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FLAT-PLATE SOLAR ARRAY PROJECT

PROCESS DEVELOPMENT AREA

PROCESS RESEARCH OF NON-CZ SILICON MATERIAL

QUARTERLY REPORT NO. 2

January 1, 1984 to March 31, 1984

CONTRACT NO. 956616

The JPL Flat-Plate 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.

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TECHNICAL CONTENT STATEMENT

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A. CONTRACT GOALS AND OBJECTIVES

The objective of this contract is to investigate high risk - high payoff research areas on advanced processing techniques for non-CZ silicon sheet material that indicate promise of improving cost effectiveness of photovoltaic module production. The specific goals are as follows.

1. Simultaneous Diffusion of Front and Back Junctions

In this part of the program, the simultaneous diffusion of liquid boron and liquid phosphorus metallorganic precursors* into N-type dendritic silicon web is being investigated. The diffusion parameters required to achieve the desired $P^{+}NN^{+}$ cell structure will be determined, and the resultant cell properties will be compared to cells produced in a sequential diffusion process.

In addition to a standard tube diffusion furnace, a series of experiments will be carried out in a belt furnace. The parameters of cells produced using this method will be compared with cell parameters of tube diffused cells.

2. Process Control Parameters and Sensitivities

During the program, the control parameters of the process will be analyzed; and the sensitivity of cell parameters to variations in these control parameters will be determined. Process control parameters to be studied are diffusion time and temperature; ambient gasses and flow rates; liquid diffusant source thickness and pre-bake conditions; and initial silicon material base resistivity.

3. Cost Analysis

A cost analysis will be performed on the simultaneous junction formation process using SAMICS-IPEG methodology. The results will be compared to a sequential diffusion process.

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*For brevity, these liquids will be referred to as liquid phosphorus and liquid boron dopants.

B. SUMMARY

This report describes work performed on JPL Contract 956615, "Process Research of Non-CZ Silicon Material," during the first three months of 1984. In this program, which started November 4, 1983, the fabrication of solar cells on N-base material using simultaneous diffusion of liquid boron and phosphorus dopants to from the desired P^+NN^+ cell structure is being studied. This simultaneous junction formation method is being compared to the sequential junction formation method where phosphorus is diffused first to form an N^+N back surface field followed by a boron diffusion for the P^+N front junction. During the contract, the sensitivity of the process parameters will also be studied; and a cost analysis of the new junction formation process will be performed using SAMICS-IPEG methodology.

The standard Westinghouse baseline sequence uses P-type dendritic web as the starting material in the fabrication of solar cells. In this baseline process, a boron compound is diffused into the back of the cell structure to form a P^+P back surface field. The second diffusion using a phosphorus compound forms the N^+P front junction. Since phosphorus diffuses more rapidly in silicon than boron, the second diffusion is carried out at about 100°C lower temperature to achieve the required 0.25 - 0.30μm junction depth. If the simultaneous diffusions were carried out on the P-type material, it would not be possible to achieve the proper junction depths for both junctions at one diffusion temperature, since to achieve the proper front junction depth (with phosphorus) would result in a very shallow (<0.1μm) back surface field. Similarly, to obtain a sufficiently deep BSF, the front junction would be too deep. For simultaneous junction formation, studies are being conducted using N-type dendritic web. With N-type web, the back N^+N junction (phosphorus doped) can be diffused deep into the web while achieving the proper shallow P^+N front junction with boron.

The N-type dendritic web for this program is being grown on standard Westinghouse dendritic web growth furnaces. The initial experiments for diffusion into N-type web have been carried out on three different resistivities of material. The growth parameters and growth characteristics of

the web have not been affected by the change from boron doped to phosphorus doped silicon charges.

The dopant sources used for both the simultaneous and sequential diffusion experiments have been metallo-organic solutions with phosphorus or boron components. When these liquids are applied to the web surface, they are baked to form a hard glass which acts as a diffusion source at elevated temperatures.

