

EXCIMER LASER ANNEALING TO
FABRICATE LOW COST SOLAR CELLS

Quarterly Technical Report No. 03
For Period Covering 1 October to 31 December 1984

Contract No. 956797

QR-10092-03
January 1985

Jet Propulsion Laboratory
Flat-Plate Solar Array Project
Module Performance and Failure Analysis Area

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Abstract

The objective of this program is to determine whether or not pulsed excimer laser annealing (PELA) of ion-implanted junctions is a cost effective replacement for diffused junctions in the fabrication of crystalline silicon solar cells. The preliminary economic analysis completed during the first quarter of this program showed that the use of ion implantation and PELA to fabricate both the front junction and back surface field (BSF) was more expensive, per wafer, than a hypothetical baseline diffusion process. However, a cost advantage may be attained if the implant-PELA process yields an improvement in the average cell efficiency from 14%, as assumed for the baseline diffusion process, to 16%. This improvement in cell efficiency would lower the overall cost of the module by about 15¢/Wp.

The technical goal of this research is to develop an optimized PELA process compatible with commercial production, and to demonstrate increased cell efficiency with sufficient product for adequate statistical analysis. During the third quarter of this program it was shown that a KrF based excimer laser, which would be the most economical to operate, can produce results equal to those seen with a XeCl laser, which was used for most experiments reported in the literature. Also during this quarter it was shown that the PELA junction can probably be improved by the time-temperature cycles typically used to sinter screen printed contacts. It was also shown that a PELA process with minimum overlap (pulsing each surface area once) is preferred for both technical as well as economic reasons. PELA of ion implanted junctions on texture-etched silicon did not yield good cells when screen printed contacts were applied.

Work planned during the fourth quarter includes optimization of the PELA process parameters for use with screen printed contacts on polished wafers, completion of the 300 wafer process demonstration task, and completion of the economic analysis.

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SECTION I INTRODUCTION

The objective of this research is to show whether or not pulsed excimer laser annealing (PELA) of ion implanted junctions is a cost effective replacement for diffused junctions in fabricating silicon solar cells. Required experiments and analysis are described below.

The first task (1A) is to select a process group which has functional equivalence to the baseline process group defined by JPL. Ion implantation and laser annealing have been used in place of diffusion of phosphorus for the front junction, and in place of aluminum drive-in for the back surface field.

The second task (1B) is to assess the sensitivity of the selected process to all significant input variables. The following parameters are being varied in this study: wavelength, beam uniformity, fluence, overlap, focusing optics, surface preparation, and ion implant species. Other parameters (for example pulse width, ion implant energy and dose) are in this work fixed, and are based on past published work. Further development of PELA is also in progress to show the compatibility of this process with commercial screen printed contact formation processes. Included in this task is the development of annealing of texture-etched surfaces.

The third task (1C) investigates the suitability of the specific excimer laser selected for this application. The KrF laser has an output power of 50 watts. This laser can anneal an area of 25 cm^2 per second, which is sufficient for the commercial application envisioned. The KrF laser has been demonstrated and this task is complete.

The fourth task (1D) is to demonstrate the achievement of a process cost reduction by producing a quantity of cells utilizing the proposed process group. The planned demonstration will comprise fabrication of 300 solar cells having diameter of 100mm as well as controls, using the equipment identified for production use. Full automation will not be used. The average cell efficiency and yield of this demonstration will be used in calculating the cost of this process.

The fifth task (3A) is to perform a preliminary economic analysis of the selected excimer laser process compared with competing technologies. The results, detailed in the first quarterly report for this contract, indicate that ion implantation and PELA of both front and back surfaces of a wafer would cost about twice as much as the equivalent baseline process group. However, since the PELA process is expected to result in more efficient cells, significant cost savings can still be realized. If the technical results of this program show that the back implant and anneal are not needed, then the cost savings would be almost \$0.32/peak watt.

The sixth task (3B) is a final economic analysis of this process using the yield and efficiency data of the demonstration experiment (Task 1D). An economic comparison between PELA and furnace annealing will be made.

The pulsed excimer laser apparatus is discussed in detail in the second quarterly report and will only be summarized here; there are no modifications to report this quarter. The lasers are made by Questek, Bedford, MA. The output pulse is reflected by a front surface mirror through a cylindrical lens to the sample wafer. The wafer is mounted horizontally, face-up on a vacuum chuck on a motorized x-y translation table located inside a small clean-air hood. For this work the wafer is moved one step, stopped, pulsed once, then moved again to a new position with a repetition rate of 2 Hz. (For production applications, the laser pulse rate would typically be over 100 Hz and the wafer would be moving continuously.)

The beam shape at the focusing lens is rectangular, approximately 10 mm x 20 mm. The fluence at the sample is adjusted by varying the focused beam width from 0.6 to 1.2 mm, and rarely changing the total pulse energy. The length of the beam at the sample position is between 25 and 30 mm. The pulse width is fixed at 20 ns. The pulsed energy at the laser is usually 400 mJ, with 86% transmission to the sample at 308 nm, and 80% transmission at 248 nm. Typical beam uniformity is ±2%.

SECTION 2

TECHNICAL PROGRESS

2.1 TASK (I) (A): SELECT PROCESS

The process chosen for the application of excimer lasers to the fabrication of silicon solar cells consists of non-mass-analyzed (NMA) ion implantation of phosphorus for the front junction followed by pulsed excimer laser annealing. For comparison, the cell processing sequence in the baseline diffusion process is:

Clean
Dry
Diffuse junction
Aluminum BSF
Clean
Print Ag Back
Print Ag Front
Cut
Test and Sort

The equivalent proposed process sequence utilizing excimer lasers is:

Clean
Dry
NMA ion-implantation of phosphorus
Pulsed excimer laser annealing
Print Al-Ag Back
Print Ag Front
AR coat
Cut
Test and Sort

The final process sequence envisioned in the first and second quarterly reports for this program indicated that a back surface field (BSF) should be formed by ion-implantation and PELA of boron. However, the gain in efficiency from such a BSF was not justified economically (see section 2.5). For this reason we have replaced the implanted BSF and Ag-printed contact with a printed Al-Ag contact.

2.2 TASK (I)(B): ASSESS EFFECT OF PROCESS VARIABLES

The objective of this task is to determine the sensitivity of the selected process, PELA of ion implanted junctions, to all significant process parameters. These parameters include laser wavelength, pulse width, beam uniformity, fluence, and percentage overlap as well as sample surface preparation, implanted ion species, ion dose, ion energy, implantation uniformity, sample temperature and atmosphere. Previously published

experimental results imply that the following parameters should be fixed: ion species, energy, dose uniformity,⁽¹⁾ and laser pulse width.⁽²⁾ For ease of processing, and because no deleterious effects have been reported,⁽²⁾ we have limited our investigation to pulsed excimer laser annealing at room temperature in atmosphere.

