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PHASE 2, AUTOMATED ARRAY ASSEMBLY, TASK IV
LOW-COST SILICON SOLAR ARRAY PROJECT

Quarterly Report No. 2, February 1—April 30, 1978

April 1978

Work Performed Under Contract No. NAS-7-100-954898

Lockheed Missiles & Space Company, Inc.
Sunnyvale, California

MASTER

U.S. Department of Energy

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Solar Energy

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Prepared by

LOCKHEED MISSILES & SPACE COMPANY, INC.
1111 Lockheed Way
Sunnyvale, CA 94086

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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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FOREWORD

The results described herein represent the work performed from February 1, 1978 to April 30, 1978 by the Manufacturing Research Organization of Lockheed Missiles & Space Company, Inc., in Sunnyvale, California. The project team, headed by Mike Lopez, is staffed with the following key personnel:

Dean Housholder, Semiconductor and Device Technology

Jerry Katzeff, Laser Technology (Annealing)

Bob Casey, Automation Processes

Harold Weinstein, R&D Staff, Photovoltaic Devices,
International Rectifier Corporation

Other principal contributors include John Knudson, Ion Implantation; and Cheryl Bostwick, Screen Printing of Contacts.

The JPL Contract Technical Manager is B. D. Gallagher.

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SECTION 1

SUMMARY

This 2nd Quarterly Report on the Phase 2, Process Development Contract on the Task IV, Low Cost Silicon Solar Array Project, covers the period February 1 through April 1978. Areas of technical discussion during this reporting period center around process verifications and critical reviews of our selected process sequence. Processes being investigated include texture etching, ion implantation, laser annealing, screen printing, sprayed-on AR coatings, and module assembly.

Three inch diameter 1:0:0 Cz silicon wafers were processed through an NaOH texturizing solution supplied as a starting point. The process was later refined deleting the initial flash etch step of nitric-hydrofluoric-acetic acid solution, simplifying the operation. Cells processed in this manner appeared acceptable. A high volume process for texture etching was conceptualized to meet the 1986 goals.

Several ion implantation runs were made on 3-inch diameter wafers using Extrion 20-200 (IR) and Acceleration, Inc., MP400 (LMSC) implanters. Implant energy level variations were made ranging from 25 to 140 KeV at fluence dosages of 1×10^{15} to 3×10^{15} ions/cm² to determine equipment parameters and cell performance effects. An oxide layer was applied on wafers for implanting at the higher energy levels to reduce bucking drift field effects.

Laser annealing work was carried out using ruby, Nd:YAG, and frequency doubled Nd:YAG lasers. It was determined that energy densities on the order of 1.5 joules/cm² are required for effective annealing of ion implanted wafers using a ruby laser. Best annealing results were achieved using a ruby laser with 4-5 joule beam energy outputs. When passed through a diffuser plate, the beam yielded an annealed spot of approximately 1.5 cm in diameter.

Scaling up laser annealing to accommodate the 3-inch diameter wafers, it was calculated that approximately a 70 joule capacity would be required. Glass rod lasers are available in these sizes; however, ruby rods have a practical size limitation of 7/8" diameter. This would yield approximately 15 joules and would require 6-8 step and repeat indexing with 50% overlap to irradiate a 3-inch diameter wafer.

Screen printing of ohmic contacts was performed using DuPont 7095 and 4021 Ag and Ag/Al pastes, respectively. Patterned grid lines of 0.5 mil thick by 10 mil wide were attained using a 325 mesh s.s. screen. Solderability proved adequate but requires further refinement for improved processing.

Additional spray-on material sources were obtained this period. These are: Owens-Illinois #650 glass resin system, and Allied Chemical Ta solutions (three) which yield Ta_2O_5 after curing. Materials are on order.

Baseline functional cells were fabricated for reference use, which yielded approximately 9% AM1 efficiency. These cells were 3-inches diameter, texture etched, ion implanted, thermal annealed, electroless nickel plated (front and back) and solder coated.

Critical reviews of our selected process sequence were performed with areas defined which required further investigations.

SECTION 2

INTRODUCTION

This is the 2nd Quarterly Report on a process development contract to verify the technological readiness of a selected process sequence from the "as-sawn" Czochiralski grown silicon wafers to the module assembly. The contract started November 1, 1977, and is of a 12 month duration. Our selected process sequence consists of working with 3-inch diameter cells, evaluating the following steps: texturizing, ion implanting, laser annealing, screen printing contacts, sprayed-on AR coating and module assembly.

