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LASER ANNEALING OF ION IMPLANTED CZ SILICON FOR SOLAR CELL JUNCTION FORMATION

Quarterly Report No. 2

By
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M. Lopez

October 1980

Work Performed Under Contract No. NAS-7-100-955696

Lockheed Missiles & Space Company, Inc.
Sunnyvale, California

U.S. Department of Energy

Solar Energy

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

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ABSTRACT

This report describes the second quarter results on a contract to evaluate the merits of large spot size pulsed laser annealing of ion implanted silicon wafers for junction formation in solar cells.

Investigations on homogenization of the laser beam were continued. In addition to the 30mm diameter fused silica rod with a 90^{o} bend configuration, quartz tubes were obtained and briefly tried. Best results were obtained with the rod homogenizer.

Laser annealing experimentation resulted in complete recrystallization of ion implanted silicon substrates as confirmed by TEM and RBS analysis.

Single pulse laser annealed, functional cells (2 x 2cm) were fabricated using varying process conditions, yielding conversion efficiencies predominantly in the 13% to slightly less than 15%.

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SECTION 1

SUMMARY

Two approaches for beam homogenization were further evaluated this reporting period. Utilization of a fused silica rod, 30mm diameter with a 90° bend configuration, yielded excellent recrystallization of ion implanted silicon across the 30mm diameter area on the substrate. This was substantiated by Rutherford Backscattering analysis.

Use of quartz tubes coated with either aluminum or silver on the exterior surface, proved unsatisfactory due to the laser energy blowing the deposited coating off the surface. This approach was abandoned at this time because it's considered to be beyond the scope of this program. However, it is believed to have merit for minimizing light transmission losses, and should be further investigated in greater depth for this application.

TEM analysis of silicon substrates laser annealed at 1.2, 1.5, 1.9 and 2.1 J/cm^2 energy densities showed defect-free and complete recrystallization and recovery of silicon from the as-implanted amorphous state.

SIMS analysis was also performed on wafers implanted at 5 and 10 KeV levels and laser annealed at the four (4) energy densities of interest. It was determined that a laser energy density not greater than 1.5 J/cm^2 would maintain junctions on the order of 3000 Å for the 5 KeV implants and 3900 Å for those 10 KeV implanted.

Functional cells, 2 x 2cm in size, were fabricated using a variety of processing conditions, including varying laser annealing energy densities, wafer surface, and with/without BSF. Cells were ohmic contacted by vacuum deposition of titanium - palladium - silver, followed by a multilayer anti-reflection coating. Most of the 58 - 2 x 2cm cells fabricated from the variety of processing conditions, exhibited conversion efficiencies of 13 % to slightly less than 15%. The results attained, though preliminary, substantiates the general acceptability of large spot size (30mm diameter) laser annealing.

SECTION 2
INTRODUCTION

This is the second quarterly report on a process development contract to evaluate the merits of large-spot pulsed laser annealing of phosphorus implanted Czochralski grown silicon wafers. The laser system used on this contract is a >30 joule Q-switched Nd:glass laser, equipped with a frequency doubler, and operates at 1064nm and 532 wavelengths. It has a pulse duration range of 20 to 50 nsec and a repetition rate of 4 pulses per minute with an effective homogenized beam diameter of 30mm. The feasibility and requirements to scale-up this type of laser to anneal 3-inch diameter at a rate of 1 wafer/sec. will also be determined.

Cell and laser annealing variables being evaluated on three-inch diameter wafers are listed below:

Wafer Specification:	CZ silicon, boron doped, 10 Ω-cm, <100> , 3-in. diameter, 0.014 in. thick.
Surface Condition:	Chem-polished, flash etched, and texture etched.
^{31}P Front Implantation:	5 KeV, 2.5 x $10^{15}cm^{-2}$ 10 KeV, 2.5 x $10^{15}cm^{-2}$ 10 KeV, 4 x $10^{15}cm^{-2}$ (texturized surfaces only)
Cell Processing:	Ion implanted, laser annealed with no back surface field. Ion implanted, laser annealed with back surface field.
Back Surface Field:	^{11}B and BF_2 implanted at 25 KeV, 5 x $10^{15}cm^{-2}$, pulsed electron beam annealed.
Front Anneal Variables:	Laser energy densities of 1.2 J, 1.5 J, 1.9 J and 2.1 J cm^{-2} (all 30mm spot size).

In the first quarterly report, it was related that good annealing uniformity was achieved over a 30mm diameter area using a fused silica rod with a right angle configuration. This was substantiated by the excellent lattice structure recovery from implant-induced damage using the pulsed laser energy as analyzed by Rutherford Backscattering techniques.