This study addresses the effect of the laser wavelength, fluence, and percent overlap on polished and texture-etched wafers, with phosphorus or boron ion implants. The effect of post-pulse thermal treatment is also discussed. Work performed during the third quarter of this contract is emphasized here.

2.2.1 Low Fluence Anneal and Effect of PELA on Minority Carrier Diffusion Length

Results of the third experiment in this program, which examined the effect of PELA at low fluence, were presented in the second quarterly report. Additional measurements show an anomaly: the minority carrier diffusion lengths (MCDL) derived from spectral response data of the laser annealed cells are lower than those of the furnace annealed control cells. In all prior experiments on this program the reverse is true with the minority carrier diffusion length being greater in laser processed material.

Two lots of wafers were prepared for this experiment. Lot 4539 had a polished front surface surface and a bright etched back surface. This material was cleaned, ion-implanted on the back with boron (see Table 1) cleaned again and annealed in a furnace. The front side was then implanted with phosphorus, cleaned, and annealed a second time using either an excimer laser or a three-step furnace anneal comprising two hours at 550°, fifteen minutes at 850°C, and two hours at 550°C. A second lot of wafers, 4540, was texture-etched on both sides, cleaned, and implanted on the back with BF_2^+ (see Table 1). The doses are increased to account for the greater surface area of the textured wafer. The change from boron to BF_2^+ was made to achieve higher implant beam current. The subsequent processing of lot 4540 was similar to that of lot 4539.

TABLE I. ION IMPLANTATION SCHEDULE

Lot #	Front Implant	Back Implant
4539	$^{31}\text{P}^+$ 10keV $2.5\text{E}15\text{ cm}^{-2}$	$^{11}\text{B}^+$ 25keV $2.5\text{E}15\text{ cm}^{-2}$
4540 (texture etched)	$^{31}\text{P}^+$ 10keV $5\text{E}15\text{ cm}^{-2}$	$^{49}\text{BF}_2^+$ 25keV $5\text{E}15\text{ cm}^{-2}$
4590 (1, 2, 3)	$^{11}\text{B}^+$ 6keV $2.5\text{E}15\text{ cm}^{-2}$	$^{31}\text{P}^+$ 25keV $2.5\text{E}15\text{ cm}^{-2}$
4590 (4, 5, 6)	$^{49}\text{BF}_2^+$ 25keV $2.5\text{E}15\text{ cm}^{-2}$	$^{31}\text{P}^+$ 25keV $2.5\text{E}15\text{ cm}^{-2}$
4573	$^{31}\text{P}^+$ 10keV $2.5\text{E}15\text{ cm}^{-2}$	none
4597	$^{31}\text{P}^+$ 10keV $2.5\text{E}15\text{ cm}^{-2}$	none

After annealing, both sets of wafers had lift-off patterned Ti-Pd-Ag evaporated contacts applied to the front and full-area Al-Ti-Pd-Ag contacts applied to the back. The contacts were sintered at 400°C for 5 minutes. Two cells, $2\text{ cm} \times 2\text{ cm}$, were sawed from each wafer and the contacts were plated to a height of 10 microns. Current voltage characteristics under AM1 illumination at 28°C were measured for all cells. Table 2 shows the values of open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF), and efficiency (EFF). The spectral response and dark I-V characteristics of selected cells were measured. Minority carrier diffusion length (MCDL), dark saturation current (J_0), and series resistance (R_s), are also presented in Table 2.

The MCDL of laser annealed cells appears to be lower than the furnace annealed controls for both lots shown in Table 2. The MCDL of cells in lot 4539 are lower than those of cells in lot 4540 with identical processing. One conjecture is that a fast-diffusing lifetime killing impurity was introduced to the surface of these wafers during the backside implant, or subsequent cleaning steps, and diffused through the bulk of the wafer during the subsequent backside furnace anneal. The furnace anneal of a high dose phosphorus implant may then acted as a gettering step for this contaminant which the laser anneal did not getter. Lot 4539 was more severely affected than lot 4540. An alternate explanation is that perhaps the back implant was improperly annealed. In such a case the subsequent furnace annealed for the controls would also re-anneal the back, but this would not occur in the laser annealed cells. A poor BSF would lead to low V_{oc} and low MCDL. This could explain the low values of V_{oc} , J_{sc} , and FF observed.

TABLE 2. THIRD EXPERIMENT ON LOW FLUENCE

ID	Fluence J/cm ²	# passes	R series ohms	MCDL μm	J ₀ pA/cm ²	V _{OC} mV	•J _{SC} mA/cm ²	FF %	EFF. %
<u>4539</u>									
23a	Furnace Anneal		.306	177	3.5	586	22.8	78.9	10.5
23b	Furnace Anneal		.394	--	--	586	22.8	78.6	10.5
24a	.5		.874	--	--	481	16.2	66.3	5.2
24b	.5	1	1.141	--	--	481	16.0	66.2	5.1
25a	.5	2	.838	.58	142.	486	18.7	71.5	6.5
25b	.5	2	.614	--	--	483	18.2	71.9	6.3
<u>4540</u>									
16a	.6	1	.502	120	217.	478	27.8	65.2	8.7
16b	.6	1	--	--	--	481	27.6	65.2	8.7
18b	.5	1	.696	155	252.	476	27.4	68.5	8.9
19a	.5	1	.553	158	260.	473	28.6	63.3	8.6
19b	.5	1	--	--	--	450	28.4	50.8	6.5
20a	.5	1	--	--	--	473	28.2	66.3	8.8
20b	.5	1	.721	167	233.	481	28.5	69.6	9.5
21a	Furnace Anneal		--	--	558	30.4	76.3	13.0	
21b	Furnace Anneal		.335	216	9.9	568	31.2	74.0	13.1

Notes: Laser wavelength was 308 nm. Overlap was 70% in all cases. No AR coatings employed.
Cell area is 4 cm².

2.2.2 Laser Wavelength

Published experimental studies of PELA were conducted using a XeCl laser at a wavelength of 308nm.⁽¹⁾ The preliminary economic study for this program, given in the first quarterly report, implied a cost saving would be attainable through the use of KrF at a wavelength of 248 nm. Recent advances in laser technology increased gas lifetime, further favoring the use of KrF for economic reasons. The objective of the fourth experiment was therefore to determine if there is a difference in PELA results using 248 nm light instead of 308 nm.