In experiments performed thus far, cells produced in sequential diffusion tests have properties essentially equal to the baseline N^+PP^+ cells. However, the simultaneous diffusions have produced cells with lower IV characteristics mainly due to cross-doping of the sources at the diffusion temperature.

C. TECHNICAL PROGRESS

1. Simultaneous Diffusion

The process sequence used in this program to simultaneous diffuse N-type web is shown in Table 1. The experiments discussed in this report are being carried out with variations within this process sequence. All previous and subsequent steps in the cell process sequence are identical to those of the baseline Westinghouse process for producing N^+PP^+ cells.

Initial tests, discussed in the first Quarterly Progress Report (WAESD-TR84-001) investigated diffusion conditions listed in Step 5 of Table 1. Proper front and back junction depths were achieved with diffusion temperatures ranging from 940 to 960°C, diffusion times ranging from 18 to 25 minutes, and with a 1000 cc/min gas ambient of N_2. In some tests, the final 5 minutes were carried out in 500 cc/min of O_2.

These diffusion conditions produced front junction depths of 0.2 - 0.3μm and back junction depths of 0.4 - 0.8μm as determined by spreading resistivity measurements.

Front and rear junction profiles are shown for a representative dendritic web cell simultaneously diffused in Figures 1 and 2, respectively. Figure 1 shows the front N^+P junction with a junction depth of 0.2μm and a surface concentration near $10^{20}/cm^3$. The slight curvature at the beginning of the curve indicates a "starved" source, i.e., there were not sufficient phosphorus atoms in the source to prevent depletion at the surface.

Figure 2 shows the back N^+N junction for the same cell. Here the junction depth is 0.8μm with a surface concentration of about $2 \times 10^{20}/cm^3$) Again, the effect of the "starved" source is seen.

TABLE 1

PROCESS SEQUENCE FOR SIMULTANEOUS DIFFUSION OF N-TYPE WEB

1. Using a P-type liquid organometallic precursor, paint dopant on defined sun-side of pre-cleaned web.

2. Dry and bake per vendor instructions.

3. Using a N-type liquid organometallic precursor, paint dopant on defined backside of web.

4. Dry and bake per vendor instructions.

5. Diffuse at predetermined temperature, time, and gas ambients. (Optimum temperature, time, and gas ambients to be determined.)