During this reporting period, work emphasis was in the development of laser annealing parameters with analytical work performed by Transmission Electron Microscopy (TEM) and Secondary Ion Mass Spectrometry (SIMS) techniques for verification of results. Functional cells were fabricated and tested, for both ion implanted/laser annealed junctions and $POCl_3$ diffused junctions (for reference).

SECTION 3

TECHNICAL DISCUSSION

3.1 BEAM HOMOGENIZATION

Two approaches to obtain satisfactory beam homogenization were evaluated in this quarterly time period. The initial approach of taking a fused silica rod bent 90^{o} in the middle with a ground input face and polished output face (see quarterly report No. 1, July 1980) and passing laser light through it yielded very uniform 30mm single pulse annealed areas on the silicon wafers. Anneal uniformity was substantiated by Rutherford Backscattering analysis which showed an almost identical spectrum across the full 30mm spot size. Typical light intensity losses experienced with this homogenizing system were approximately 37%.

To minimize light losses, it was decided to evaluate another system consisting of a plano concave lens placed in front of a quartz tube coated with either aluminum or silver. Laser light diverged by the lens would be contained by the quartz tube with final spot size to be determined by the diameter of the tube. Size tubes obtained and tried were eight (8) inches in length by 30, 35, 40 and 45mm inside diameters with wall thicknesses of 2mm. Difficulties were experienced with this approach due to blow-off of the coatings on the tube and constant propagation of high intensity spots onto the silicon substrate with subsequent wafer surface damage. It was decided at this point to utilize the bent fused silica rod as a homogenizing medium in all future investigations. Additional work on other approaches, including tubes, should be undertaken; however, it is not within the scope of this investigation.

3.2 TEM AND SIMS ANALYSIS

TEM analysis was performed to evaluate the recovery of laser annealed substrates from implant induced damage. Wafers utilized consisted of chemically polished surfaces implanted at 5 KeV and 10 KeV, $2.5 \times 10^{15}/cm^2$. Four samples in each implant group (5 KeV and 10 KeV) were prepared. The samples were annealed utilizing a 30mm beam homogenizer at energy densities of 1.2 J/cm^2, 1.5 J/cm^2, 1.9 J/cm^2, and 2.1 J/cm^2. Within each anneal energy setting, approximately 25% of the energy was at $\lambda = 532nm$ and the rest at $\lambda = 1064nm$. Figure 1 contains TEM results which typified the laser annealed specimens even at the lowest laser anneal energy density.