The wafers used for this experiment were from the same lots of ion-implanted material used in experiment three and were processed in identical fashion, as reported in the previous section. It can be seen by comparisons drawn in Table 3 that cells annealed at 248 nm perform better than cells annealed at 308 nm. For polished wafers, from lot 4539, those annealed with KrF laser are better at higher fluences (1.5 and 2.0 J/cm²) while those annealed with the XeCl laser are better at the low fluence (1J/cm²). The tentative conclusion is that the use of KrF is not disadvantageous.

2.2.3 Effect of Post-PELA Heating

The objective of experiment five was to test the effect of short-time moderate temperature heating on wafers already excimer laser annealed. A thermal cycle of 650°C for five minutes was selected after consideration of other PELA results,⁽³⁾ experiments previously reported in this program in which aluminum alloyed back contacts were sintered at 620°C, and the similarity of this thermal cycle to that used to fire screen printed contacts.

As in experiments three and four, wafers for this experiment were prepared in lots 4539 and 4540. The processing sequence for this experiment was exactly the same as previously described, except that to test post-PELA heating, some wafers were heated in a sintering furnace tube after laser annealing. Note that the MCDL of all laser annealed cells in lot 4539 (Table 4) was lower than the MCDL for furnace annealed controls, as previously mentioned. Cell 1b in Lot 4540 implies that the 650°C thermal treatment may also have lowered the MCDL relative to laser annealed cells that were not heated (4540-10a). However, the data from lot 4539 in Table 4 is scattered and no conclusion should be drawn.

TABLE 3. FOURTH EXPERIMENT: EFFECT OF WAVELENGTH

ID	Fluence J/cm ²	λ (nm)	Overlap %	# passes	Post PELA temp	R series ohms	MCDL μm	J _o pA/cm ²	V _{oc} mV	J _{sc} mA/cm ²	FF %	EFF. %
4539												
13a		Furnace Anneal				--	--	--	590	23.4	78.0	10.8
13b		Furnace Anneal				.349	155	3.2	591	23.3	78.7	10.9
14a	1.3	248	75	1	--	.333	79	67.1	508	22.5	75.4	8.6
14b	1.3	248	75	1	--	--	--	--	509	22.5	73.6	8.4
15a	1.5	248	70	1	--	--	--	--	568	21.3	75.8	9.1
15b	1.5	248	70	1	--	.319	59	6.4	568	21.3	76.8	9.3
16a	2.0	248	60	1	--	--	--	--	565	20.3	72.5	8.3
16b	2.0	248	60	1	--	.256	31	6.6	565	20.2	74.5	8.5
17a	1.0	248	75	1	--	--	--	--	494	20.9	74.7	7.7
17b	1.0	248	75	1	--	.478	56	112.	494	20.8	75.7	7.8
18a	1.3	308	75	1	--	.318	60	9.3	554	21.2	71.1	8.4
18b	1.3	308	75	1	--	--	--	--	553	21.2	68.9	8.1
19a	1.5	308	70	1	--	2.9	14	7.0	549	19.6	48.4	5.2
19b	1.5	308	70	1	--	--	10	9.2	489	20.7	32.6	3.3
20a	1.5	308	70	1	--	.329	58	6.4	560	20.6	61.0	7.0
20b	1.5	308	70	1	--	--	--	--	555	20.7	56.1	6.4
21a	2.0	308	60	1	--	.264	62	6.1	562	20.4	52.5	7.2
21b	2.0	308	60	1	--	--	--	--	549	20.1	49.5	5.5
22a	1.0	308	80	1	--	--	--	--	528	21.2	73.3	8.2
22b	1.0	308	80	1	--	.341	52	24.6	531	21.2	75.6	8.5
4540												
2a	1.3	248	75	1	--	--	--	--	506	27.6	66.9	9.4
2b	1.3	248	75	1	--	.378	129	54.6	514	28.1	72.5	10.5
3a	.8	248	75	1	--	--	--	--	483	27.7	71.0	9.5
3b	.8	248	75	1	--	.435	89	158.	488	27.8	72.4	9.8
22a	1.0	308	80	1	--	--	--	--	527	27.7	60.5	8.8
22b	1.0	308	80	1	--	.463	128	42.7	522	27.1	68.4	9.7
23a	1.3	308	75	1	--	--	--	--	499	24.6	44.1	5.4
24a	1.0	308	75	1	--	.294	134	25.2	509	27.1	47.8	6.6
25a	.8	308	75	1	--	--	--	--	512	28.9	61.2	9.0
25b	.8	308	75	1	--	.334	137	54.9	509	28.1	64.1	9.1

Note: No AR coatings employed. Area is 4 cm².

TABLE 4. FIFTH EXPERIMENT EFFECT OF POST-PELA HEATING

ID	Fluence J/cm ²	λ (nm)	Overlap %	# passes	Post PELA temp	R series ohms	MCDL μm	J _O pA/cm ²	V _{OC} mV	J _{SC} mA/cm ²	FF. %	EFF. %
4539												
5a		Furnace Anneal				.250	149	3.7	584	23.3	75.7	10.3
5b		Furnace Anneal				.290	145	4.0	577	23.1	64.3	8.6
6a	1.5	308	60	1	--	.330	43	6.2	565	20.4	73.0	8.4
6b	1.5	308	60	1	--	--	--	--	557	20.4	59.2	6.7
7a	1.5	308	60	1	650	--	--	--	575	21.9	60.8	7.7
7b	1.5	308	60	1	650	.176	97	4.3	577	21.8	75.0	9.4
8a	1.5	308	60	1	--	.269	41	6.7	565	20.2	76.8	8.7
8b	1.5	308	60	1	--	--	--	--	561	20.2	72.6	8.2
9a	1.8	308	50	1	650	--	--	--	570	20.3	75.0	8.7
9b	1.8	308	50	1	650	.205	56	5.6	571	20.4	75.8	8.8
10a	.9	308	85	1	--	1.980	46	42.9	516	21.5	72.8	8.1
10b	.9	308	85	1	--	--	--	--	510	21.1	70.1	7.5
11a	.9	308	85	2	650	.378	65	6.9	568	22.2	73.9	9.3
11b	.9	308	85	2	650	.407	70	7.1	564	22.3	69.8	8.8
12a	1.5/.9	308	60/85	2	--	.276	74	6.1	568	21.1	72.7	8.7
12b	1.5/.9	308	60/85	2	--	--	--	--	564	21.4	64.4	7.8
4540												
1a	1.1	308	80	1	650	--	--	--	525	26.1	57.6	7.9
1b	1.1	308	80	1	650	.258	87	18.8	539	27.0	64.5	9.4
7a	1.1	308	80	1	650	--	--	--	512	25.6	50.1	6.6
7b	1.1	308	80	1	650	--	--	--	523	26.2	42.9	5.9
8a		Furnace Anneal			--	--	--	553	29.0	61.1	9.8	
8b		Furnace Anneal			.301	192	11.1	567	28.4	21.2	11.5	
10a	1.1	308	80	1	--	.255	132	32.4	523	28.1	62.5	9.2
10b	1.1	308	80	1	--	--	--	--	521	27.8	63.3	9.2
12b	1.1	308	80	1	--	--	--	--	508	28.1	46.0	6.6
15a	1.1	308	80	1	--	--	--	--	509	27.4	57.3	8.0

