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

Sixth Quarterly Report, January 1, 1977—March 31, 1977

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

**Dow Corning Corporation
Hemlock, Michigan**

**ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
Division of Solar Energy**

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1 January 77 - 31 March 77

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NEW TECHNOLOGY

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

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1 January 77 - 31 March 77
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1. SUMMARY

Preliminary studies have been conducted to develop a foundation for the work to be carried out in Phase II of the program, which is designed to investigate the effects of processes and impurities on terrestrial silicon solar cells.

Solar cells nearly 10% efficient (without AR coatings) can be made on p-type material with resistivities down to about 0.2 Ω -cm using a process similar to that employed during Phase I of the program. As resistivity falls below about 0.1 Ω -cm cell efficiency also falls and process instabilities become more prevalent. For this reason the resistivity of the baseline material chosen to study the combined effects of boron and metal doping will probably be in the 0.1 to 0.3 Ω -cm range.

Initial studies on n-base material indicate that 0.2 μ m deep junctions with adequate sheet resistivities can be obtained by boron diffusion from BBr_3 at 875°C. Slow cooling from the diffusion temperature appears necessary to maintain good lifetime and I_{sc} values. $p^+/n/n^+$ cells fabricated on a Westinghouse internal program using this type of processing produce coated cells with 16% efficiencies.

Future studies will focus on metal impurity doping of low resistivity p-type and n-type substrates and on gettering and heat treatment effects in standard 4 Ω -cm p-type material.

2. INTRODUCTION

The first part of this program, Phase I, was primarily concerned with determining how specific metal contaminants affected the performance of terrestrial silicon solar cells. Phase II of the program is an extension of that work designed to investigate the effects of processes, as well as impurities, on solar cell performance so that purity requirements for solar grade material can be defined. The methodology for carrying out the experimental effort is substantially that described in previous reports, e.g., Ref. 1; new analytical or experimental techniques will be described as they are introduced to the program.

The overall content of the program falls into several broad categories outlined below. The details and timing of the effort are subject to modification pending the signing of a contract with JPL.

Processing. Our previous experiments indicate that the performance of metal-contaminated silicon solar cells is to some extent dependent on the processing history of the silicon.¹ For this reason, a significant part of the continuing program will be devoted to clarifying the effects of processes and impurities on cell performance. We include in this category the effect of heat treatment, gettering, the effect of crystal growth parameters, and the degree to which impurity effects depend on the efficiency of the baseline solar cell itself.

We plan to examine the response of various impurities to heat treatment times and temperatures relevant to process history in order to identify the effects of processing on the electrical activity of contaminants. Similarly, gettering treatment type, time, and temperatures will be examined as a means for controlling the harmful effects

of impurities present in the silicon. As growth rate can affect the segregation of impurities, as well as impurity distribution in a crystal, a series of experiments will be carried out on Czochralski and silicon web crystals to determine the sensitivity of the material device performance to this variable. Finally, solar cells fabricated by a process designed to yield higher efficiencies than present baseline cells will be tested to assess the effects of impurities in these more efficient devices.

Resistivity. The base resistivity likely to characterize future silicon solar cells is yet unknown. There is some theoretical justification to expect efficiency to peak at lower resistivities than commonly employed.² Also, since boron is difficult to remove during semiconductor processing, economics may dictate that Solar Grade material contain considerable boron and hence display low resistivity.³ For these reasons we will explicitly examine the combined effects of metal impurities and high boron concentrations on solar cell performance. The initial silicon resistivity will be in the range 0.05 to 5 Ω -cm, the final choice of baseline resistivity depending on obtainable device performance and process reliability.

n-Base Cells. Depending on the distribution of energy levels relative to the valence and conduction bands, some metal impurities may act differently as carrier recombination centers in an n-base silicon solar cell than they do in the p-base device. Thus, a portion of this program is planned to investigate what effects metal impurities have on solar cells made from phosphorus-doped material. To facilitate comparison with the work done on the boron-doped substrates, the metal and metal concentrations will be similar to those employed before.¹

Matrix Extension. The data base on impurity effects in p-base material is sufficiently detailed with respect to most of the single metal contaminants in metallurgical grade silicon that further work will be focussed primarily in two areas: (1) measurement and modeling of

boron-doped ingots containing two or more metal contaminants, and (2) study of contaminants which may enter the solar cell process sequence from sources other than the metallurgical grade starting material. Some experiments will also be conducted to fill in gaps in the present single element data base.

The above studies will comprise most of the initial effort in Phase II. As the program evolves, we also expect to examine the effects of oxygen and carbon interaction with the metal contaminants using float-zoned crystals as a vehicle for the comparison studies. Some experiments on the introduction of controlled amounts of metal impurities into polycrystalline p-base silicon may also be conducted.

Since the studies on low resistivity and n-base material represent some significant departures from past methodology, most of the work during the past quarter has centered on the growth of crystals for these studies and the development of experimental techniques for processing and characterizing samples and devices. In particular, the standardization of reliable solar cell fabrication sequences for low resistivity and n-base cells with efficiencies comparable to the cells used in past studies¹ was an important part of these first studies in Phase II. Some additional solar cell data for metal contaminants in 4 Ω -cm p-base silicon have also been collected and are reported below.

3. EXPERIMENTAL RESULTS

3.1 Silicon Preparation and Analysis

3.1.1 Czochralski Ingots

During the first phase of this effort, the effect on solar cell performance of impurities most likely to occur in solar grade silicon was investigated. P-type silicon having an acceptor concentration in the 2.5×10^{15} to 7×10^{15} atoms/cm³ was selected as baseline material, process standards, and as the background doping concentration for all multiple doped ingots. The selection of this acceptor concentration insured excellent cell performance in baseline material while providing a sufficiently high acceptor concentration to minimize variations in resistivity due to trap impurities. Boron was used as the acceptor dopant. Metal contaminants chosen from the impurity matrix in Fig. 1 were added singly or in combination, along with boron in order to assess their effects on cell performance.

Phase II will proceed in the same manner as in the past with Dow Corning preparing specially-doped ingots and characterizing them according to impurity concentration and crystal structure. Solar cell fabrication and evaluation along with additional material analysis will be conducted at Westinghouse. Based on initial material performance, subsequent impurity concentrations are established until an adequate trend is apparent which will permit estimating cell performance under various conditions of impurity type and concentration. The impurity matrix for the first low resistivity and n-base studies will be the same as in Fig. 1. Planned extensions of the impurity matrix include the elements calcium, carbon, and others likely to form materials of construction in silicon processing.