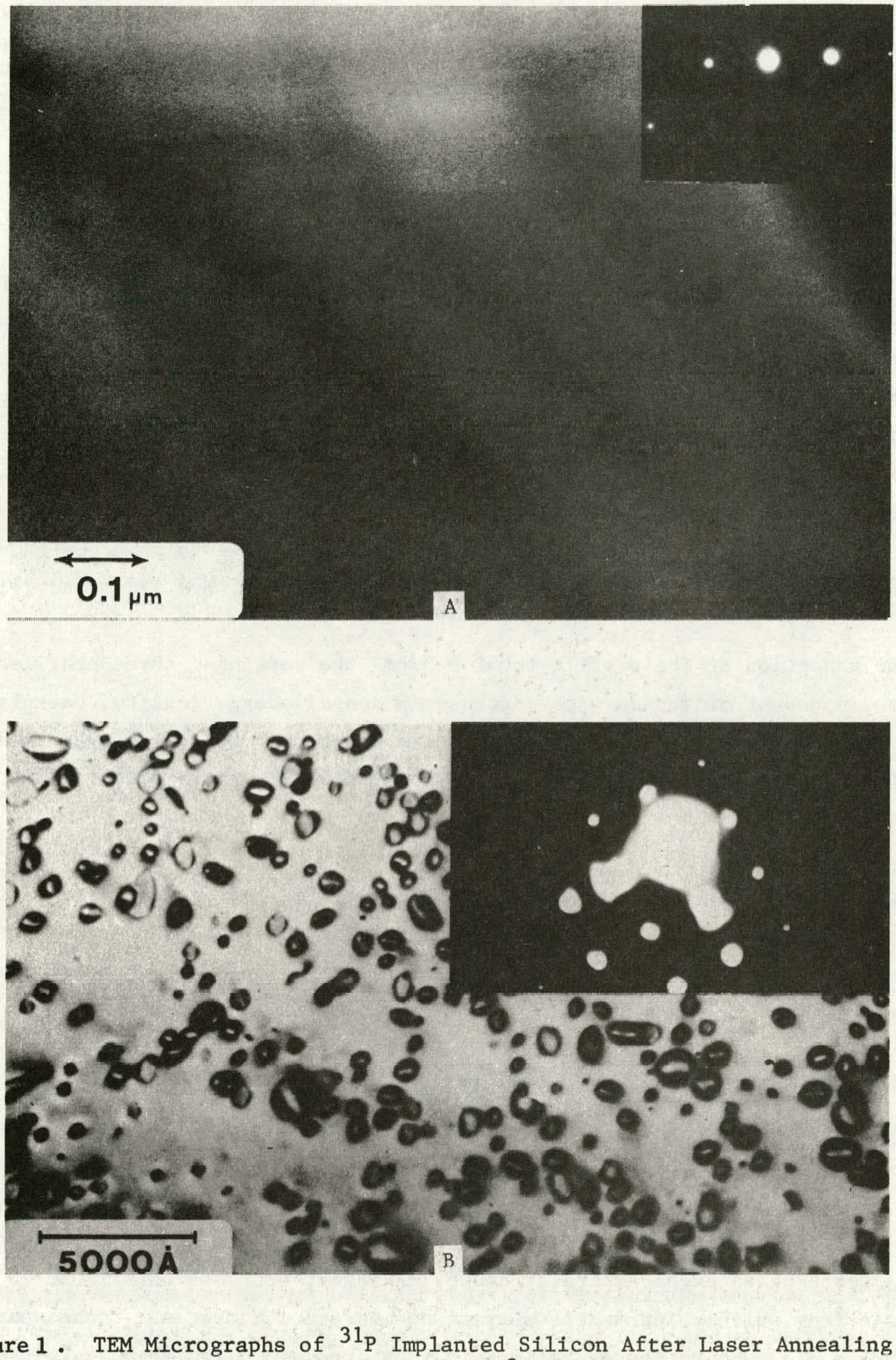


Figure 1. TEM Micrographs of ^{31}P Implanted Silicon After Laser Annealing (A), and After Furnace Annealing 900°C / 20 minutes (B).

For comparison, a TEM micrograph of a furnace annealed (900^{o}C/20 min.) sample is also included. Single crystal diffraction patterns (upper-right insert) were obtained indicating complete recrystallization and recovery from the amorphous state during laser annealing. The laser-annealed implant is found to be defect free, whereas a very high residual defect density in the form of dislocation loops is found in the furnace annealed specimen.

The obtained TEM data, coupled with previously reported (first quarterly report, July 1980) Rutherford Backscattering data indicated that excellent crystallographic recovery is obtained in ion implanted substrates as a result of exposure to laser irradiation. In selecting an optimum laser anneal parameter, additional data, namely ^{31}P dopant diffusion as a function of laser anneal energy density was required. The necessity for this data arises from the requirement of maintaining a shallow junction in the cell for improving its response in the blue end of the spectrum. To this end SIMS analysis was performed, Figures 2 and 3, on samples annealed at the four laser anneal energy densities: 1.2 J/cm^2, 1.5 J/cm^2, 1.9 J/cm^2 and 2.1 J/cm^2.

With the exception of the profile for 1.9 J/cm^2 the remaining three profiles show increase in dopant diffusion with increase in anneal energy density. Unexplainably the dopant profile at 1.9 J/cm^2 was almost identical to one at 1.5 J/cm^2 and consequently was not included in the figures. Additional work is forthcoming to verify this condition.

The impurity concentration (atoms/cm^3) in as implanted and annealed states for 10 KeV implants was found to be higher than for the 5 KeV counterparts. This is puzzling since the reverse should be true. An evaluation of this phenomenon is also forthcoming.

The standard approach in determining impurity depth following SIMS analysis is to measure the depth of the crater sputtered by the action of the ion microprobe primary beam, and relate that to sputtering time. Attempts at measuring crater depth using a Dektak and Tencor proficorders failed due to the fairly rough chemically polished surface of the wafers. From obtained plots it was evident that wafer surface peaks exceeded crater depth, making it extremely difficult to ascertain from which point on the surface to measure the crater. Consequently, the depth scale on the figures reflects a less accurate calculated scale based on the known projected range of the as-implanted dopant profile. Based on this scale