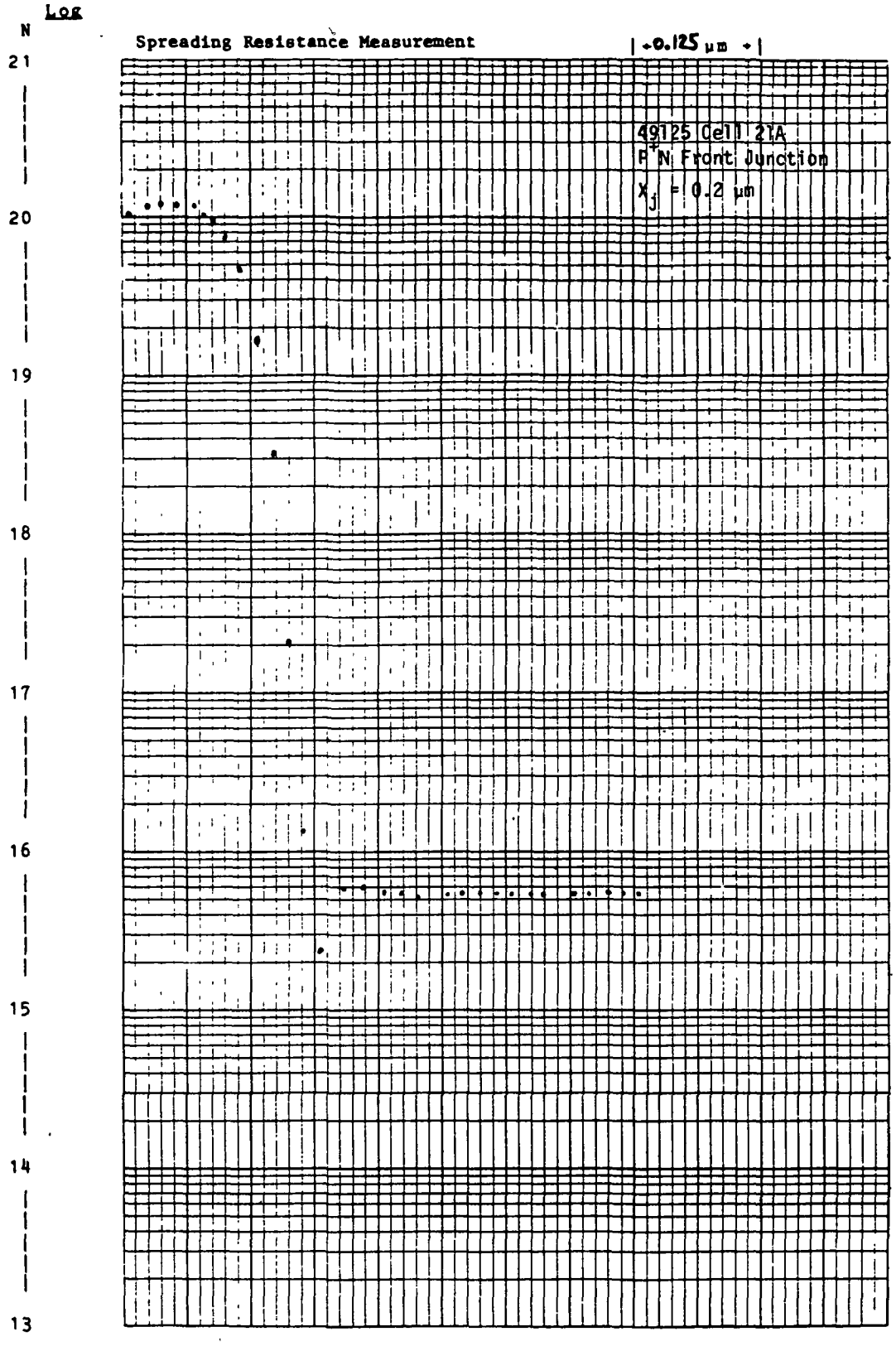

Figure 1. P^+N Front Junction Profile Measured on Simultaneously Diffused Web Strip #49125-21A