Note: No AR coatings employed. Area is 4 cm².

In this experiment wafers 1, 7, 10, 12 and 15 in lot 4540 were laser annealed at what was believed to be the optimum fluence for texture-etched material. Originally we intended to anneal the polished wafers in Lot 4539 at 0.9 and 1.8 J/cm², but the higher fluence damaged the surface, and so the fluence was reduced to 1.5 J/cm². Also, in Lot 4539, the poor fill factor for cells 5b, 6b, 7a, and 12b could be due to slight plating of silver on the edges of the cells after sawing. We discuss this possibility later.

To further test the effect of post-PELA thermal cycling, the cells were fabricated from 3 inch diameter 0.3 ohm-cm p-type float zone silicon with starting MCDL of about 150 microns. This material is identical to that used by Spire to fabricate very high efficiency silicon solar cells (over 18%) using oxide passivation and thermal annealing. For this experiment, (lot 4573) wafers were cleaned and implanted on the front with phosphorus (see Table 1), and annealed either by the excimer laser or in a furnace. No back surface implant was used. Wafers numbered 2 and 4 were subsequently heated to 650°C for 5 minutes. Front contacts comprised of lift-off patterned evaporated Ti-Pd-Ag. The back contacts were full-area evaporated Al-Ti-Pd-Ag. Contacts were sintered at 400°C for 5 minutes. Six cells, each 2 cm x 2 cm, were sawed from each wafer and then the metal contacts thickness was increased to 10 microns by plating. A letter suffix in the cell ID is used to differentiate cells from the same wafer. Results are shown in Table 5 for the best and worst cell from each wafer.

The best laser annealed cell (4573-3a) has an efficiency of 10.9% without an AR coating, which would be about 15.2% with a good AR coating. This efficiency was better than any of the furnace annealed control cells in this lot. The poor cells in this lot, after inspection, appeared to have some plated metal shunting the junction at the edge of the cell. A few cells were edge etched and the remeasured efficiency is shown, much improved, in Table 5. Edge etching did not change cell 3a.

The average minority carrier diffusion length (MCDL) of the laser annealed cells, 155 microns, is greater than the 133 micron MCDL of the furnace annealed controls, and much greater than 79 micron average MCDL of laser annealed cells that were heated to 650 °C. The causes of the variation in MCDL are difficult to identify. That the laser-processed cells have the highest MCDL is reasonable, since no thermal processing is used. Whether the reduced MCDL in one thermal anneal or post-PELA heating causes structural defects or introduces impurities cannot be determined.

TABLE 5. PELA PROCESSING IN VERY HIGH QUALITY SILICON

. ID	Fluence J/cm ²	λ (nm)	Overlap %	Post PELA Temp	# Passes	R series Ohms	MCDL μ m	J_o pA/cm ²	V_{oc} mV	J_{sc} mA/cm ²	FF %	* EFF %	
												EFF %	EFF %
4573													
1c		Furnace Anneal				.73	128	2.6	594	23.2	76.4	10.5	--
1f		Furnace Anneal				.30	138	2.8	568	22.9	48.2	6.3	--
2c	1.5	308	40	650	2	.22	56	3.8	580	20.9	77.0	8.8	--
2a	1.5	308	40	650	2	.19	72	3.5	566	19.8	50.1	5.9	9.6
2g	3a	1.5	308	40	--	.25	166	1.8	603	23.2	77.7	10.9	--
3b	1.5	308	40	--	2	.24	165	1.9	595	23.3	67.4	9.3	--
4b	1.5	308	40	650	1	.26	85	3.8	582	21.7	76.6	9.7	--
4a	1.5	308	40	650	1	.28	101	3.9	571	22.2	58.6	7.4	9.3
5b	1.5	308	40	--	1	.50	147	6.0	563	23.2	73.8	9.6	--
5a	1.5	308	40	--	1	.37	141	7.4	557	23.1	62.9	8.1	--

Notes: * Efficiency after edge etching, other results before edge etching. No AR coatings employed. Cell area is 4 cm².

2.2.4 Fluence

As shown in Tables 2 through 5, the fluence (total energy/unit area) used to anneal ion implanted silicon wafers was varied from 0.5 to 1.8 J/cm². The best results on polished material are obtained with fluences in the range of 1.5 to 1.8 J/cm². The best results on texture-etched material are obtained with fluences in the range from 0.8 to 1.3 J/cm². The optimum fluence on textured material is lower because reflected light will be incident on the material at least twice before reflection away from the surface, thus increasing the absorbed energy (Figure 1). This is important because the reflectivity of molten silicon is over 60% and the near surface material will be melted during most of the irradiation pulse (20 ns). The effect shown in Figure 1 implies that the total incident light energy is greater near the bottom of the pyramids than near the top. This non-uniform irradiation of the surface of textured material makes it very difficult to completely anneal all of the implanted area without overheating any part. The proposed use of screen printed contacts requires deep junctions to prevent shunting. Such junctions cannot be easily formed with laser annealing of texture-etched surfaces without damaging some part of the surface. Ion-implanted, pulsed excimer laser annealed, texture-etched wafers are not considered compatible with screen printed contacts. Therefore polished or bright-etched wafers will be used for the demonstration.