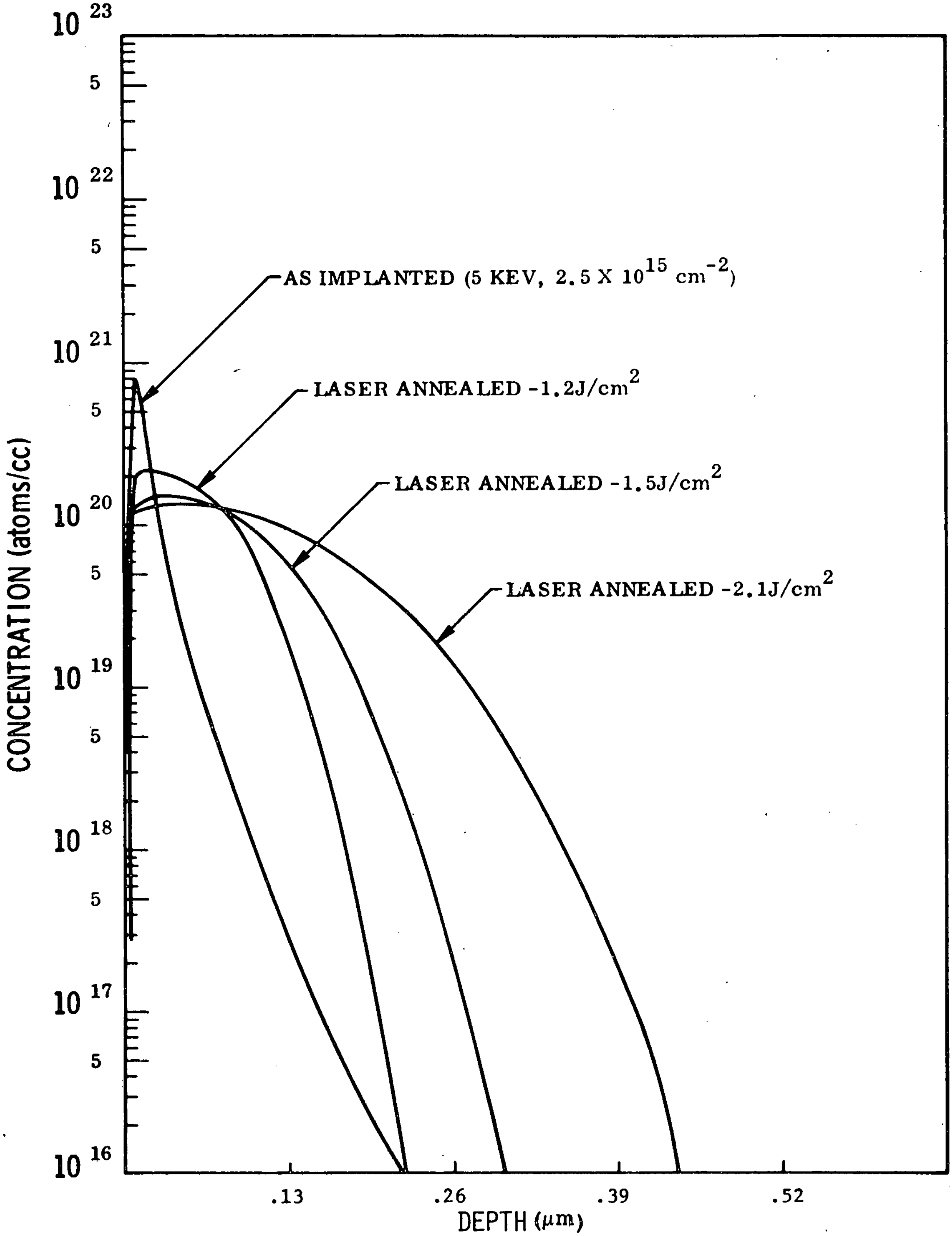


Figure 2. SIMS profiles of 5KeV phosphorus in silicon for as implanted and laser annealed specimens.