Concentration Range Impurity Element	Less than 10^{13}	$10^{13} - 10^{14}$	$10^{14} - 5 \times 10^{14}$	$5 \times 10^{14} - 5 \times 10^{15}$	$5 \times 10^{15} - 10^{16}$	Greater than 10^{16}
Aluminum				X		X
Chromium		X	X	X		
Copper			X	X	X	
Iron		X	X	X		
Magnesium	X		X			
Manganese		X	X	X		
Nickel			X	X		
Titanium	X	X	X			
Vanadium	X	X	X			
Zinc	X					
Zirconium		X				

Figure 1. Impurity Matrix

As in the past program, the majority of ingots will be prepared using the Czochralski crystal growth method. Modified NCR-2805 and HAMCO-800 crystal pulling furnaces are being used for ingot preparation. The operation of the units is quite similar (both units are resistance heated) and has been described previously.⁴ All graphite furnace parts are changed for each impurity as well as for n-type and p-type material. While this procedure is costly and time-consuming, it has been successful in avoiding contamination by unintentionally added impurities.

In general, impurities with high melting points and low vapor pressure are added prior to melt-down. Regardless of when materials with high vapor pressure are added, substantial material is lost by evaporation. During the present program, the use of oxides of several impurities will be evaluated in an attempt to retain an adequate impurity concentration in the melt. The amount of impurity added to the melt is based on the target concentration for the ingot and equilibrium segregation of the impurity (if known). When no data are available on segregation coefficients, some preliminary ingots are grown from doped melts to collect the necessary information. Effective segregation coefficients currently being used are shown in Table 1. Typical growth parameters are:

Pull rate:	7 cm/h
Seed rotation:	10-15 rpm cw
Crucible rotation:	2-4 rpm ccw
Charge Weight:	0.85 kg - 2.0 kg
Ingot Diameter:	3.2 cm (nominal)
Atmosphere:	1 atm Argon

A total of thirteen ingots were prepared during the first quarter. These thirteen ingots consisted of the following:

p-type (4 ohm-cm) baseline	1 ingot
p-type low resistivity	3 ingots
n-type (1.5 ohm-cm) baseline	1 ingot

Table 1. Segregation Coefficients

<u>Element</u>	<u>Segregation Coefficient</u>
Al	$3 \times 10^{-2} / 2.8 \times 10^{-3} \dagger$
C	0.05
Cu	6.9×10^{-4}
Cr	1.1×10^{-5}
Fe	6.4×10^{-6}
Mg	3.2×10^{-6}
Mn	1.3×10^{-5}
Mo	$\sim 10^{-6}$
Ni	3.2×10^{-5}
Ta	$\sim 10^{-7}$
Ti	3.6×10^{-6}
V	4×10^{-6}
Zr	$< 1.5 \times 10^{-7}$
Zn	$\sim 10^{-5}$

$\dagger$ Value of 2.8×10^{-3} based on resistivity while
value of 3×10^{-2} is based on SSMS.

Table 2. Ingot Resistivity and Etch Pit Density

<u>Ingot Identification</u>	<u>TGT Resistivity (ohm-cm)</u>	<u>Actual Resistivity (ohm-cm)</u>	<u>Etch Pit Density (/cm³)</u>
W-054-00-000	4.0 (B)	4.3 - 3.8	0 - 4.25 K *
W-055-Cu-004	4.0 (B)	4.1 - 3.7	0.5 K - 25 K
W-056-Cu-005	4.0 (B)	4.4 - 3.75	2.5 K - 10 K
W-057-00-000	0.5 (B)	0.46 - 0.47	0.5 K - 1.25 K
W-058-00-000	0.2 (B)	0.22 - 0.18	0 - 0.2 K
W-059-00-000	0.05 (B)	0.05 - 0.053	0 - 2 K
W-060-00-000	1.5 (P)	2.1 - 1.0	0 - 1 K
W-361-Cr/Ti-001	4.0 (B)	5.0 - 4.0	3 K - Clusters
W-362-N/Cu-001	1.5 (P)	2.0 - 0.95	0.4 - 4 K
W-363-N/Cr-001	1.5 (P)	2.2 - 1.7	1 K - 40 K
W-064-N/Mn-001	1.5 (P)	2.2 - 1.35	1 K - 3 K
W-065-N/Ti-001	1.5 (P)	1.9 - 1.7	0 - 2 K
W-066-Ti-005	4.0 (B)	6.0 - 3.9	1 K - 4 K

doubly-doped n-type	4 ingots
doubly and multiply-doped p-type	4 ingots

All thirteen ingots have been sliced and forwarded to Westinghouse for cell fabrication and evaluation.

The resistivity and etch pit density determined for slices taken from the seed and tang ends of each ingot are summarized in Table 2. No problems were encountered in achieving proper donor and acceptor concentrations. A relatively larger variation in resistivity is observed along the length of n-type ingots due to the smaller effective segregation coefficient of phosphorus compared to boron. All n-type material was grown for an average resistivity of 1.5 ohm-cm. As before, the resistivity of p-type material which is relatively heavily doped with a transition element is somewhat higher than baseline material, e.g., W-061 and W-066.

Although no attempt has been made to produce dislocation free crystals, several of the ingots were free of dislocations as revealed by lack of etch pits. The values shown in Table 2 are for the seed end and tang end of the ingot. The solar cell material is in general taken from areas toward the seed end of the ingots so the first value of etch pit density is more indicative of the actual material from which solar cells are fabricated.

Target impurity concentrations, calculated concentrations based on melt analysis and measured impurity concentrations (SSMS data), are compiled in Table 3 for all ingots produced this quarter. Calculated concentrations based on melt analysis continue to be in excellent agreement with targeted values. Reasonable agreement also exists between measured impurity concentration and calculated impurity concentration for all but ingot W-064 for which we have measured an extremely high manganese concentration. Additional SSMS measurements are planned on samples from all doubly and multiply-doped ingots as time permits and upon reaching a contractual agreement, samples from these ingots will be

Table 3. Ingot Impurity Concentration

<u>Ingot Identification</u>	<u>Target Concentration</u> <u>10^{15} atoms/cm³</u>	<u>Calc. Concentration</u> <u>10^{15} atoms/cm³</u>	<u>Measured Concentration</u> <u>10^{15} atoms/cm³</u>
W-054-00-000	N/A	N/A	N/A
W-055-Cu-004	0.05	0.034	<1
W-056-Cu-005	25	39	70
W-057-00-000	N/A	N/A	N/A
W-058-00-000	N/A	N/A	N/A
W-059-00-000	N/A	N/A	N/A
W-060-00-000	N/A	N/A	N/A
W-061-Cr/Ti-001	1.0/0.02	0.91/0.017	1.0/<1
W-062-N/Cu-001	1.0	0.86	2.0
W-063-N/Cr-001	0.8	0.85	1.0
W-064-N/Mn-001	1.0	0.64	8.0
W-065-N/Ti-001	0.35	0.28	Incomp.
W-066-Ti-005	0.06	0.048	Incomp.