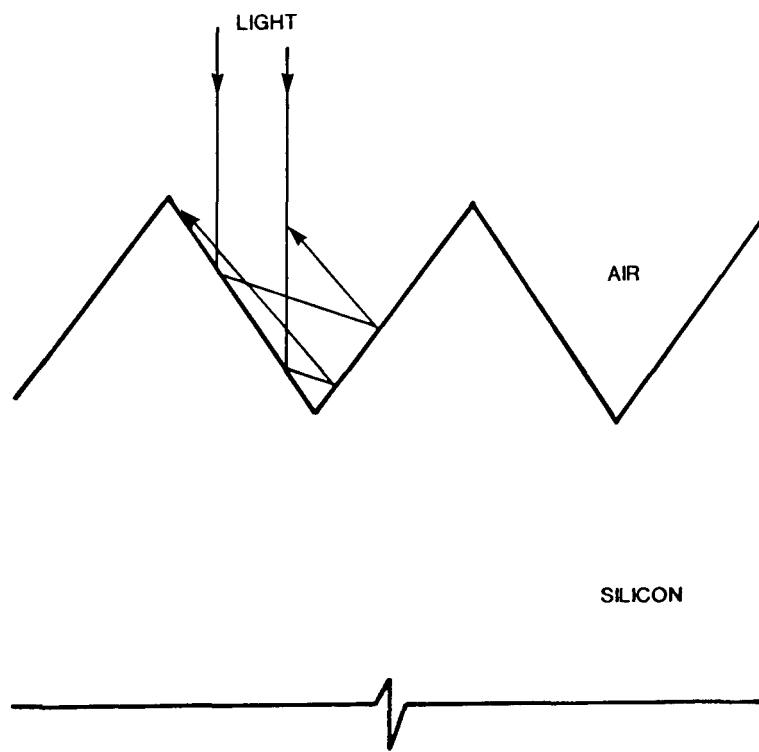


FIGURE 1. INCIDENT LASER LIGHT ON TEXTURE-ETCHED SILICON SURFACE SHOWING WHY ABSORBED FLUENCE IS GREATER NEAR BOTTOM OF PYRAMIDS.

The uniformity of the irradiation upon the wafer surface is more important at higher fluences since hot spots will create damaged regions. An example of damage from a hot spot focused into a line by the cylindrical lens is shown in Figure 2. This is wafer number 9 from lot 4539. The average fluence was 1.8 J/cm^2 . The hot spot created a shallow depression about 10 microns wide which recurs every 200 microns (0.010 inch), the distance the wafer was moved between pulses. The metallization of the front contact passes over several of these damaged areas as seen in Figure 2. The efficiency of the cell did not seem to be much affected as the fill factor and open current voltage of this cell are good. It is possible that the poor MCDL of this lot of wafers reduces performance more than the surface damage.

2.2.5 Overlap

The annealing pattern of the laser beam used in these experiments is a long thin rectangle, 25 to 30 mm long and 0.5 to 1.5 mm wide. This pattern was scanned over the surface of a wafer as shown in Figure 3. Typical step distances were 0.5 mm and 24 mm in the short and long directions, respectively. These step distances adjusted for different beam widths so that no region on the wafer was left unannealed. Because the beam had low fluence tails which do not anneal silicon (see the second quarterly report for this contract) typical patterns must overlap by about 50%. This implies that each point of the sample surface is pulsed twice, once at low fluence and once at a higher fluence in random order. Increasing the overlap or pulsing a sample twice (two passes) improved results for low fluence irradiation (see Table 2, wafers 4539-24 and 25). At higher fluence, over 1.5 J/cm^2 , there was no discernable improvement in average cell performance. Based upon this finding, and on the fact that processing costs increase with any increase in overlap, the demonstration experiment will use minimum overlap, and only one annealing pass.

2.2.6 Annealing Boron Implants

As originally envisioned the process sequence included back boron or boron-trifluoride implantation and pulse excimer laser annealing (PELA) to form a back surface field. Because the effect of a BSF is minimal in the low resistivity material being used, experiment six used the reverse type of cell structure, p^+nn^+ , to determine the electrical characteristics of PELA for boron implants. All of these wafers (N-type, float

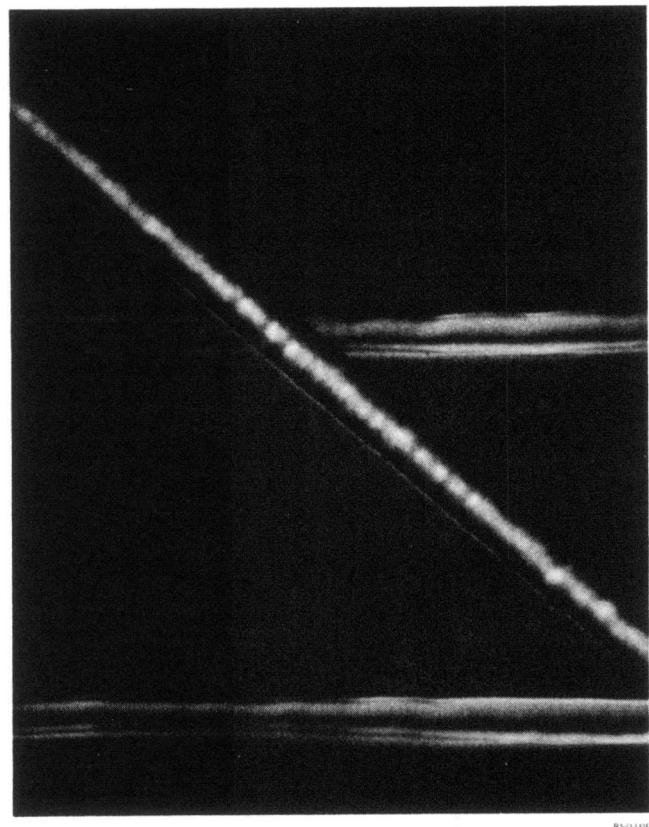


FIGURE 2. DAMAGE TO POLISHED SILICON SURFACE FROM PELA DUE TO HOT SPOTS. (Damage areas are horizontal features, solar cell metallization is diagonal line, magnification 200x, cell 4539-9a.)