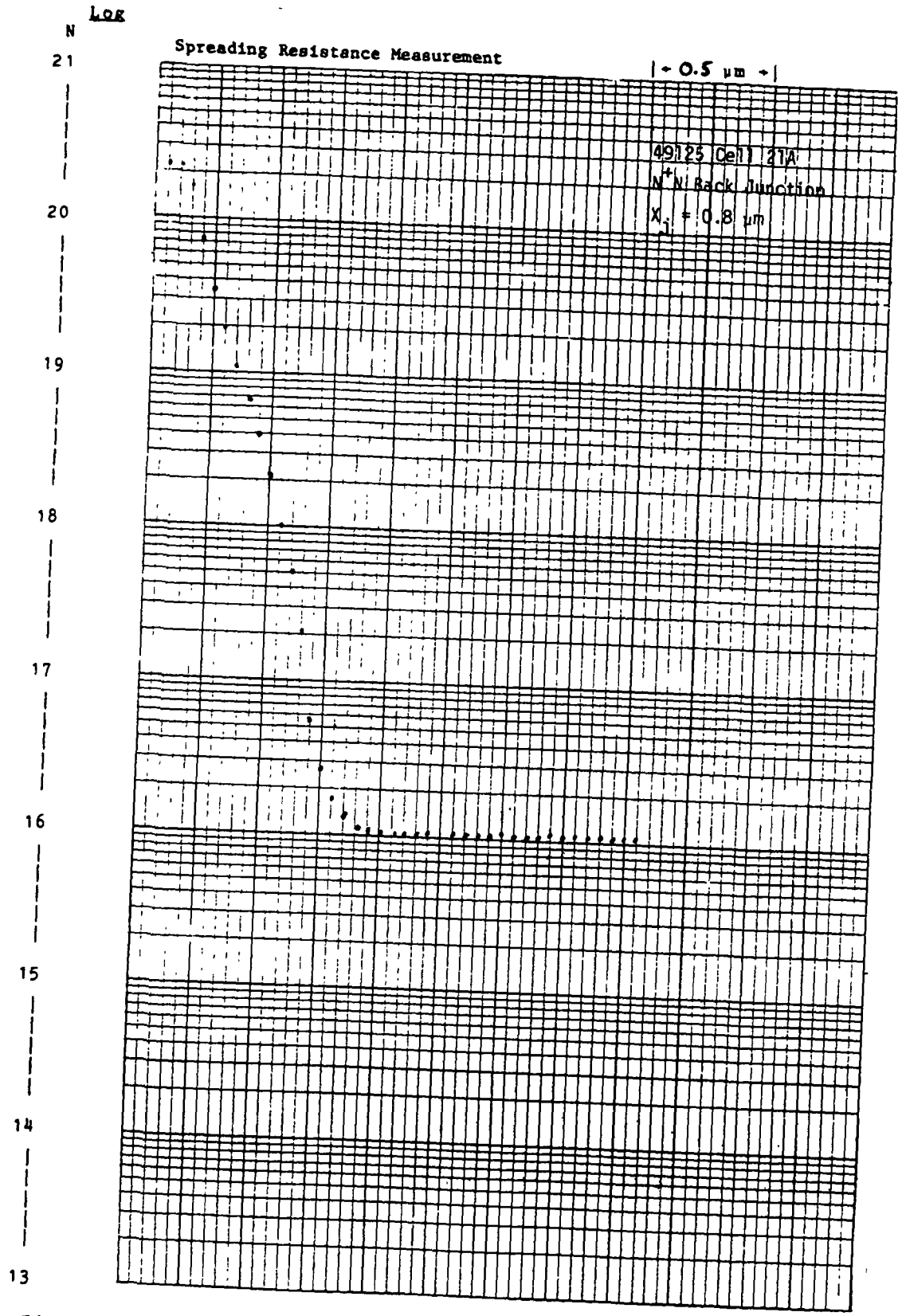

Figure 2. N^+N Back Junction Profile Measured on Simultaneously Diffused Web Strip #49125-21A

These figures indicate that proper diffusion conditions have been obtained to achieve a P^+NN^+ cell by simultaneous diffusion.

Table 2 lists diffusion conditions and results achieved in a number of simultaneous diffusion experiments conducted during this reporting period. In the previous quarterly report it was shown that during diffusion the liquid dopants, in addition to diffusing into the surface to which they were applied, would also contaminate and diffuse into the opposite side. Because of this, the experiments listed in Table 2 were carried out with one or both of the liquid dopants masked with an undoped SiO_2 glass to inhibit or control this cross-doping.

Several different SiO_2 glasses were used in these tests. U1A is used as a diffusion mask in the baseline process for N^+PP^+ cells. X600 and NP-5R are experimental SiO_2 solutions obtained from Allied Chemical Corporation and require baking at higher temperatures to achieve a hard glass.

Experiment 47748 was diffused in Ar to determine if there was any interaction between the N_2 ambient and the dopant/mask layers which would cause out-diffusion of the dopants.

As seen in Table 2, the maximum cell efficiency obtained in these experiments was 11%; however, the majority of the cells have much lower efficiency (<1% - 4%). In all cases when the shunt resistance of the low efficiency cells was measured, it was found to be unacceptably low, generally in the 1-10Ω-cm^2 range.

After testing, the metal and antireflection coating was removed from a number of cells in the experiments listed in Table 2. These cell blanks had the same sheet resistivity as was measured after diffusion, but a careful point-by-point scan with a conductivity probe showed small N-type areas in the P-type front surface. These areas would be sufficient to short-out the cell causing the very low shunt resistance and the low IV parameters.