Table 4. Web Melt Analysis

<u>Sample I.D.</u>	<u>Impurity/Concentration (% Atomic)</u>
DW-32	Cu/ 6.16×10^{-3} Ti/ 8.85×10^{-3}
DW-35	Cu/ 2.64×10^{-3}
DW-36	Cu/ 2.64×10^{-3}
DW-37	Cr/ 3.24×10^{-3}
DW-38	Cu/ 4.84×10^{-2}
DW-39	Ni/ 1.4×10^{-3}
DW-40	Ni/ 5.28×10^{-3}
DW-42	Cr/ 1.03×10^{-2}
DW-43	Mn/ 7.14×10^{-3}
DW-44	Ti/ 7.09×10^{-3}

submitted for neutron activation analysis. This will permit establishing more reliable impurity concentration for these ingots.

Some additional comments regarding the impurity analysis are pertinent here. The performance of the spark source mass spectrometer (SSMS) is monitored periodically to determine what background conditions exist due to machine history and/or sample preparation. During this quarter, there has been a background present at copper and titanium mass/charge ratio at a concentration of 5×10^{14} to 1×10^{15} atoms/cm³. For this reason, certain samples intentionally doped with the above impurities were not evaluated. These samples will be evaluated in the future when this background level is reduced.

3.1.2 Dendritic Web Crystals

Dendrites, central web sections, and melt samples were analyzed for impurity concentration this quarter. No problems were encountered in the melt analysis effort and these results, Table 4, remain consistent with the values calculated from weighed impurity additions. Considerable difficulty has been encountered in both the analysis of dendrites and central web sections. Spark source analysis of the central web sections is hampered by the sample geometry. Due to the thin nature of these samples, breakage often occurs during equipment loading or during spark generation. Samples which are not broken are consumed very rapidly so there is insufficient material to develop the required long exposures required for trace impurity determination. Although adequate material exists in the dendrites, analysis to date indicates some non-uniformity in the impurity distribution. This might be expected from the type of segregation known to occur during dendritic growth.⁴

The results of dendrite analyses, Table 5, are quite similar to those reported previously.¹ Concentration of impurities appears to be in the 10^{15} - 10^{16} atoms/cm³ range with the exception of DW-034 and DW-040. DW-034 contained no intentionally added metal and the failure to detect nickel in DW-040 is not surprising since the detection limit

Table 5. Analysis of Web Dendrites

<u>Sample Identification</u>	<u>Impurity Concentration 10¹⁵ atoms/cm³</u>
DW-034-2D (D)	None
DW-034-2E (D)	None
DW-035-1C (D)	1.2 (Cu)
DW-037-1D (D)	0.3 - 3.0 (Cr)
DW-037-1C (D)	0.3 - 3.0 (Cr)
DW-040-1D (D)	None (Ni <3)
DW-040-1F (D)	None (Ni <3)
DW-042-1E (D)	0.6 (Cr)
DW-043-1E (D)	8 (Mn)

for nickel is relatively high. Previous analyses¹ indicate that the web itself usually contains lower impurity levels than the dendrites so the data in Table 5 may roughly be taken as upper limits on the impurity content of the webs.

3.2 Silicon Evaluation

3.2.1 Low Resistivity Studies

Our initial experiments were designed to identify potential problems in processing low resistivity p-type silicon, to assess the effects of base resistivity on cell performance and then to develop a reliable, but unoptimized, process to produce cells with efficiencies comparable to our standard 4 Ω -cm baseline material ($\sim 10\%$ at AM1 illumination without AR coatings). From this point controlled amounts of metal impurities will be added to the baseline material, and the effects of base resistivity and metal impurity content on cell performance will be evaluated relative to the higher resistivity baseline material.

P-type silicon wafers with resistivities spanning the range 0.05 to 50 Ω -cm were diffused at 825°C for 50 minutes, following our standard procedure,¹ and fabricated into solar cells. Two difficulties involving diffusion and metallization developed during these experiments. First, we observed that the apparent sheet resistance of the diffused layer increased with substrate resistance, Fig. 2, suggesting that the junction might be deeper in the lower resistivity material. This is contrary to existing diffusion theory and with later impurity profile measurements which indicate that surface concentration and junction depth are in all likelihood independent of substrate resistivity in the range of interest. A probable explanation for the data in Fig. 2 is that the measuring probes punched partially through the thin ($\sim 0.3 \mu\text{m}$) diffused layer, so that the apparent sheet resistivity measured is the sum of two parallel resistances due to the layer and substrate.

We also found that solar cells made from heavily-doped substrates were more sensitive to metallization sintering conditions

Fig. 2. Variation of the sheet resistance of the n^+ diffused layer with boron doped substrate resistivity using POCl_3 at 825°C for 50 minutes; nominal junction depth is about $0.3\text{ }\mu\text{m}$.

