile, e.g. Figure 6. The low temperature data shown suggest values for $N_o \approx 1 \times 10^{14}/\text{cm}^3$ and $N_g^o = 5 \times 10^{12}/\text{cm}^3$. It is assumed the gettering surface, where N_g is applicable, is located at the n-p junction. The gettering process for this sample consisted of an 825°C, 50 min phosphorus diffusion.

A fit of the data to the series solution described above, assuming diffusion-controlled drift of V to the surface, indicates a value of the diffusion constant at 825°C of about $8.5 \times 10^{-10} \text{ cm}^2/\text{sec}$. This is more than an order of magnitude greater than the value obtained for Ti, suggesting that V diffuses more rapidly in silicon than does Ti.

3.5 The Permanence of Impurity Effects in Silicon Solar Cells

Experimental evidence^(1,2) shows that solar cell performance is a function of device process history. Since the operating life of solar cells in the field is expected to be over twenty years, it is important to determine how stable the performance of cells made on impure silicon will be over extended periods. That is, how permanent are the characteristics of solar cells fabricated on solar grade silicon?

The time period involved is extremely long compared to practical test times, 50 accelerated testing is required to predict aging behavior. This can be accomplished by adjusting the level of the stress to which the specimen is exposed. On the basis of our earlier results we believe that the temperature is likely to dominate the degradation related to impurities. Thus, in these first aging experiments this parameter has been given priority.

3.5.1 Experimental Method

Prediffused silicon wafers containing single impurities are subjected to temperature stress at several elevated temperatures. The rate of property degradation is determined at each temperature, assuming that, at least in the initial stages, cell efficiency decreases linearly with time. A linear least squares fit to the efficiency-time data gives estimates of η_0 (the initial efficiency) and $1/\eta_0 \, d\eta/dt$ (the normalized rate of change of efficiency). From these parameters determined at different temperatures, an Arrhenius plot is developed to express the temperature dependence of impurity degradation for a particular impurity.

Ingots which have so far been used in permanence studies are listed in Table 9.

3.5.2 Interpretation of Data

In the investigations conducted during this reporting period, pre-diffused cells were thermally stressed at 400°C (for 0, 10, 50, and 200 hours), at 600°C (for 0.5, 2, and 24 hours), and at 800°C (for 0.17, 0.5, and 1 hours). Cells were subsequently contacted and measured. In no case did the efficiency decreased by more than 10% of its original value, so the assumption of linear rate of change is justified. A compilation of these measurements appears in Table 10. These data plus those from earlier measurements were used to construct Table 11.

3.5.3 Behavior of Cells Containing Iron

The effects of iron on solar cells are complex, including excessive junction shunting and depletion region recombination.^(3,4) Our preliminary investigation has shown that the time-efficiency behavior of iron-contaminated cells can also be quite complex. Cells from each of the two ingots W135Fe005 ($7.8 \times 10^{14} \text{ Fe cm}^{-3}$) with W166Fe007 (1.06×10^{15}) sometimes exhibited an increase in cell efficiency with time. This effect might be due to dispersion of iron precipitates or to gettering of iron-induced recombination centers. In any case, such behavior is not amenable to analysis by the same method as is applied to cells containing other impurities which mainly degrade bulk lifetime. This is indicated by the dashes in Table 11.

3.5.4 General Observations

As noted previously, neither Ti nor Mo show serious aging effects of the concentrations we have studied. We expect little or no change in cell performance due to the impurities themselves over periods projected beyond 20 years.^(3,4) However, if the initial data in Table 11 are confirmed, cells doped with other impurities will begin to show degradation within the 20 year period. Cr shows the lowest "time to failure" followed by Ag and Nb. As Cr and Ag are expected to diffuse more rapidly in silicon than do Ti or Mo this is perhaps to be expected.

TABLE 9

INGOTS USED IN PERMANENCE STUDIES

Ingot Identification	Impurity Concentration (cm ⁻³)
*W09700000	Baseline
*W077Mo001	4.2×10^{12} Mo
*W123Ti008	1×10^{14} Ti
*W072Cr005	4×10^{14} Cr
W192Ag001	2.2×10^{15} Ag
W183Nb002	$< 9 \times 10^{12}$ Nb
W135Fe005	7.8×10^{14} Fe
W166Fe007	1.06×10^{15} Fe
W167Nb001	$< 4.4 \times 10^{13}$ Nb

*For earlier data see previous reports^(3,4)