TABLE 2

SIMULTANEOUS DIFFUSION EXPERIMENTS AND RESULTS

Run ID	P^+ Dopant	N^+ Dopant	Diffusion Conditions	Sheet Resistivity (Ω/□) P^+	Sheet Resistivity (Ω/□) N^+	Cell Data (Efficiency)	Comments
49133	B150	PX10	960°C/20 min	>1K	8-10	No PN Junction	B150 masked with U1A (SiO_2)
49137	Dil B150	PX10	960°C/20 min	40-60	6-15	<2%	PX10 masked with U1A
49138	B120	PX10	960°C/20 min	>10K	5-10	No P-N Junction	B120 masked with U1A
49147	Dil B150	PX10	960°C/20 min	10-60	10-15	1-11%	PX10 masked with U1A after 400°C bake
50801	B156	PX10	960°C/20 min/N_2	8-12	8-12	Poor (<3%)	PX10 baked in air for 1 hour before diffusion
50806	B150	PX10	950°C/20 min/N_2	10-60	10-15	1%-8%	PX10 masked wit U1A
50805	B60	PX10	960°C/20 min/N_2	50-60	10-15	5%-8%	PX10 masked with U1A; N^+ areas on P^+ surface
50831	B120	PX10	960°C/20 min/N_2	some low, 90-100	6-10	Poor (<3%)	PX10 and B120 masked with U1A; last 5 min. of diffusion in O_2
50962	B120	PX10	960°C/20 min/N_2	10-1000	6-10	Poor (<3%)	PX10 and B120 masked with U1A; last 5 min. of diffusion in O_2
50838	"Diffusol" P	"Diffusol" N	950°C/20 min/N_2 + O_2	Unable to strip diffusion glass			
50976	Dil B150	PX10	940°C/20 min/N_2 - 18 min + O_2 5 min	50-200	6-10	0	PX10 masked with X600 experimental SiO_2
50980	B60	PX10	950°C/20 min/N_2	-	-	2-5%	PX10 and B60 masked with NP-5R, baked at 400°C
47748	B60	PX10	950°C/20 min/Ar	Generally 10-40, some 80-120	8-20	1-4%	PX10 and B60 masked with NP-5R, baked at 400°C

Dopant Identification

B120, B150, PX10, NP-5R, X600 } Allied Chemical Corporation

U1A, B60 } Diffusion Technology, Inc.

Diffusol "N", Diffusol "P" } Transene Co., Inc.

A tentative model for the results of the simultaneous diffusions thus far is that the phosphorus species diffuse both into the silicon forming the N^+N back junction and outward through the mask. These phosphorus species then migrate (in a gas or along the surface of the web) and diffuse into the front surface of the cell. This excess phosphorus concentration at the surface and into the silicon prevents the boron from compensating the web and forming the P^+N junction. This explanation is somewhat validated by spreading resistance measurements. In some areas on the front surface, the spreading resistance profile is similar to Figure 2, that is, an N^+N junction structure.

2. Simultaneous Diffusion Using a Belt Furnace

One objective of the program is to show the feasibility of carrying out the simultaneous diffusions in a belt furnace.

During this period, such a test was made at Radiant Technology Corporation, Cerritos, California, using an IR heated belt furnace in which the diffusion gaseous ambient was controlled to several parts per million. Mr. Paul Alexander, JPL contract monitor, assisted in this test.

For this experiment, the web strips were pre-diffusion cleaned at the Westinghouse facility in Pittsburgh, Pennsylvania, and then packed to minimize contamination before the test. At Radiant Technology Corporation, the liquid dopants (Phosphorus, PX10 and Boron, B120 and B150 from Allied Chemical Corporation) were applied using a sponge-squeegee. The strips were pre-baked at 200°C after an air dry. The strips were placed on a quartz boat for carrying through the furnace.

The major results of this test were as follows:

1. The proper diffusion temperature (960°C) was obtained for 19 minutes with belt moving at 7 cm/min (slowest speed).

2. The cooling rate was faster than desired (46°C/min between 960°C and 720°C). This can be adjusted with an additional zone on the furnace.

3. No breakage was noted.

4. The diffusion glasses were stripped after the web strips were returned to Pittsburgh (a 30 hour delay). Some staining was noted on both front and back surfaces of the web strips. Staining was caused by the excessive time lag between diffusion and stripping.