Table 6

EFFECT OF DIFFERENT METALLIZATION ON SOLAR CELL PARAMETERS^{*}

Resistivity of P-Base Si ohm-cm	Metal System	Sintering Conditions	I _{SC} mA	V _{OC} Volts	FF	Efficiency η (No AR Coating)
3.5	Ti Pd Ag	Before Sintering	23.05	0.555	0.730	9.88
		550°C/H ₂ /15 min.	22.93	0.561	0.759	10.32
3.5	Ti Pd Ag	Before Sintering	22.83	0.558	0.751	10.11
		300°C/H ₂ /10 min.	22.77	0.546	0.731	9.62
0.2	Ti Pd Ag	Before Sintering	21.18	0.587	0.736	9.67
		550°C/H ₂ /15 min.	21.72	0.574	0.547	7.22
0.2	Ti Pd Ag	Before Sintering	20.98	0.577	0.706	9.06
		300°C/H ₂ /10 min.	21.81	0.574	0.697	9.26
0.05	Ti Pd Ag	Before Sintering	17.45	0.552	0.686	7.02
		550°C/H ₂ /15 min.	17.18	0.247	0.449	2.02
0.2	Al Si	Before Sintering	21.50	0.585	0.685	9.12
		500°C/H ₂ /10 min.	22.40	0.579	0.517	7.12
3.5	Cr Pd Ag	Before Sintering	23.25	0.556	0.749	10.24
		300°C/H ₂ /10 min.	22.83	0.547	0.723	9.55
0.2	Cr Pd Ag	Before Sintering	21.57	0.582	0.722	9.62
		300°C/H ₂ /10 min.	22.26	0.589	0.734	10.19
0.05	Ti Pd Ag	Before Sintering	17.87	0.553	0.744	7.75
		300°C/H ₂ /10 min.	18.27	0.559	0.654	7.06
0.45	Ti Pd Ag	Before Sintering	22.13	0.585	0.708	9.70
		300°C/H ₂ /10 min.	22.63	0.586	0.719	10.09
0.2	Ti Pd Ag	Before Sintering	20.87	0.579	0.708	9.06
		300°C/H ₂ /10 min.	22.33	0.579	0.701	9.62
10.00 FZ	Ti Pd Ag	Before Sintering	22.97	0.524	0.743	9.46
		300°C/H ₂ /10 min.	23.20	0.513	0.704	8.87
50.00 CZ	Ti Pd Ag	Before Sintering	22.85	0.469	0.712	8.07
		300°C/H ₂ /10 min.	23.10	0.412	0.654	6.57

* The data points represent an average of 4 wafers per resistivity.

Resistivity of P-Base Si ohm-cm	Metal System	Sintering Conditions	I _{SC} mA	V _{OC} Volts	FF	Efficiency η (No AR Coating)
3.5	Ti Pd Ag	Before Sintering 300°C/H ₂ /10 min.	22.43	0.553	0.746	9.79
			22.70	0.542	0.745	9.70
	Cr Pd Ag	Before Sintering 300°C/H ₂ /10 min.	22.33	0.553	0.755	9.86
			22.63	0.542	0.734	9.52
	Al Si	Before Sintering 300°C/H ₂ /10 min.	23.45	0.552	0.723	9.89
			23.38	0.544	0.722	9.72
0.2	Ti Pd Ag	Before Sintering 300°C/H ₂ /10 min.	20.90	0.587	0.774	10.04
			21.62	0.590	0.775	10.46
	Cr Pd Ag	Before Sintering 300°C/H ₂ /10 min.	20.72	0.567	0.662	8.26
			21.56	0.579	0.691	9.13
	Al Si	Before Sintering 300°C/H ₂ /10 min.	20.98	0.592	0.747	9.80
			22.43	0.593	0.727	10.21

than their more lightly-doped counterparts. Data from several sintering experiments, Table 6, and some unreported studies, indicate that at sintering temperatures of 550°C or higher TiPdAg metallization causes slight degradation in the cell performance provided the substrate doping level is not too high. In comparison, CrPdAg system essentially shorts out the junction, indicating a much higher diffusivity and/or chemical interaction of Cr with silicon. Our high temperature sintering data on Al-Si system are more limited and this system deserves further experimentation. Based on our experience on the integrated circuit industry, Al-Si metallization, sintered at $\leq 400^\circ\text{C}$, should provide acceptable results for shallow junction devices.

For cells from heavily doped substrates all three metallization systems at high sintering temperature (550°C) cause severe degradation in the fill factor, viz., Table 6. A possible explanation for this behavior can be deduced from the variation of the junction depletion width and electric field as a function of the base acceptor concentration, as shown in Fig. 3. As the doping level increases, the effective width of the junction region narrows and there is an increased probability of junction penetration and shorting by defects or precipitates. Even if such defects only partially penetrate into the high field depletion region, significant field emission currents will result. The effect on solar cell performance of junction shorting or field emission current is a degradation of the fill-factor and open circuit voltage, precisely what we have observed. One source of defects in the low resistivity material could be the formation of boron phosphide and an associated dislocation network in the phosphorus diffused n^+ region. This mechanism becomes increasingly likely as the substrate boron concentration is made larger. The dislocations provide enhanced diffusion paths for the contact metal as well as sites where the metal can precipitate. This sequence of events is consistent with the cell performance data which in turn indicates the need for lower sintering temperature on cells from heavily doped substrates. Under a Westinghouse-funded program

Fig. 3. Solar cell junction depletion width and electric field vs. base acceptor concentration.

some transmission electron microscopy work is being carried out to identify the defects in the n^+ region. At a sintering temperature of 300°C the differences among the three metallization systems are small, Table 6. Thus, we have tentatively elected to continue use of the TiPdAg system. It is, however, necessary to develop data on long term reliability, adherence, and stability.

Conventional n^+p cells were fabricated using different resistivity Czochralski and float zoned silicon to establish an upper limit in the boron doping of the p-base material at which reasonable cell performance can be obtained. Figures 4 through 6 show the open circuit voltage, short circuit current and the cell efficiency data as a function of resistivity. V_{oc} exhibits a broad maximum value of about 0.57V at doping concentrations in the range of 10^{16} to 10^{17} cm^{-3} (i.e., 0.2 to 1.0 ohm-cm). The short circuit current decreases gradually with increasing doping, and falls off rapidly at doping level above 10^{17} cm^{-3} due to decrease in the minority carrier lifetime and mobility.

These data cannot be explained by classical photodiode theory which predicts a monotonic increase in open circuit voltage and cell efficiency as the substrate resistivity is decreased.⁵ However, by including the effects of high junction fields and high carrier concentration effects in the base, an acceptable model can be obtained. As shown in Fig. 7, carrier-carrier (Auger) recombination reduces the base lifetime for acceptor concentrations above 10^{17} cm^{-3} and at the same level mobility begins to drop, Fig. 8, as carrier-carrier scattering begins to dominate. These two mechanisms largely account for the loss in carrier collection efficiency and short circuit current, Fig. 5. The observed reduction of open-circuit voltage with concentration is partially explained by the reduced collection efficiency but dominantly voltage loss is associated with a decrease of the silicon band gap at high impurity concentrations. At very high concentrations impurity banding results in a band gap reduction^{6,7,9} but at solar cell concentrations, the predicted effect is insufficient by itself to account for the observed voltage loss.

Fig. 4. Dependence of open circuit voltage, V_{OC} , on substrate resistivity of n^+p solar cells.

Curve 689844-A

Fig. 5. Dependence of short circuit current, I_{sc} , on substrate resistivity of n^+p solar cells.

Fig. 6. Variation of the cell efficiency, η , with substrate doping of n^+p cells.

Fig. 7. The dependence of the lifetime in boron-doped Si.

Curve 689847-A

Fig. 8. Electron mobility, μ_e , in silicon at 300K as a function of impurity concentration.