A compilation of these measurements is made in Table 10

TABLE 10

PERMANENCE STUDIES DATA

		$\frac{1}{\eta_0} \frac{d\eta}{dt} \text{ (hr}^{-1}\text{)}$		
Ingot	η_0 (%)	400°	600°	800°
192Ag001	9.29	-1.506×10^{-3}	-3.802×10^{-3}	-8.288×10^{-2}
183Nb002	8.28	-9.884×10^{-4}	-2.614×10^{-3}	-1.919×10^{-1}
135Fe005	7.43	-6.717×10^{-4}	$+3.948 \times 10^{-3}$	$+4.762 \times 10^{-3}$
166Fe007	8.57	-1.288×10^{-3}	$+5.099 \times 10^{-4}$	-1.261×10^{-1}
167Nb001	7.66	-9.335×10^{-4}	-3.190×10^{-3}	-2.037×10^{-1}

Combined data from these measurements and those described in references 3 and 4 were used to construct Table 11.

TABLE 11

PROJECTED BEHAVIOR OF SOLAR CELLS

<u>Ingot</u>	<u>E_a (eV)</u>	<u>Time to failure at 100°C (hrs)*</u>
Baseline	1.42	6.3×10^{12}
W077Mo001	2.03	4.4×10^{19}
W123Ti008	3.47	7.6×10^{39}
W072Cr005	0.25, 0.55	$1.0 \times 10^{5**}$
W192Ag001	.5872	3.3×10^5
W183Nb002	.7665	7.4×10^6
W135Fe005	-	-
W166Fe007	-	-
W167Nb001	.7891	1.0×10^7

* Time to failure is defined as the time in which the cell efficiency will be reduced to 90% of its initial value.

** Based upon $E_a = 0.55 \text{ eV}$

Note that twenty years is equivalent to 1.75×10^5 hours.

4. CONCLUSIONS

The microstructural stability of polycrystalline silicon material grown by the Czochralski process is more sensitive to metallic impurities than is single crystal silicon; grain boundaries initiate cellular breakdown and second phase formation. The distribution of impurities in those polycrystalline ingots with cellular breakdown is nonhomogeneous, impurity segregation occurring in clusters mainly associated with grain boundaries. When the melt impurity concentration is reduced, millimeter-size grains are readily produced and the impurity distribution is much more uniform.

Vanadium impurity in polycrystalline silicon forms a deep level trap which is the same as that formed in single crystal silicon. Vanadium is getterred by the phosphorus diffusion process; the phenomenon is consistent with a vanadium diffusion model.

Elevated temperature stress measurements indicate that the presence of slow diffusing species such as Mo and Ti will not affect the long term efficiency of solar cells operating at a practical temperature. The effects of Cr, Ag, and Nb will be more pronounced. The effect of Fe is so far nonpredictable, due to multiple cell degradation mechanisms.

5. PROGRAM STATUS

The program is on schedule with respect to assumed milestones.

5.1 Present Status

During the last reporting period

- Fifteen new ingots, both single and polycrystalline, were grown, and characterized with respect to impurity concentration.
- Molybdenum and vanadium containing polycrystalline materials were evaluated by optical microscopy, deep level spectroscopy and solar cell I-V measurements.
- Gettering of vanadium by phosphorus diffusion was measured and quantitatively described.
- Causes of extremely low efficiency in Mo and V contaminated polycrystalline material were identified and ascribed to second phase formation.
- Preliminary projections of effects of Ag and Nb impurities on the long term efficiency of solar cells were made. Anomalous behavior of Fe in solar cells was documented.

5.2 Future Activity

During the next quarter we expect to continue the evaluation of impurity effects in polycrystalline solar cells, extend the gettering studies to other impurities and to initiate work on impurity behavior in high efficiency devices. The details of the studies are pending signing of the contract for the total Phase IV contract with JPL.

6. REFERENCES

1. R. H. Hopkins, et al., 11th Quarterly Report and Summary, Silicon Materials Task (Part 2) DOE/JPL 954331-78/c, July 1978.
2. R. H. Hopkins, et al., 5th Quarterly Report and Summary, Silicon Materials Task (Part 2) DOE/JPL 954331-77/1, January, 1977.
3. R. H. Hopkins, et al., 17th Quarterly Report and Summary-Volume 1., Silicon Materials Task (Part 2) DOE/JPL 954331-80/9, January , 1980.
4. Ibid., Volume 2.

7. ACKNOWLEDGEMENTS

We would like to thank the following individuals whose contributions have been important to the success of this program: D. N. Schmidt (cell processing and testing), B. F. Westwood (process experiments and photolithography), A. M. Stewart (material characterization and web growth), H. F. Abt (metallization), C. F. Seiler (device measurements), S. Karako (DLTS measurements), T. Zigarovich (mask preparation), D. Lahor (manuscript preparation), and S. Farukhi (manuscript editing).