5. Sheet Resistivity Measurements

   - Back surface (PX10 as N^+ dopant) - All strips in 8-12Ω/□ range as desired. All strips N type.

   - Front surface (B120 as P^+ dopant) - About half the strips had low sheet resistivities (5-10Ω/□) and a mixture of N and P type conductivity. The remainder of the strips had high sheet resistivity (>1KΩ/□) and had mixed N and P type conductivity.

   - Front (B150 as P^+ dopant) - All strips were in the 45-60Ω/□ range (as desired). They were generally of P-type conductivity with some strips having spots of N-type conductivity.

6. On fabricated cells, the AR coating and plating was generally irregular mainly due to the noted stains (See #4).

7. The cell IV parameters were poor with the maximum cell efficiency being 3%.

After fabrication and testing, the metal was stripped off three cells; and the sheet resistivity and conductivity was mapped on the front and back surfaces.

The back surface of all cells was found to be N-type with a sheet resistivity of 8-12Ω/□ as previously measured. The front surfaces had sheet resistivities generally in the 45-55Ω/□ range, but the surface also showed small areas of N-type conductivity. The sheet resistivity of these small areas was in the 10-20Ω/□ range.

On several cells, dark IV and spreading resistance measurements were made. The cells all had low shunt resistances of less than 5 ohm-cm^2. Due to this low shunt, the other dark IV parameters such as saturation current and carrier lifetime were not measurable. The spreading resistance data was similar to that shown in Figures 1 and 2.

From this belt furnace tests, it is concluded:

1. A belt furnace can be used to perform simultaneous diffusions and achieve junction depths in the proper range.

2. The cell properties were poor due to the same contamination problem encountered in the diffusion furnace experiments and discussed previously in this report.

3. Sequential Diffusion

The major thrust of the program is to prove the feasibility of simultaneous diffusion, therefore only limited effort has been spent on sequential diffusion. The specific sequence, diffusion materials, and results of several such runs are shown in Table 3.

Although the number of cells produced using this technique is small (<30), the data indicate that cells can be produced on N-type web with comparable efficiencies of those achieved on P-type when cross-contamination is controlled.

TABLE 3

SEQUENTIAL DIFFUSION OF N-TYPE WEB

1.	First Diffusion -	Back junction using PX10 with U1A mask on front surface. Xj = 0.5 - 0.8μm; diffused at 950°C/20 min.
2.	Second Diffusion -	Front junction using B150 with U1A mask on back surface. Xj = 0.2 - 0.3μm; diffused 950°C/20 min.
3.	Cell Efficiency Range -	11.0 % - 14.5% on 20 cm^2 cell
4.	Average Efficiency -	>13%

D. ACTIVITIES PLANNED FOR NEXT PERIOD

1. Continue experiments to eliminate cross-doping during simultaneous diffusion. The experiments will focus on obtaining hard, impermeable glass masks.

2. Continue sequential diffusion runs as baseline checks.

E. PROGRAM DOCUMENTATION AND DELIVERABLES STATUS

All programmatic and technical documentation specified in the subject contract (956616) have been prepared and submitted in accordance with contract schedular requirements. Table 4 summarizes submittal status of all routine reports (financial and monthly/quarterly technical reports). Table 5 summarizes submittal status of contract required documentation. All milestones scheduled to date have been met as shown on the Program Milestone Chart, Figure 3.

TABLE 4

ROUTINE PROGRAM DOCUMENTATION SUBMITTAL STATUS

Item	Submittal Date
1. Monthly Technical Reports	
A. November 1983	December 12, 1983
B. January 1984	February 8, 1984
C. February 1984	March 15, 1984
2. Financial Management Reports	
A. November 1983	December 12, 1983
B. December 1983	January 20, 1984
C. January 1984	February 15, 1984
D. February 1984	March 21, 1984
3. Quarterly Progress Reports	
A. No. 1	January 15, 1984
B. No. 2	April 15, 1984