A second mechanism is proposed by Rittner based on a thermal analog of the Franz-Keldysh effect, which describes a lowering of the optical bandgap in the presence of large electric fields.⁸ The change in bandgap is given by

$$\Delta E_g = [(h/2\pi m^*)(qE)^2]^{1/3} \quad (1)$$

where h = Planck's constant
 m^* = combined effective mass for electrons and holes
 E = the electric field.

The thermal bandgap for silicon should exhibit similar behavior and experimentally bandgap reductions from 0.05 eV to 0.15 eV were observed for electric fields from 10^4 to 5×10^4 V/cm,¹⁰ in close agreement with the predicted values. The peak electric field in a solar cell junction, viz., Fig. 3, is large enough that a significant portion of the depletion volume experiences gap reduction.

The relationship between gap reduction and solar cell behavior can be developed from the classic double exponential model of Sah, Noyce and Shockly,¹¹ which expresses the cell current density as:

$$J = J_{sc} - J_r(e^{qV/2kT} - 1) - J_d(e^{qV/kT} - 1), \quad (2)$$

where J_{sc} is the light generated short circuit current density, V the cell voltage, J_d the saturation current density associated with the base, and J_r is the saturation current generated within the depletion region. In the classical derivation J_d is given by:

$$J_d = qD_n n_i^2 / (N_A W_B),$$

and J_r is:

$$J_r = (qn_i kT(\pi/2)) / ((\tau_p \tau_n)^{1/2} E) \quad (3)$$

If the bandgap change is incorporated, J_r becomes

$$J_r' = J_r e^{\Delta E_g / 2kT} \quad (4)$$

Substituting J_r' in Eq. (2) permits calculating the voltage-current characteristic. The effect of increasing ΔE_g is to increase J_r which in turn reduces cell voltage and fill factor. This analysis overestimates the volume governed by Eq. (1) and therefore predicts cell voltages which are too small. However, despite these approximations, the agreement with experimental data is quite good. With further refinement, this model should be capable of explaining most of the resistivity dependent cell behavior.

At this point it appears that cells with comparable efficiency to those made on 4 Ω -cm baseline can be fabricated from material with resistivity near 0.2 Ω -cm using TiPdAg contacts and a reduced sintering temperature. Assuming these results hold under further testing, and we expect they will, the nominal 0.2 Ω -cm material will form the baseline resistivity for subsequent metal doping experiments.

3.2.2 n-Base Studies

As in the low resistivity work, our preliminary efforts were directed toward developing reliable process techniques, including the choice of an appropriate boron diffusion source, diffusion temperature and time. The first experiments employed both BN and BBr_3 sources and were carried out with p-type silicon to facilitate diffusion profile measurements. Since the lifetime of the p-type material had been previously well characterized,¹ effects of diffusion on silicon lifetime could also be evaluated in these tests.

BBr_3 diffusions at 960°C initially degraded the lifetime of the p-base material, typical values after a standard cycle being about 0.15 μ sec. The lifetime could be restored to nearly the original value by a post-phosphorus diffusion at 825°C. Possible contamination from the BBr_3 source was eliminated as a cause for the low lifetime by measuring the lifetime of wafers subjected to identical thermal cycles, but with the BBr_3 source bypassed. The lifetimes of wafers diffused from BBr_3 and BN sources also showed only small differences. Boron-diffused wafers were finally processed through the standard 825°C thermal cycle

without the POCl_3 source being turned on to determine if annealing or gettering was effective in restoring lifetime. The lifetime was restored to 4.1 μsec during these tests and we concluded that the normal cooling rate after the BBr_3 diffusion had been excessive. Further experiments verified that the lifetime could be preserved during the BBr_3 diffusion cycle if very slow withdrawal of the wafers from the furnace was performed. The results of this series of experiments are listed in Table 7.

When a profile of the standard 960°C BBr_3 cycle was obtained by the anodic oxidation and incremental sheet resistance method, Fig. 9, it was evident that the junction depth was excessive. The furnace temperature was reduced to 875°C and a time cycle of 2-20-2 minutes yielded an average sheet resistance of 34 ohms per square. A profile of a junction formed with the revised diffusion cycle, Fig. 10, illustrates that an appropriate depth for cell fabrication had been achieved. The characteristic parameters for the two diffusion cycles are listed below.

Characteristic Boron Diffusion Profile Parameters

Temp (°C)	Time Cycle (Preheat-Deposition-Soak)	R_s $\Omega/\square$	C_o cm^{-3}	X_j μm	D^* cm^2/sec
960	2-12-2	18.71	2.1×10^{20}	0.41	5.40×10^{-14}
875	2-20-2	34.4	1.7×10^{20}	0.18	7.71×10^{-15}

* calculated from $X_j = 2\sqrt{D_t} \text{erfc}^{-1} (N_t/N_o)$.

A lot of p^+/n solar cells were fabricated using the 875°C diffusion cycle and the n-type wafers from baseline ingot W060-00-000. The data for this run are compiled in Table 8 along with the results for some $p^+/n/n^+$ cells fabricated on an internal Westinghouse program.

The good I_{sc} values obtained for the cells on W060-00-000 indicate that adequate lifetime can be maintained by slow cooling the wafers after the BBr_3 diffusion. The low efficiency of these first

Table 7. Boron Diffusion Recombination Lifetime Measurements

Silicon Material	Diffusion Temp/Time	Atmosphere & Sources	Cooling Rate	τ_r (μ sec)
EBr ₃	SOURCE			
*P, 1-3 Ω -cm, 1:1:1	960/2-12-2	Std [†]	Std	0.15
*P, 1-3 Ω -cm, 1:1:1	960/24-15-100	Std [†] (no BBr ₃)	5 min Slow Manual	0.86
*P, 1-3 Ω -cm, 1:1:1	960/2-12-2	Std [†]	Slow Pull (5 min)	3.9
*P, 1-3 Ω -cm, 1:1:1	960/2-12-2	Std [†]	Slow Pull (5 min) Annealed @ 820°C	4.1
*Gettered 825°C/50 min	960/2-12-2	Std [†]	Very Slow (5 min)	3.2
*Gettered 825°C/50 min	920/2-12-2	Std [†]	Very Slow (5 min)	3.9
*Gettered 825°C/min	875/2-20-2	Std [†] ($R_s = 47.3$)	Very Slow Pull	2.8
EN	SOURCE			
*P, 1-3 Ω -cm, 1:1:1	920/50 min	N ₂	Std	0.89
*P, 1-3 Ω -cm, 1:1:1	920/50 min	N ₂ No Source	Std	0.463
*P, 1-3 Ω -cm, 1:1:1	920/50 min	N ₂ No Source	Program Cooled Furnace	0.92

* τ_r of non-diffused material = 4.38 to 8.33 μ sec.