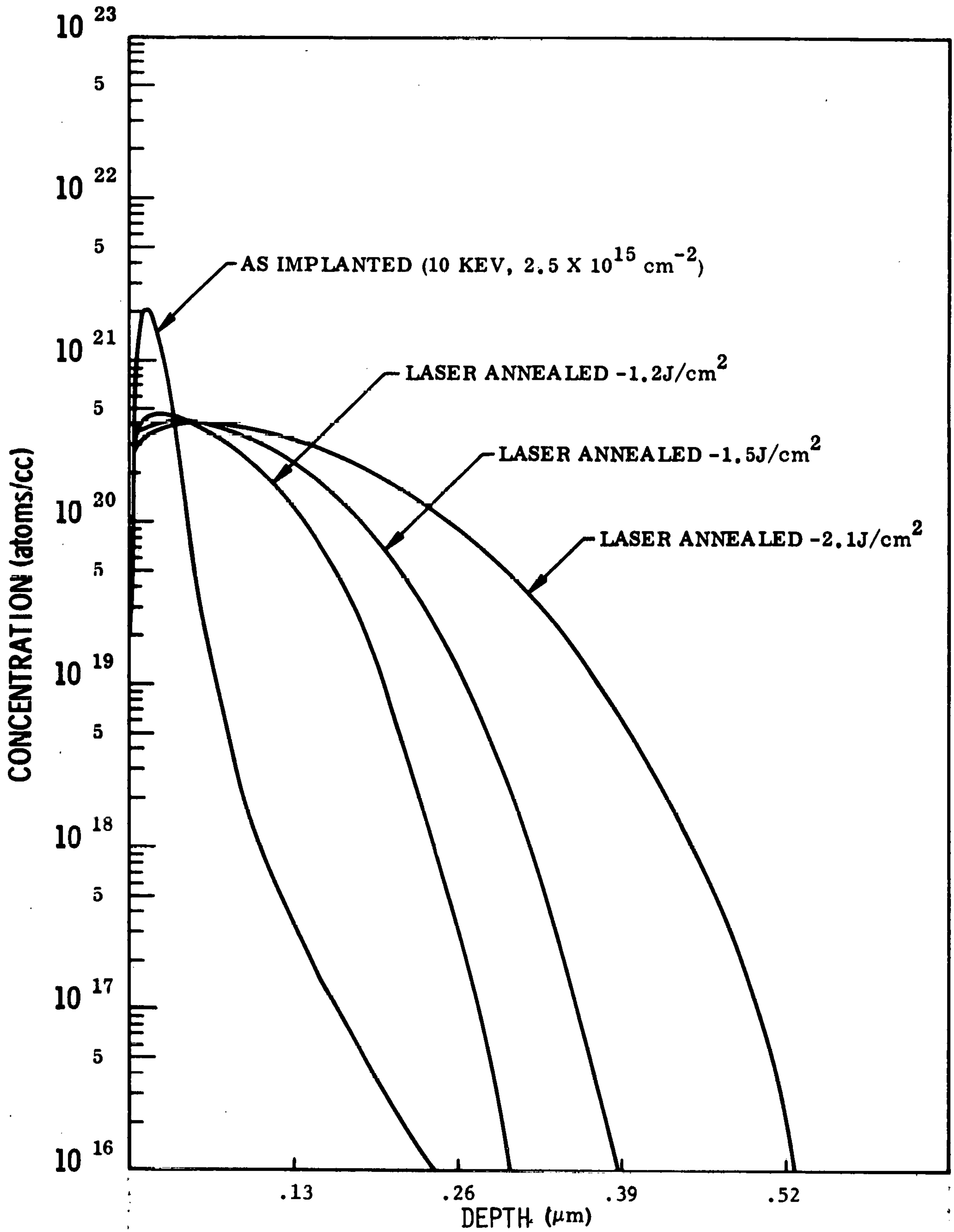


Figure 3. SIMS profiles of 10KeV phosphorus in silicon for as implanted and laser annealed specimens.

it appears that to maintain shallow junction conditions in the cell, annealing should be carried out at laser energies no greater than 1.5 J/cm^2. At this energy density junction depth was approximately 3000Å for the 5 KeV implanted specimens and 3900Å for the 10 KeV implanted specimens.

3.3 CELL FABRICATION

The obtained TEM, SIMS, and RBS data verified that laser annealing yields an electrically active, defect free, shallow junction device. To further determine optimum fabrication parameters and conditions, 2 x 2cm cells were fabricated using a variety of processing conditions. The processing conditions and AM 1 electrical output results are shown in Table 1. All laser annealing was performed with the 30mm diameter fused silica rod with a 90° bend configuration (described in section 3.1). Ohmic contacting and multilayer anti-relfective coating (MLAR) operations were performed by Applied Solar Energy Corporation (ASEC). Contacts were formed by vacuum deposited titanium - palladium - silver. Anti-reflective coating was evaporated TiO_2 and Al_2O_3. Cells with texture etched surfaces are in process of fabrication by ASEC and were not available for inclusion in this report. Also in process are 2 x 2's with screened on aluminum for BSF, and 3-inch diameter cells which were implanted and furnace annealed for reference.

The data presented in Table 1 can only be considered as preliminary indicators at best, due to the small number of cells processed. However, it does substantiate the general acceptability of the large spot size laser annealing process.

As a means of comparison, three (3) inch diameter cells were fabricated by ASEC using their standard $POCl_3$ diffusion process. Cells were made from similar CZ silicon as used for those laser annealed, namely, 10 Ω-cm, <100> , 0.014" thick, chem-polished surfaces, Ti-Pd-Ag contacts and MLAR. Table 2 shows the results of these cells.

The data shown in Table 3 was extracted from Table 1, and was ordered by type of cell construction, irrespective of material surface conditions and laser energy densities. It is presented for purposes of reflecting an overview comparison on work performed to date.