The 1st quarter's work addressed technology and economic evaluations of the select process sequence. It was concluded that best suited lasers for annealing consist of Argon, ruby and Nd:YAG with wavelengths of .5 μm , .694 μm , and 1.06 μm , respectively. Areas requiring additional significant technology advancements include screened ohmic contacting and module configurations to reduce material costs, and pulse annealing.

This report focuses on process verifications and process critical reviews.

SECTION 3

TECHNICAL DISCUSSION

3.1 PROCESS VERIFICATION

Experimental work commenced this reporting period to verify the adequacy of each process step in the manufacture of functional cells.

3.1.1 Texture Etch

The texture etch procedure as supplied for use in processing as-sawn wafers, called for a flash etch step consisting of a nitric (HNO_3) - hydrofluoric (HF) - acetic acid (CH_3OOH) solution, followed by sodium hydroxide (NaOH) texturizing and a neutralizing step of hydrogen peroxide (H_2O_2) - sulfuric acid (H_2SO_4) rinse. The flash etch step was deemed too costly to meet the overall project cost objectives, and was subsequently eliminated without any apparent deleterious effects on the performance of the cells. The procedure used calls for a 1% solution of NaOH followed by the H_2O_2 neutralizing step and DI water rinses. The detailed procedure was submitted to JPL.

Wafers processed by this modified texture etch process are typified in the SEM photomicrograph shown in Figure 1.

It is also believed that the post texturizing hydrogen peroxide step can be replaced with a fully integrated in-line force-flush water spray system. This would eliminate the use of environmentally undesirable chemicals, simplifying the process and lowering costs.

A projection was made of this texture etch process into one of high volume, high throughput magnitude as would be required for the 1986 production quantities. This high throughput process is described in the following paragraphs.

IR3-6

2000X

60° Tilt

Figure 1. SEM Photomicrograph of Typical Texture-Etched <100> Silicon Wafer Using 1% Solution of NaOH

The hydrogen peroxide neutralizing rinse has been eliminated in our projected process, as we believe that the simpler acid rinse will suffice if followed by multiple DI water sprays. The system defined here is configured for pilot evaluation. In this regard, it provides for excess capability in terms of sodium hydroxide concentration, immersion time and/or processing temperature. Optimum process parameters for an automated system must necessarily be established during a period of trial operation of the actual system. It will be simpler at that time to reduce the value of one or more of the variables than to effect an increase. Impact of this approach on overall cost estimates is minimal. Provisions necessary to minimize downtime and maintain real time process control have been considered.

The large number of wafers to be run through a wet system argues convincingly for processing of the work pieces while they are held in cassettes. Accordingly, we have defined a special open frame cassette configuration for wet processing. The 3/16-inch wafer spacing is retained but the length is increased to approximately 12-inches to hold a quantity of 50 wafers. The cassettes are assumed to be loaded by Waferco and entered directly into the Cellco production sequence at this texture etch station. They are automatically clamped to holding devices attached on 6-inch centers to dual conveyor chains which carry the cassettes through the etching steps. Conveyor speed is assumed at 2 feet per minute. Masking of the wafers by the cassette retaining slots is avoided by a technique proven by the SILTEC Corporation, Cassette Etch Station, Model 2001, where the cassette is slowly rotated on an eccentric longitudinal centerline. This causes the wafers to move back and forth in their retaining slots, exposing the entire surface to the processing liquids. In this application, the rotation is achieved by spur gears on the end(s) of the cassette holders. The gears engage stationary gear racks as the conveyor chain moves. The conveyor path and the several process steps are shown schematically in Figure 2.

The first step in the etching process is an alcohol rinse, agitated by submerged jets to direct the flow between the wafers. Vapors are recondensed and returned to a reservoir which provides makeup alcohol. Cassettes are then carried directly into the etchant tank and through the hot, two percent (for higher etch rate) sodium hydroxide solution. Agitation is similarly provided. Level, pH, temperature and specific gravity sensors control the makeup system. The solution is circulated in reverse flow direction and filtration is accomplished by De-Laval centrifuges which do not require consumable filters or labor intensive servicing. Vapors may be allowed to vent to the atmosphere carrying sodium carbonate salts, which are slightly basic. The next step is a tap water rinse with sufficient acid added to neutralize the drag-out from etching tank. Ten percent of the outflow is brought to neutral pH and discarded to control the salt concentration. Makeup acid and water are added to the remainder which is recirculated. The wafers are then carried through a series