† Standard Atmospheres: Preheat, Argon + Oxygen - Deposition,
Argon + Oxygen + BBr₃ Vapor - Flush, Oxygen only.

Fig. 9. Boron diffusion profile obtained by incremental resistivity measurements.

Fig. 10. Boron diffusion profile selected for fabrication of p⁺/n and p⁺/n/n⁺ solar cells during Phase II.

Table 8
 p^+/n and $p^+/n/n^+$ Solar Cell Performance

Type of Cell (Lot Identification)	I_{sc} (mA)	V_{oc} (volts)	F.F.	η (%)
<u>p^+/n</u>				
W060-00-000	23.38	0.513	0.563	7.14
<u>$p^+/n/n^+$</u>				
SOLEP 118*	23.73	0.584	0.776	11.36
SOLEP 119*	24.78	0.579	0.771	11.71

* SOLEP - Westinghouse supported solar cell study. The data represent averages of several cells.

cells follows from their poor fill factors, an effect attributed to metallization problems. The $p^+/n/n^+$ cells have uncoated efficiencies over 11%. One cell from SOLEP 119 was coated with 850 Å of SiO which raised its efficiency by 38% to 16%. Two additional lots from W060-00-000 are being fabricated into p^+/n and $p^+/n/n^+$ cells so that a standard process for the n-base experiments can be chosen. The fabrication of impurity doped n-base solar cells will be started once the testing of these two lots confirms the fact that a repeatable process exists for the fabrication of efficient n-base solar cells.

3.2.3 Extension of p-Base Data

Some additional cell runs have been made on doubly-doped 4 Ω -cm p-base silicon to fill in gaps in the data base and to extend our experiments on multiply-doped ingots. These data appear in Tables 9 to 11 below.

Table 9. Solar Cell Data for Cu-Doped Ingot W055-Cu004

61213 W055CU004 (1E14) W020 00 000

SOL3 4 /25/77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IF	LOC(10)	N	R	FF	EFF	OCD	PCDA	PCDE
1R*	22.50	.553	20.24	-6.410	1.94	-.36	.723	9.51	.00	.00	.00
1B	22.90	.555	20.92	-7.065	1.71	-.55	.754	10.13	4.29	7.30	7.00
3B	22.90	.557	21.17	-7.903	1.49	-.34	.771	10.40	5.20	7.30	7.00
5B	22.70	.556	20.57	-6.519	1.90	-.97	.748	9.98	3.90	7.30	7.00
1C	22.70	.552	20.62	-6.634	1.85	-.93	.751	9.95	3.90	.00	.00
2C	23.20	.553	20.96	-6.352	1.96	-1.00	.743	10.08	4.55	.00	.00
3C	23.20	.553	21.14	-6.828	1.78	-.81	.755	10.24	5.20	.00	.00
4C	23.20	.553	20.96	-6.352	1.96	-1.00	.743	10.08	2.86	.00	.00
5C	22.70	.551	20.80	-7.180	1.66	-.72	.763	10.09	4.16	.00	.00
2S	22.80	.552	20.97	-7.479	1.58	-.54	.766	10.19	4.42	.00	.00
3S	23.20	.554	21.35	-7.549	1.56	-.42	.764	10.39	4.94	.00	.00
1T	23.00	.555	21.12	-7.361	1.62	-.57	.763	10.31	4.81	.00	.00
2T	22.90	.553	20.94	-7.070	1.70	-.67	.758	10.15	4.55	.00	.00
3T	23.20	.554	21.30	-7.331	1.62	-.60	.764	10.38	5.20	.00	.00
4T	23.40	.551	21.17	-6.457	1.91	-.85	.743	10.13	3.90	.00	.00

AVERAGES: 61213 BASELINE W020 00 000

22.83 .556 20.89 -7.162 1.70 -.62 .757 10.17 4.46 7.30 7.00

STD .09 .001 .24 .569 .17 .26 .010 .17 .54 * *

61213 W055CU004 (1E14)

23.05 .553 21.03 -6.963 1.75 -.74 .756 10.18 4.41 .00 .00

STD .23 .001 .20 .436 .14 .19 .009 .13 .65 * *

PERCENT OF BASELINE

100.0 29.4 100.7 102.8 103 81.6 99.8 100.1 98.8 .0 .0

STD% 1.4 .4 2.2 14.3 20 92.6 2.5 3.0 28.5 .0 .0

Table 10. Solar Cell Data for Cu-Dop-d Ingot W056-Cu005

70201A W056CU005 AFTER SINTER (50E15) W020 00 000

SOL3 4 /25/77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(10)	N	B	FF	FFF	OCB	PCDA	PCDB
1R*	22.50	.558	20.32	-6.657	1.86	-.14	.725	9.63	.00	.00	.00
2B	22.40	.558	20.24	-6.350	1.98	-1.14	.746	9.86	4.29	7.30	7.00
3B.*	22.50	.556	20.06	-5.707	2.29	-1.62	.732	9.68	3.25	7.30	7.00
1C	22.20	.549	20.24	-6.897	1.75	-.75	.754	9.71	3.51	4.85	6.66
2C	22.50	.553	20.52	-6.990	1.73	-.56	.751	9.88	3.51	4.85	6.66
3C.*	22.70	.544	18.10	-3.290	5.49	-6.75	.643	8.39	1.95	4.85	6.66
4C	22.60	.550	20.50	-6.685	1.82	-.64	.743	9.77	3.51	4.85	6.66
5C	22.60	.551	20.75	-7.433	1.59	-.40	.760	10.00	3.90	4.85	6.66
1S	22.40	.547	19.86	-5.551	2.34	-1.56	.722	9.36	2.99	4.85	6.66
2S	22.50	.548	20.47	-6.804	1.78	-.71	.750	9.78	3.51	4.85	6.66
3S	22.30	.547	20.29	-6.801	1.77	-.77	.751	9.69	3.90	4.85	6.66
1T	22.30	.549	20.44	-7.257	1.64	-.57	.760	9.83	3.90	4.85	6.66
2T.*	22.40	.537	17.51	-3.134	5.99	-7.36	.624	7.94	1.69	4.85	6.66
3T	22.20	.544	19.81	-5.759	2.21	-1.52	.731	9.34	3.25	4.85	6.66
4T	22.60	.547	19.08	-4.365	3.36	-2.34	.663	8.66	2.60	4.85	6.66
AVERAGES: 70201A BASELINE W020 00 000											
	22.40	.558	20.24	-6.350	1.98	-1.14	.746	9.86	4.29	7.30	7.00
STD	.00	.000	.00	.000	.00	.00	.000	.00	.00	*	*
70201A W056CU005 AFTER SINTER (5E15)											
	22.42	.549	20.20	-6.454	2.00	-.98	.738	9.60	3.46	4.85	6.66
STD	.15	.002	.46	.897	.51	.59	.028	.37	.40	*	*
PERCENT OF BASELINE											
	100.1	98.3	99.8	98.4	101	113.8	99.0	97.4	80.6	66.4	95.1
STD%	.7	.4	2.3	14.1	26	51.6	3.7	3.8	9.3	.0	.1