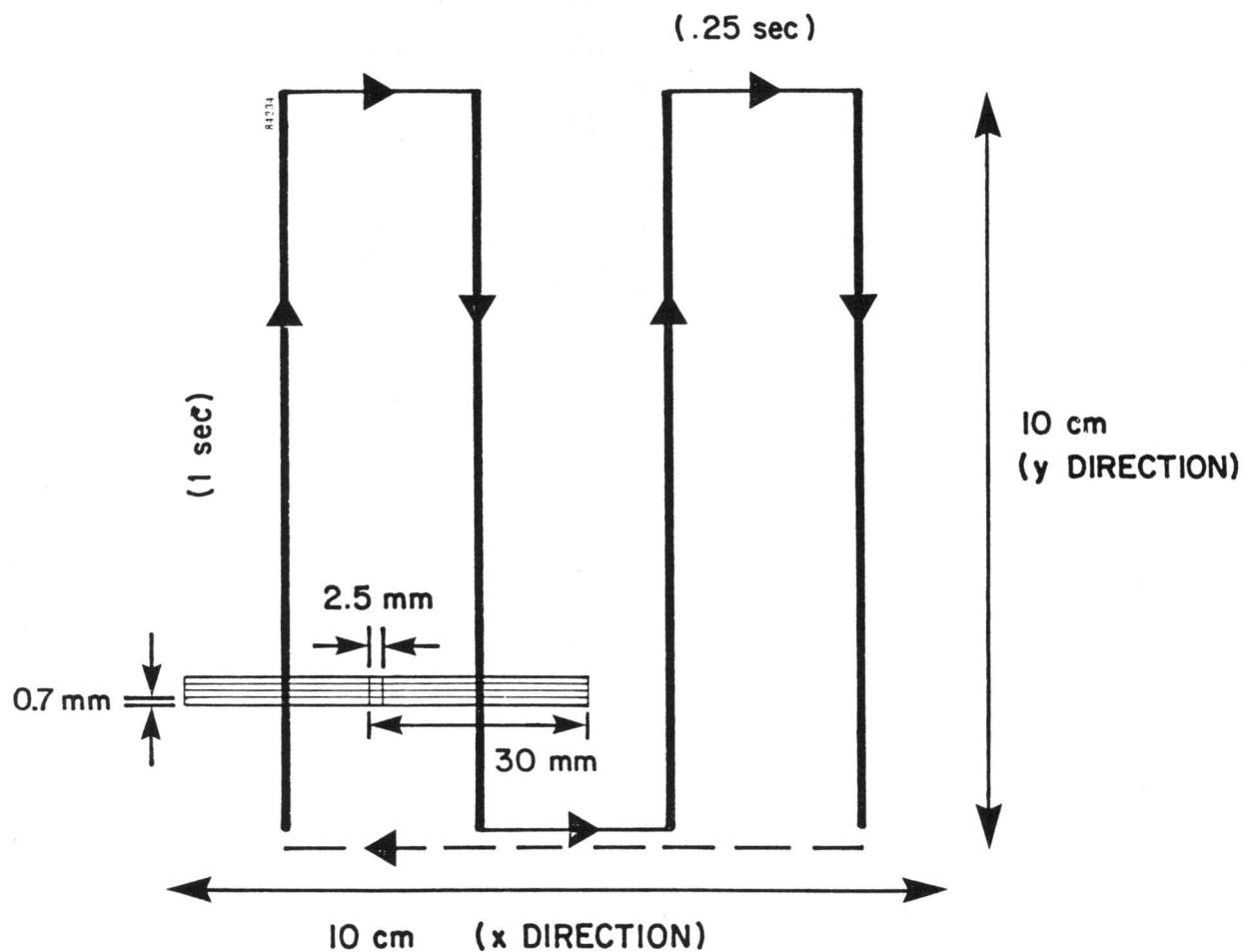


FIGURE 3. SCANNING PATTERN FOR ANNEALING A 100 cm^2 SQUARE WAFER OR 10 cm DIAMETER ROUND WAFER (Total transit time at 10 cm/sec is 5.5 seconds.)

zone, 4 ohm-cm, polished) are implanted on the back and then annealed in a furnace before implanting the front with either boron or BF_2^+ (see Table 1). One wafer of each type was annealed in the furnace a second time, while the other two wafers were pulsed excimer laser annealed at different fluence levels. Cell measurements are shown in Table 6.

Comparing the two furnace annealed controls, wafer 1 and 4, the cells fashioned from BF_2 implants are better. This could be due to the fact that the BF_2 implant created an amorphous surface due to heavy ion damage, which can lead to improved structure and greater dopant activation after annealing than the boron implant which did not have as much crystal damage and was not completely amorphous at the surface. Alternately, there could have been a contaminant in the boron implant which reduced the MCDL after furnace annealing. With PELA, the MCDL of all wafers is high. Annealing the boron implant at higher fluence (1.6 J/cm^2) appears better, comparing 4590-2b with 3a or b, possibly due to removal of deep lying defects with a greater melt depth. It is not clear why the open circuit voltage of PELA of BF_2 implanted cells (4590-5a, b and 6a, b) is so low.

These results are interpreted to imply that the laser parameters for adequate activation of boron or BF_2 implants to form a back surface field are nearly identical to the laser parameters to anneal a phosphorus implanted front junction. However, because adequate cells were made in the test material with sintered Al-Ti-Pd-Ag contacts on lapped surfaces for the back contact, ion-implantation of boron or BF_2 on the back will be dropped from the demonstration experiment. The economics of PELA will be more favorable in this case (see Section 2.5).

2.2.7 Surface Preparation

The materials used for lots 4539 and 4540 are identical, except that lot 4539 has a polished front surface and lot 4540 has a textured-etch surface on both sides (1-3 micron pyramids). The low reflection of the texture-etched surface (Figure 1) reduces the fluence needed to anneal this material. However, the pyramid tops receive half of the laser fluence that the pyramid bottom areas receive. Maintaining the laser illumination below the damage and excess melting threshold results in shallow junction depth near the

TABLE 6 EXPERIMENT SIX
BORON-IMPLANTED p⁺nn⁺ CELLS

ID	Fluence J/cm ²	λ (nm)	Ion	R series ohms	MCDL μm	J _o pA/cm ²	V _{oc} mV	J _{sc} mA/cm ²	FF %	EFF. %
4590										
1a	Furnace Anneal	11B		.82	75	25.0	535	21.6	71.9	8.3
1b	Furnace Anneal	11B		--	--	--	532	21.5	70.7	8.1
2a	1.6	308	11B	--	--	--	542	17.0	34.4	3.2
2b	1.6	308	11B	.37	144	14.1	548	24.0	73.1	9.6
3a	1.3	308	11B	--	--	--	537	23.9	70.0	9.0
3b	1.3	308	11B	.41	163	21.7	537	24.0	72.5	9.4
41	Furnace Anneal	49BF ₂		--	--	--	548	23.6	71.8	9.3
4b	Furnace Anneal	49BF ₂		.70	154	16.3	548	23.7	73.1	9.5
5a	1.6	308	49BF ₂	--	--	--	488	23.6	70.1	8.1
5b	1.6	308	49BF ₂	.50	126	90.8	491	23.9	69.9	8.2
6a	1.3	308	49BF ₂	--	--	--	481	24.3	70.0	8.2
6b	1.3	308	49BF ₂	.46	144	116.	483	24.0	70.6	8.2

Notes: No AR coatings employed. Area is 4 cm².