TABLE 5

SUMMARY PROGRAM DOCUMENTATION STATUS

Initial Baseline Cost Estimate	November 17, 1983
Program Plan	November 17, 1983

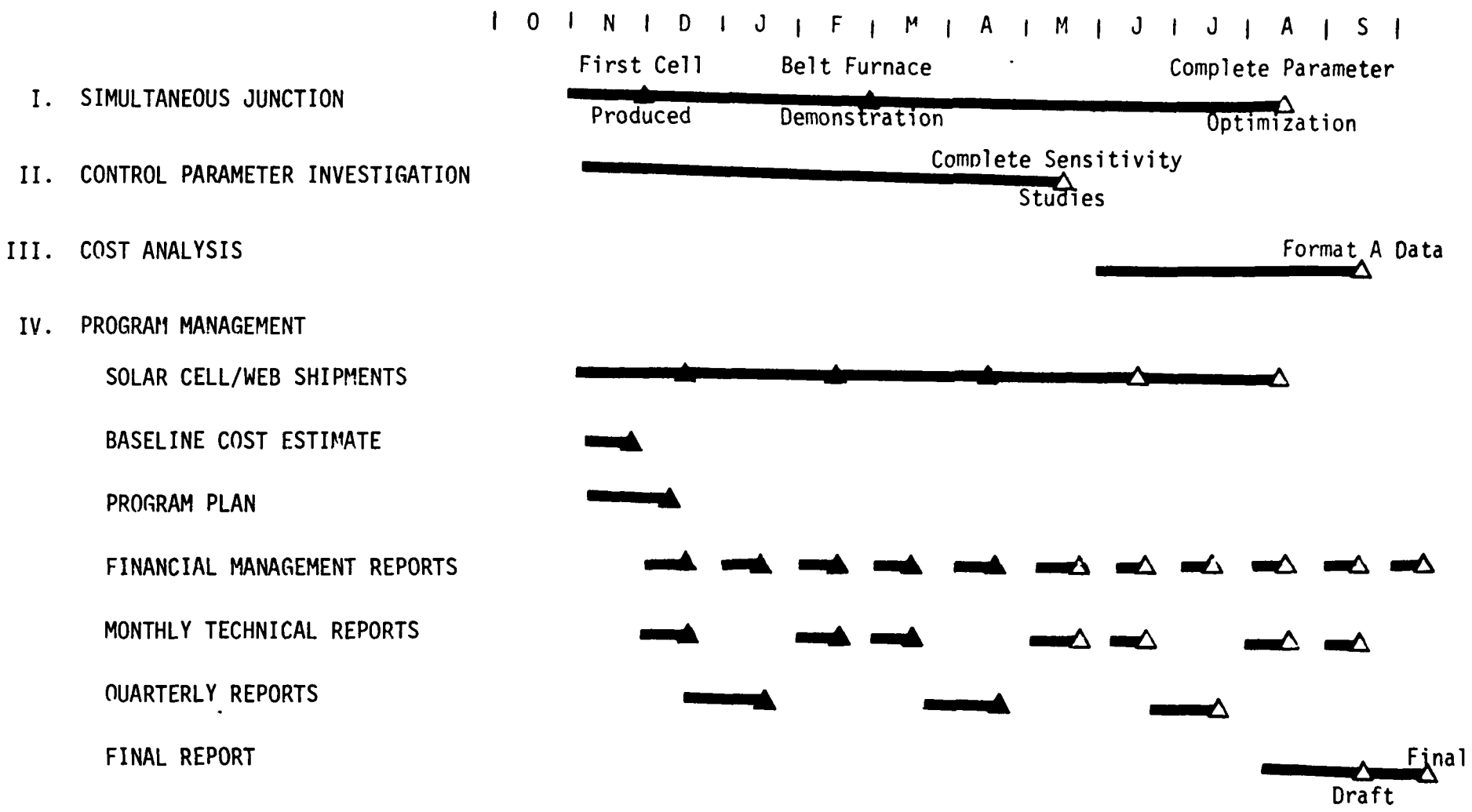

Figure 3. Process REsearch of Non-CZ Silicon Material Milestone Chart