TABLE 1
FUNCTIONAL CELLS - PROCESSING CONDITIONS AND TEST RESULTS

FRONT IMPLANT (2.5×10^{15} cm^{-2})	① WAFER SURFACE CONDITION	FRONT LASER ENERGY (J/cm^2)	② PULSE CONDITION	③ BSF	NO. CELLS PROCESSED	Voc RANGE (mV)	Isc RANGE (mA)	CFF RANGE (%)	CONV. EFF. RANGE (%)	Jsc RANGE (mA/cm^2)
10 KEV	PO	FURNACE 875°C/20 min		NONE	2	550,553	126.5,127.5	77,78.6	13.7	31.6,31.9
5 KEV	PO	1.5	SINGLE	NONE	3	552-556	133.6-134.8	74.9-77.1	13.8-14.5	33.4-33.7
5 KEV	FE	1.5	SINGLE	NONE	3	539-546	134-136	72.3-77	13.3-14.1	33.5-34
10 KEV	PO	1.2	SINGLE	NONE	3	543-549	125.7-128	73.8-75.5	12.9-13.1	31.4-32
10 KEV	FE	1.2	SINGLE	NONE	3	530-539	132-133.5	70.5-72.3	12.5-12.8	33-33.4
10 KEV	PO	1.5	SINGLE	NONE	3	549-555	126-127.5	72.8-77.9	12.9-13.6	31.5-31.9
10 KEV	FE	1.5	SINGLE	NONE	3	549-554	131.5-132	74.2-75.8	13.5-13.9	32.9-33
10 KEV	PO	1.5	DOUBLE	NONE	1	554	127	76.5	13.5	31.8
10 KEV	PO	1.5	2 STEP OVERLAP	NONE	1	550	125.5	76.3	13.8	31.4
10 KEV	FE	1.5	2 STEP OVERLAP	NONE	1	545	136	[illegible]	10.4	[illegible]
10 KEV	PO	1.9	SINGLE	NONE	3	549-556	125-126.5	75.8-77.1	13.3-13.4	31.3-31.6
10 KEV	FE	1.9	SINGLE	NONE	3	550-555	131-131.5	76.3-77.3	13.8-14.1	32.8-32.9
10 KEV	PO	1.9	DOUBLE	NONE	2	550	125	74.3,76.3	12.8,13.1	31.3-31.6
10 KEV	PO	1.9	2 STEP OVERLAP	NONE	1	549	130.5	72.9	13.1	32.6
5 KEV	PO	1.5	SINGLE	BF_2, PEBA	2	555	132.7,133.6	76.9,77.6	14.2,14.4	33.2,33.4
5 KEV	PO	1.5	SINGLE	BF_2,PEBA + LASER	1	575	139	73.6	14.7	34.8
5 KEV	PO	1.9	SINGLE	BF_2,PEBA + LASER	1	573	136	73.8	14.4	34.0
10 KEV	PO	1.2	SINGLE	BF_2,PEBA	3	545-550	127-128.3	76.7-78.2	13.3-13.8	31.8-32
10 KEV	FE	1.2	SINGLE	^{11}B,BF_2, PEBA	3	534-545	131-132.5	72-77.1	12.6-13.9	32.8-33.1
10 KEV	PO	1.5	SINGLE	BF_2,PEBA	3	540-557	127-127.5	68.9-78.1	11.8-13.8	31.8-31.9
10 KEV	FE	1.5	SINGLE	^{11}B,BF_2, PEBA	3	552	130.5-131	76.7-77.6	13.9-14.0	32.6-32.8
10 KEV	PO	1.5	SINGLE	BF_2,PEBA + LASER	2	560	127.5,128.5	78.3,78.7	14.0,14.2	31.9,32.1
10 KEV	FE	1.5	SINGLE	^{11}B,BF_2, PEBA + LASER	2	565,571	134	74,74.5	14.1,14.2	33.5
10 KEV	PO	1.9	SINGLE	BF_2,PEBA	3	552-556	126-127	77.3-78.2	13.5-13.7	31.5-31.8
10 KEV	FE	1.9	SINGLE	^{11}B,BF_2, PEBA	3	553	131-132	71.4-77.2	12.9-14.0	32.8-33
10 KEV	PO	1.9	SINGLE	BF_2,PEBA + LASER	1	565	126.7	78.1	14.0	31.7
10 KEV	FE	1.9	SINGLE	^{11}B,BF_2, PEBA + LASER	1	560	133.0	72.9	13.6	33.3

LEGEND:
① PO (CHEM POLISHED)
FE (FLASH ETCHED)
② SINGLE PULSE: IRRADIATED ENTIRE 2X2 CM AREA WITH ONE PULSE.
DOUBLE PULSE: SAME AS SINGLE EXCEPT TWO PULSES ON SAME AREA.
2 STEP OVERLAP: TWO PULSES WITH 50% OVERLAP.
③ ^{11}B, BF_2 IMPLANTED AT 25KEV, 5×10^{15} CM^{-2}. PEBA: PULSED ELECTRON BEAM ANNEALED.