Table 11. Solar Cell Data for Cr/Ti-Doped Ingot W061-Cr/Ti001

70211 W061 CR-TI 001 (1E15-2E13) BEFORE SINTER W020 00 000
 SOL3 4 /25/77 AM1: P0=91.60MW/CM² NO AR COATING

ID	ISC	VOC	IP	LOG(I0)	N	R	FF	EFF	OCD	PCDA	PCDE
1R*	22.50	.557	20.40	-6.889	1.78	-.05	.730	9.68	.00	.00	.00
1B	22.80	.557	20.82	-7.268	1.65	-.01	.741	9.95	4.55	7.30	7.00
2B	23.10	.558	21.06	-7.192	1.68	.02	.738	10.06	4.42	7.30	7.00
3B	23.10	.552	20.82	-6.595	1.86	-.04	.720	9.71	3.90	7.30	7.00
4B	23.20	.554	20.77	-6.125	2.06	-.58	.719	9.78	4.16	7.30	7.00
5B.*	23.70	.551	20.43	-4.866	2.84	-1.40	.678	9.36	3.25	7.30	7.00
1C	17.10	.498	15.33	-6.579	1.73	.23	.707	6.36	.13	.00	.00
2C	17.10	.495	15.22	-6.315	1.82	.27	.695	6.22	.13	.00	.00
3C	17.30	.495	15.34	-6.119	1.90	.08	.692	6.27	.13	.00	.00
4C	17.30	.495	15.42	-6.380	1.79	.34	.696	6.30	.13	.00	.00
5C	17.30	.497	15.43	-6.474	1.76	.59	.693	6.30	.13	.00	.00
1S	16.10	.497	13.55	-4.607	2.95	-1.94	.647	5.47	.13	.00	.00
2S	18.20	.501	15.78	-5.148	2.46	-1.39	.682	6.58	.13	.00	.00
3S	17.60	.500	15.14	-4.903	2.65	-2.00	.679	6.32	.13	.00	.00
1T	15.70	.491	13.87	-6.161	1.88	.56	.680	5.54	.13	.00	.00
2T	17.30	.496	15.42	-6.210	1.86	-.27	.706	6.40	.13	.00	.00
3T	17.30	.496	15.39	-6.263	1.84	.13	.697	6.32	.13	.00	.00
4T	17.10	.493	15.26	-6.295	1.82	-.17	.706	6.30	.13	.00	.00

AVERAGES: 70211 BASELINE W020 00 000

23.05 .555 20.87 -6.795 1.81 -.15 .730 9.88 4.26 7.30 7.00

STD .15 .002 .11 .466 .16 .25 .010 .14 .25 * *

70211 W061 CR-TI 001 (1E15-2E13) BEFORE SINTER

17.12 .496 15.10 -5.955 2.04 -.30 .690 6.20 .13 .00 .00

STD .62 .003 .64 .638 .39 .90 .016 .32 .00 * *

PERCENT OF BASELINE

74.3 89.4 72.3 112.4 112 6.8 94.5 62.8 3.1 .0 .0

STD% 3.2 .9 3.5 16.1 34 ***** 3.5 4.2 .2 .0 .0

3.2.4 Lifetime Studies

3.2.4.1 n-Base Material

Several attempts were made to measure the surface recombination velocity for n-type silicon, so that recombination lifetime measurements could be initiated on recently grown n-type ingots. The techniques used were similar to those used to measure the lifetime of p-type silicon.¹ The primary method involves finding a value of S which yields a calculated value of τ_r that is independent of sample thickness. The second technique requires a knowledge of τ_r , then calculating S from the measured value of τ_r' according to the equation,

$$S = \sqrt{D \left(\frac{1}{\tau_r'} - \frac{1}{\tau_r} \right)} \tan \sqrt{\frac{d^2}{D} \left(\frac{1}{\tau_r'} - \frac{1}{\tau_r} \right)} \quad (5)$$

when $D(\tau_o^2/d^2) \gg 1/\tau_r$, Eq. (5) may be simplified to

$$S = \sqrt{\frac{D}{\tau_r'}} \tan \sqrt{\frac{d^2}{D\tau_r'}} \quad (6)$$

Figure 11 depicts how normalized lifetime, τ_r/τ_r ($d = 0.133$ mm), varies for a single sample of 72 ohm-cm n-type silicon as the thickness is reduced by etching. The plot shows that the calculated value of τ_r can only be made independent of thickness for specimens less than 0.28 mm (11 mils) thick. The reason for the thickness dependence of τ_r above 0.28 mm is believed to result from insufficient penetration of the LED source light into the sample. A scatter in the data of about $\pm 5\%$ is representative of the accuracy of PCD measurements. The value of S required for zero slope below 10.5 mils was determined by linear regression and found to be about 690 cm/sec. The resulting value for the recombination lifetime was found to be 20 μ sec. The requirement that $D(\tau_o^2/d^2) \gg 1/\tau_r$ is not met for samples as thin as 3 mils, so no attempts were made to determine S by the simpler technique of Eq. (6).

Fig. 11. Determination of surface recombination velocity for n-type silicon (LED source).

Fig. 12. Determination of surface recombination velocity for PCD measurements with 1.06 μ m laser (Nd:YAG) pulsed light source.