Overlap was 75% with one pass laser anneal in all cases.

pyramid top. Since the tops of these pyramids are subject to damage during processing, the shallow junction makes a wafer with this surface treatment more susceptible to shunting. From the data for lot 4540 shown in Table 2 shunting of the junction in texture etched wafers is more of a problem than for polished wafers (lot 4539). Additionally, a lot of nine 100mm texture-etched wafers (10 micron pyramids), ion-implanted with phosphorus as lot 4540, pulsed excimer laser annealed, with screen printed contacts were all very badly shunted. This result militates for the use of polished or bright-etched wafers for the demonstration experiment.

2.2.8 Demonstration Experiment

The objective of the seventh experiment was to test the material selected for use for the demonstration of product experiment, and to test the optimized laser processing parameters. The 100mm diameter material was cleaned, implanted on one side (Table 1) and laser annealed. Two wafers were heated to 650°C after annealing. Front contacts comprised evaporated Ti-Pd-Ag patterned by photolithography. Back contacts were Al-Ti-Pd-Ag. All contacts were sintered at 400°C for 5 minutes. Six cells, each 2x2 cm, were sawed from each wafer and contacts were plated up to 10 microns. Measured values for the best and worst cell from each wafer are shown in Table 7.

Compared to Lot 4573, there was no problem with metallization shunting the junction. The spread in characteristics is small. The MCDL of the laser annealed cells exceeds that of the furnace annealed cells. The 650°C post-PELA treatment had no apparent effect on the MCDL. However, the 650°C thermal treatment did improve the V_{oc} and relative efficiency of cells from wafers so treated. The cells laser annealed with only one pass are better than cells similar processed but subjected to two laser passes. Note that the better PELA cells from wafer 4 are as good as those from either furnace annealed control wafer.

2.3 TASK (1)(C): DEMONSTRATE APPROPRIATENESS OF SOURCE

This task is considered complete and details are given in the second quarterly report for this poroject. A 50 watt KrF pulsed excimer laser can anneal six hundred,

TABLE 7
TEST PELA ON MATERIAL INTENDED FOR DEMONSTRATION OF PRODUCT EXPERIMENT

ID	Fluence J/cm ²	(nm)	Post PELA temp	# passes	R series ohms	MCDL m	J _O pA/cm ²	V _{OC} mV	J _{SC} mA/cm ²	FF %	EFF. %
<u>4597</u>											
1a	Furnace Anneal				.47	86	6.0	574	22.8	78.5	10.3
1f	Furnace Anneal				--	--	--	573	22.8	76.9	10.0
2f	Furnace Anneal				.44	--	5.9	573	22.3	77.8	10.0
2c	Furnace Anneal				--	--	--	571	22.1	77.9	9.8
3c	1.5	308	--	1	.48	--	17.2	538	22.9	73.5	9.1
3f	1.5	308	--	1	--	--	--	541	22.8	69.8	8.6
4d	1.5	308	650	1	.41	136	5.3	579	23.3	77.6	10.4
4f	1.5	308	650	1	--	--	--	574	22.8	75.0	9.8
5f	1.5	308	--	2	.33	124	9.5	554	22.5	71.4	8.9
5b	1.5	308	--	2	--	--	--	559	22.3	61.0	7.6
6b	1.5	308	650	2	.36	121	5.6	575	22.6	75.6	9.8
6f	1.5	308	650	2	--	--	--	569	22.5	64.2	8.2

2-17

Notes: No AR coatings employed. Area is 4 cm².
Overlap for all laser annealed cells is 60%.

100 mm diameter wafers per hour. For comparison to entries in Table 2 through 7, the parameters used for this production speed demonstration were: 160 Hz pulse rate, 312 mJ per pulse (measured at the laser, 80% of this at the ample), a focal width of 0.7 mm by 30 mm length, and a scan rate of 10 cm/second (see Figure 3).

2.4 TASK (1)(D): DEMONSTRATE PRODUCT

The objective of this task is to produce a quantity of product so that the achieved yield and cell efficiency may be used to demonstrate process cost reduction. The material and equipment needed to complete this task are available. The parameters for material preparation (polished front, lapped back surface or as-cut), ion-implantation (2.5×10^{15} ions/cm², 10 keV, $^{31}P^+$, normal to surface), and pulsed excimer laser annealing (1.8 J/cm², 0.7 mm x 30 mm beam spot, 248 nm radiation) are determined. The only parameters that still need to be fixed are the time-temperature profiles for firing of screen printed contacts.

2.5 TASK (3)(B): FINAL ECONOMIC ANALYSIS

It was assumed in the preliminary economic analysis that the ion-implanter and laser annealing systems, each with an output of 600 wafers per hour, would be run for a sufficient time to match the 5 MW/yr output of the baseline process line proposed by JPL. If it is assumed that each shift will work only 1850 hours/year, then the implanter-laser annealer combination will produce about 1MW output per year per shift with 16% efficient round cells, or a total of 3 MW/year.

The final economic analysis will use this 1 MW output per shift per line. Preliminary calculations are shown in Table 8. Note that the cost of the PELA process is driven mostly by the cost of the ion implanter, so that comparison of the costs of laser annealing and furnace annealing should be included in the final analysis.

TABLE 8. ECONOMIC ANALYSIS

ASSUMPTIONS: 1985 dollars
 80% up time
 .886 yield
 600 wafers/hour throughput
 1850 hours/shift/year
 3 shifts
 100 mm diameter, as-cut, silicon wavers

ION IMPLANTATION AND PULSED EXCIMER LASER ANNEALING

Capital Equipment Price	\$1,856,000 x 0.59 =	\$1,095,040.
Floor Area	850 sq. ft. x 4136/sq. ft. =	\$115,600
Direct Labor	\$624,375 2.02 =	\$1,261,238.
	per shift (17 @ \$5/hr, 1 @ \$7.50/hr, 2 @ \$10/hr)	
Materials		
(2,664,000 wafers @ \$3.25 each; \$.919/wafer for all else)		
	\$10,886,456 x 1.17 =	\$12,713,754.
Utilities	\$23.006 x 1.17 =	\$26,917.
Total Price		\$15,212,549.
for 2,360,304 wafers/year		
encapsulated in modules.		