TABLE 2

$POCl_3$ DIFFUSED CELLS (3 IN. DIA.)

Qty. Cells		Voc (mV)	Isc (A)	CFF (%)	η (%)	(mA cm^{-2})
48	Mean :	542.9	1.496	73.4	13.1	32.8
	Range:	540-545	1.46-1.53	71.1-74.6	12.6-13.3	32.-33.6

TABLE 3

OVERVIEW OUTPUT COMPARISON BY CELL CONSTRUCTION

Type Construction	Size Cells	Qty. Cells	Voc (mV)	Isc (mA)	CFF (%)	η (%)	Jsc (mA cm^{-2})
Laser Annealed, No BSF	2 x 2cm	30	530-556	125-136	69.9-77.9	12.4-14.5	31.3-34
Laser Annealed With PEBA BSF	2 x 2cm	20	534-557	126-133.6	68.9-78.2	11.8-14.4	31.5-33.4
Laser Annealed With PEBA & Laser Pulsed BSF	2 x 2cm	8	560-575	126.7-139	72.9-78.7	13.6-14.7	31.7-34.8
Furnace Annealed, No BSF	2 x 2cm	2	550, 553	126.5, 127.5	77, 78.6	13.7	31.6, 31.9
$POCl_3$ Diffused, No BSF	3 in. dia.	48	540-547	1460-1520	71.1-74.6	12.6 13.3	32-33.6

From the preceding data, it is apparent that the contribution of the PEBA formed BSF was insignificant when compared with the no BSF devices. When followed by laser pulsing there is a slight increase in the Voc, leading to the observation that additional work should be performed on the PEBA and/or laser pulsing for the BSF formation.

3.4 DELIVERED HARDWARE

Two hundred and fifty (250) ion implanted, unannealed, 3-inch diameter wafers were delivered to JPL for their discretionary subsequent processing. The wafers consisted of:

- 50 ea. chem-polished surfaces, 5 KeV, 2.5 x 10^{15} cm^{-2} ^{31}P implants.
- 50 ea. chem polished surfaces, 10 KeV, 2.5 x 10^{15} cm^{-2} ^{31}P implants.
- 50 ea. flash etched surfaces, 5 KeV, 2.5 x 10^{15} cm^{-2} ^{31}P implants.
- 50 ea. flash etched surfaces, 10 KeV, 2.5 x 10^{15} cm^{-2} ^{31}P implants
- 50 ea. texture etched surfaces, 10 KeV, 4 x 10^{15} cm^{-2} ^{31}P implants.

SECTION 4

CONCLUSIONS

4.1 Large spot size, single pulse laser annealing yields active, defect free, shallow junction silicon substrates from which high efficiency solar cells can be fabricated.

4.2 Low cost flash etching techniques for saw damage removal on the solar cell silicon substrates appear to be compatible with laser processing.

4.3 Five (5) KeV ion implanted/laser annealed solar cells appear to exhibit increased conversion efficiency coupled with shallower junction in comparison to 10 KeV implanted cells.

4.4 Additional work on annealing back surface field implants is required for optimization of cell output.

SECTION 5

RECOMMENDATIONS

5.1 It is recommended that additional work be performed to assess the best suited process for back surface field formation for the LSA program. Processes for consideration include: (1) ion implanted ^{11}B or BF_2 followed by PEBA or laser pulse; (2) screened-on and fired aluminum in conjunction with laser annealed front junctions.

SECTION 6

NEW TECHNOLOGY

Single pulse laser annealing of 2 x 2cm size cells was demonstrated with electrical output characteristics similar or superior to conventionally processed cells.