The experiment for which the calculations are shown in Fig. 11 was repeated twice to evaluate the reproducibility of the measurements. Considerable scatter and variation in the value of S ensued and it has been concluded that a more penetrating type light source is required so that the thickness range can be increased significantly. For this reason, and also to extend the range of measurement to lower lifetimes, a new PCD instrument is being readied for use. The new equipment employs an Nd-doped YAG laser which produces monochromatic radiation at $1.06\text{ }\mu\text{m}$. The absorption coefficient α of silicon at $1.06\text{ }\mu\text{m}$ is approximately equal to 25 cm^{-1} and the depth of penetration ($1/\alpha$ concentration) is $400\text{ }\mu\text{m}$. The intensity of the radiation will be sufficient to effectively modulate silicon with a resistivity of $1 \times 10^{-3}\text{ ohm-cm}$. The results of the first tests of the equipment, for measurement of S for p-type silicon, are shown in Fig. 12. Although the data show considerable scatter, the anomaly for thicker samples has disappeared as expected. The scatter is largely due to difficulties in reading the half amplitude time on the oscilloscope because of random variations in the radiation energy per pulse, and poor control of the injection level. Present efforts are being devoted to solving these equipment problems. The surface recombination velocity assumed for the calculations shown in Fig. 12 was $4 \times 10^4\text{ cm/sec}$. This value is larger than that necessary (8.99×10^3) for the LED source. The reason for the difference is that the depth of penetration for the LED light is only about $50\text{ }\mu\text{m}$, and the resulting gradient in minority carriers produces a diffusion current in opposition to the effects of surface recombinations. This reduces the effective surface recombination velocity for the LED radiation. We will delay the measurement of τ_r for n-type silicon, and low resistivity p-type silicon until the new PCD instrument is operating as expected.

3.2.4.2 p-Base Material

Czochralski Wafers. Table 12 contains bulk PCD lifetime measurements (LED source) for recently grown ingots; data for ingots W001-W052 appear in the last quarterly report.¹

Table 12. Bulk Lifetimes (PCD) of Silicon Ingots
Before and After Phosphorus Diffusion

Ingot Identification	Best Estimate of Impurity Conc. (10^{15} atoms/cm)	Lifetime (As-Grown)		Lifetime (Diffused)	
		τ (μ sec)	σ (Note 1)	τ (μ sec)	σ (Note 1)
W053-00-00	--	6.6	0.1 (2)	--	--
W054-0000	--	6.3	0.4 (2)	--	--
W055-Cu004	0.05	6.2	0.1 (2)	7.8	0.6 (2)
W056-Cu005	25	6.7	0.3 (2)	5.6	1.7 (4)
W057-0000	--	Note 2	--	4.6	0.7 (2)
W058-0000	--	Note 2	--	Note 2	--
W059-0000	--	Note 2	--	Note 2	--
W060-000 (n type)	--	Note 3	--	Note 3	--
W061-Cr/Ti001	1/.02	--	--	--	--

Note 1. Sample size shown in parentheses.

Note 2. Lifetime measurements not practical due to low resistivity.

Note 3. Surface recombination velocity has not been measured for n-type.

Web Crystals. Table 13 contains recent PCD measurements on
web samples before and after diffusion.

Table 13. Recombination Lifetime and Solar Cell Short
Circuit Current for Silicon Dendritic Web Specimens

Web Run Number	Impurity Type	τ_r (As-Grown) (μ sec)	τ_r (Diffused) (μ sec)	I_{SC}^* (mA/cm ²)
DW039-2	Ni	0.34	2.4 (2)	20.9 (2)
DW040-1	Ni	0.49	3.2 (2)	20.25 (4)
DW042-1	Cr	0.31	2.0 (3)	20.65 (2)
DW043-1	Mn	0.65	2.8 (2)	--
DW044-1	Ti	0.47	1.2 (5)	17.40 (2)

Sample size shown in parentheses.

* Solar Cell 0.5 x 2.0 cm.

4. CONCLUSIONS

Preliminary studies on cell processing for low resistivity p-type silicon and for n-type silicon are nearly completed. For ingots with resistivities down to about 0.2 Ω -cm, reasonably efficient cells can be fabricated with essentially the same process used for the standard 4 Ω -cm baseline material: 825°C phosphorus diffusion for fifty minutes and TiPdAg contacts. The contact sintering temperature will probably have to be lowered to 300°C to give reliable results. Below about 0.2 Ω -cm, I_{sc} and V_{oc} fall and typical (uncoated) cell efficiencies for 0.05 Ω -cm material are about 7%. Process instability also seems to increase with diminishing resistivity, an observation which can be explained by the narrowing of the depletion width in the low resistivity material coupled with the enhanced penetration of the junction by defects.

Slow cooling of wafers after boron diffusion appears necessary to maintain good lifetime and I_{sc} values in n-base material. 16% efficiencies in $p^+/n/n^+$ baseline cells have been achieved (with anti-reflective coating) using BBr_3 diffusion at 875°C.

Lifetime measurements in thick samples and in low resistivity samples require modification of our present PCD apparatus to improve penetration of the light into the samples. A laser-activated system is under construction.

5. FUTURE ACTIVITY

It is expected that following the signing of the contract for Phase II of the program, activity will move forward in several areas including studies of metal-doped low resistivity silicon, metal-doped n-base silicon, studies of gettering and heat treatment in p-base silicon using impurities from the initial impurity matrix and expansion of the impurity matrix to include other impurities.

6. REFERENCES

1. R. H. Hopkins et al., Fifth Quarterly Report, Silicon Materials Task (Part 2), ERDA/JPL-954331-77/1.
2. P. M. Dunbar and J. R. Hauser, Proceedings of IEEE Photovoltaic Specialists Conf., p. 13 (1975).
3. J. R. McCormick, L. D. Crossman, and A. Raucholz, Proceedings of IEEE Photovoltaic Specialists Conf., p. 270 (1975).
4. R. H. Hopkins et al., Second Quarterly Report, Silicon Materials Task (Part 2), ERDA/JPL-954331-76/1.
5. P. A. Isles, S. I. Socloff, 11th Proc. IEEE Photovoltaic Specialists Conference, p. 19 (1975).
6. M. P. Godlewski, H. W. Brandhorst, C. R. Barona, "Effects of High Doping on Silicon Solar Cell Performance," 11th Proc. of the IEEE Photovoltaic Specialists Conf., pp. 32-35 (1975).
7. M. P. Godlewski, H. W. Brandhorst, F. W. Lindholm, and C. T. Sah, 1976 Conf. Proc. Am. Inst. Mining, Metallurgical and Petroleum Eng.
8. E. S. Ritner, J. Energy 1, 9 (1977).
9. S. M. Sze, Physics of Semiconductor Devices, Wiley & Sons, pp. 151-156 (1969).
10. K. I. Britsyn, A. A. Smirnov, Fizika Tverdogo Tela 8, 163-165 (Jan. 1966).
11. C. T. Sah, R. N. Nayce, and W. Shockley, Proc. IRE 45, 1228-1243 (Sept. 1957).