TABLE 8 (continued)

POCl₃ DIFFUSION

Capital Equipment Price	\$1,552,000 x .59 =	\$915,680.
Floor Area	900 ft ² x \$136/ft ² =	\$122,400
Direct Labor	\$721,500 x 2.02 =	\$1,457,480.
	(23 @ \$5/hr, 2 @ \$7.50/hr, per shift)	
Materials	\$10,751,904 x 1.17 =	\$12,579,728.
	(2,664,000 wafers @ (\$3.25 + \$.786 all else)	
Utilities	23,710 x 1.17 =	\$27,740
	Total Price	\$15,103,028
	for 2,360,304 wafers/year	
	encapsulated in modules	

Efficiency %	PELA \$/watt	Diffusion \$/watt	Output MW/Yr.
12	6.85	6.79	2.22
13	6.32	6.27	2.41
14	5.87	5.82	2.59
15	5.48	5.44	2.78
16	5.14	5.10	2.96

SECTION 3

CONCLUSIONS AND RECOMMENDATIONS

The determination of whether or not pulsed excimer laser annealing (PELA) is an economic alternative method of fabricating silicon solar cells will be decided entirely on the estimated achievable efficiency of the process in production. The cost per wafer of implementing this process may be twice the cost of the equivalent element in the baseline process, but significant savings are realized for even marginal improvements in cell efficiency.

Experiments show that the PELA process is sensitive to surface preparation and fluence, but insensitive to wavelength (248 vs. 308 nm), overlap (providing the entire surface is annealed), sample temperature, ambient and possibly contamination. Alignment and care of internal laser optics is critical to prevent beam non-uniformities which are damaging at the preferred high fluence. Post-PELA heating may be beneficial.

The maximum solar cell efficiency achieved by PELA equals that of furnace annealed, ion-implanted controls that have no passivating oxide. There is no evidence that PELA is better than this control process. However, the relative insensitivity of pulsed excimer laser annealing to many important process parameters implies that it has strong advantages over other pulsed annealing techniques such as Q-switched ruby or Nd:Yag lasers, and pulsed electron beams.

SECTION 4
PLANNED WORK IN THE NEXT REPORTING PERIOD

The research program is on schedule (Figure 4). Experiments to define screen printed contact parameters should be complete by late February. Processing of the demonstration experiment lot of 300 wafers, plus controls, will begin the second week in February. Completion of the fabrication of these solar cells should be achieved by the second week of March. The preliminary or draft final report is expected to be complete on time, on or about April 1st.

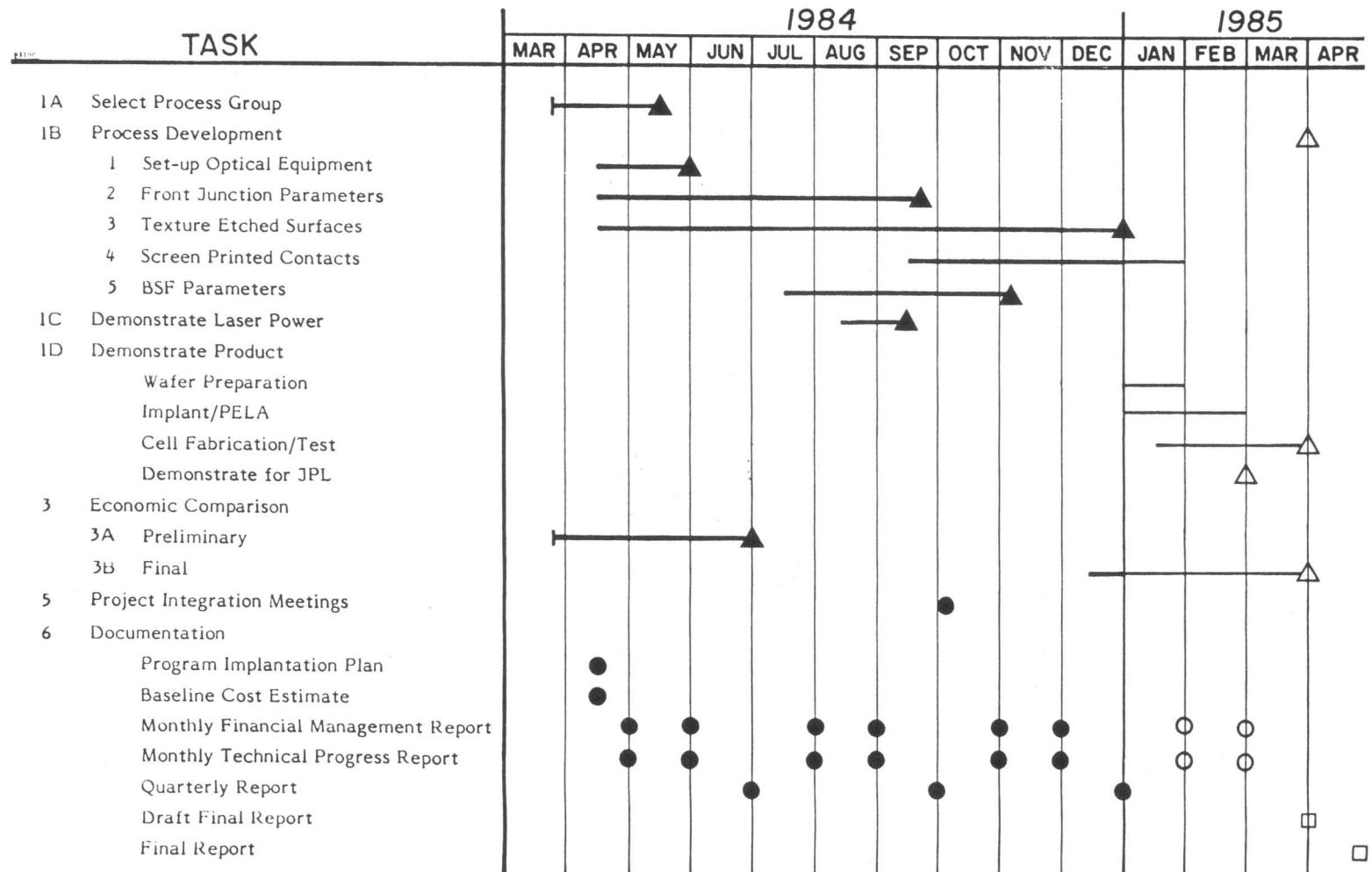


FIGURE 4. PROGRAM SCHEDULE.

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