SECTION 7

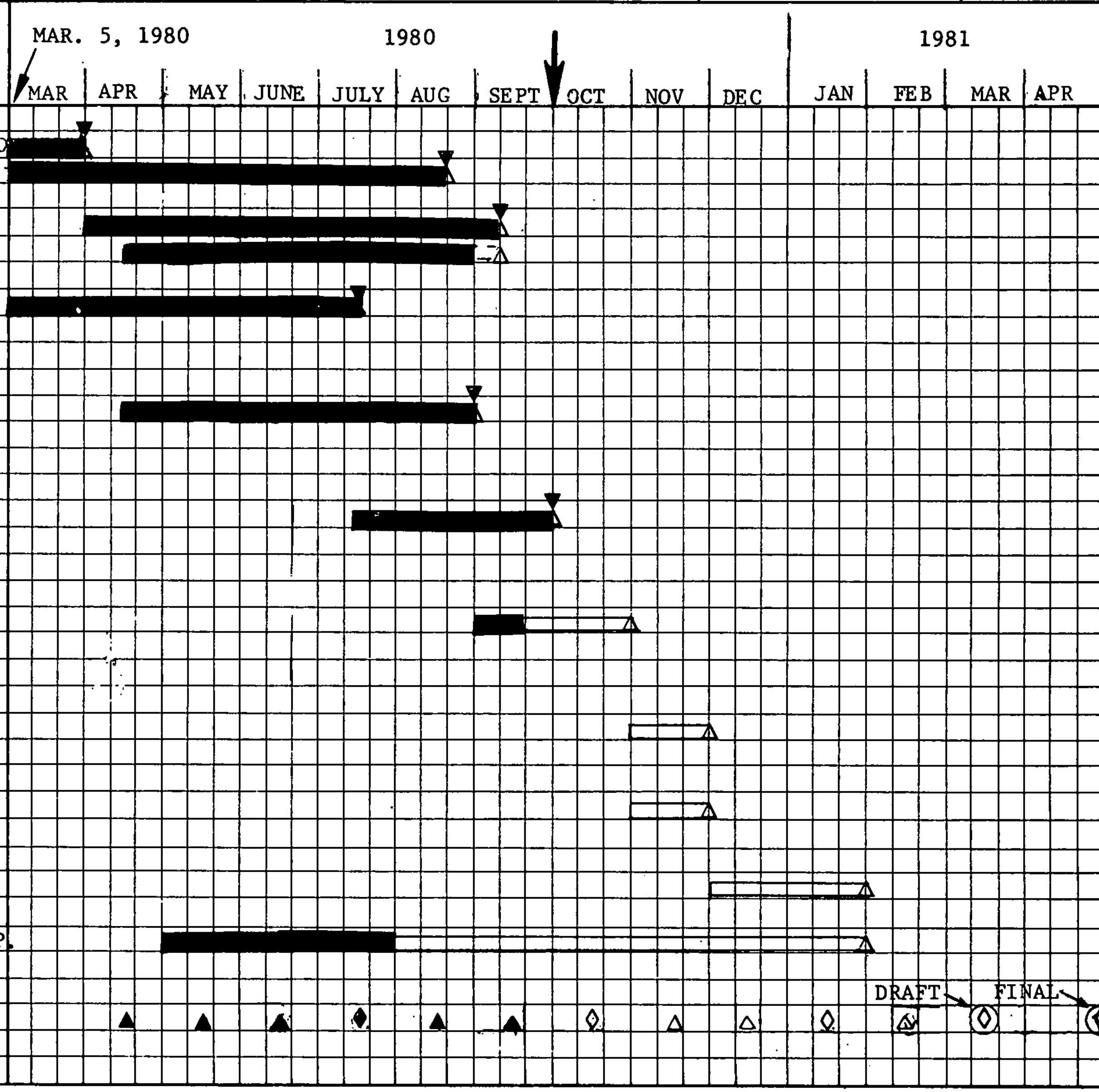
PROGRAM SCHEDULE

Progress to date is shown in the following Program Plan Chart.

SCHEDULE PLAN

MODEL	PLAN	TITLE	PREPARED BY:	DATE
		LASER ANNEALING EVALUATION OF ION IMPLANTED SOLAR CELLS	M. Lopez	11-12-79
ISSUE NO.	REFERENCE		APPROVED BY:	DATE
	JPL 955696		Rev.	5-30-80

1.0	MTL PROCUREMENT & PROJ CONT.
1.1	SUBMIT DEV. PLAN FOR JPL APPRO
1.2	PURCHASE WAFERS
1.3	ION IMPLANT WAFERS. DELIVER UNANNEALED WAFERS TO JPL
1.4	PROCESS CONTROL (REF) CELLS
2.0	HOMOGENIZE BEAM
3.0	DETERMINE SINGLE & MULTI-STEP LASER PARAMETERS AT 532, 1064 nm & COMB. ANALYZE
4.0	OPTIMIZE SINGLE PULSE ANNEAL & FABRICATE ~2 x 2 cm CELLS. ANALYZE & CORRELATE
5.0	OPTIMIZE MULTI-STEP ANNEAL & FABRICATE 2 x 4 cm CELLS ANALYZE & CORRELATE
6.0	VERIFY PROCESS-SINGLE/MULTI PULSE BY FAB. SMALL (2x2 cm) CELLS & LARGER.
7.0	REPEAT PROCESS VERIFICATION USING 3.0 IN. DIA. WAFERS
8.0	FABRICATE 3.0 IN. DIA. CELLS & DELIVER TO JPL FOR EVAL.
9.0	DETERMINE LARGE DIA. PULSE EQUIP.
10.0	DOCUMENTATION ① -SAMICS, TECH. PROGRESS & FINAL REPORTS.



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