Figure 2. Schematic - Texture Etch Process

of four atomizing spray chambers where they are washed with reverse cascaded DI water. Waste water from the rinse may be used to heat the first spray station through a heat exchanger. This wash water is also reprocessed through filtration and deionizing steps. Finally, the wafers are dried by passing through Freon evaporates. Vapors rising into the hood are recondensed and returned to the system. Displaced water is removed from the Freon to maintain system balance. The cassettes are then fixed in an upright position and disengaged from their holders for transfer to the next operation.

The system will require computer control to maintain the several variables within pre-established limits. Quality of the etch will be sensed by test of the reflectivity of wafers leaving the station with automatic corrective action programmed. It has been suggested by IR that laser induced fluorescent spectroscopy may also be employed to check for contamination levels with automatic correction or shutdown procedures incorporated in the control system.

This texture etch station will process 4 cassettes or 200 wafers per minute. Four parallel stations will be required. Recycling subsystems will be cross-manifolded between stations to minimize downtime. All tanks will be castored and configured for quick-disconnect to allow rapid replacement and offline cleaning and/or refurbishment.

3.1.2 Ion Implantation

Several runs of wafers were processed through the ion implantation step during this period using Extrion 20-200 (IR) and Acceleration, Inc. MP400 (LMSC) implanters. Variations in implant energy levels were made ranging from 25 KeV to 140 KeV to determine equipment parameters and cell performance effects. The high implant levels were performed through an SiO_2 oxide layer to reduce the bucking drift field effects prevalent in implanting impurities into silicon. Fluence dosages of 1×10^{15} to 3×10^{15} ions/cm² were used during this experimentation.

Table I shows some of the specifics of wafers implanted during this period.

A concern in ion implantation is the extent of the bucking current drift field. One method to minimize the drift field is to tailor the impurity profile during implanting. A preliminary equation has been worked out by International Rectifier to be applied to a programmed implant cycle that would vary implant beam energy and time, at constant (maximum) beam current. This would tailor an optimized impurity profile for solar cell structures. The value of such an implant technique is that the desired profile could be obtained without the energy loss accompanying implanting through a dielectric. Also, an improved cost efficiency can be realized through the use of a progressively diminishing beam energy during the implant cycle. A limitation to this work will be the 20 KeV minimum of the Extrion and Acceleration MP400 Implanter equipment. Development of an optimum profile will require equipment with lower (<10 KeV) acceleration capability.

TABLE I
WAFER IMPLANTATION PARAMETERS

Surface Condition	Beam Energy/Dosage	Implanter		Disposition (Intended Use)
		Extrion (IR)	Acceleration (LMSC)	
TE, No Oxide	50 KeV/1 x 10 ¹⁵ 31P	X		Reference/ Laser Anneal
TE, Oxide	125 KeV/1 x 10 ¹⁵ 31P		X	Laser Anneal
TE, Oxide	125 KeV/1 x 10 ¹⁵ 31P 150 KeV/5 x 10 ¹⁴ 11B		X	Laser Anneal
Pol. Oxide	125 KeV/1 x 10 ¹⁵ 31P		X	Laser Anneal
TE, Oxide	125 KeV/1 x 10 ¹⁵ 31P		X	Laser Anneal
TE, Oxide	125 KeV/1 x 10 ¹⁵ 31P 200 KeV/1 x 10 ¹⁵ 11B		X	Laser Anneal
TE, Oxide	140 KeV/2 x 10 ¹⁵ 31P Evap. Alum. BSF		X	Reference
TE, Oxide	140 KeV/2 x 10 ¹⁵ 31P 200 KeV/1 x 10 ¹⁵ 11B		X	Reference
TE, Oxide	25 KeV/1 x 10 ¹⁵ 31P	X		Reference/ Laser Anneal
TE, No Oxide	25 KeV/3 x 10 ¹⁵ 31P 150 KeV/5 x 10 ¹⁵ 11B		X	Laser Anneal
FE, Oxide	65 KeV/3 x 10 ¹⁵ 31P	X		Laser Anneal
FE, Oxide	25 KeV/1 x 10 ¹⁵ 31P Evap. Alum. BSF	X		Reference/ Laser Anneal

NOTE: All Wafers 3" diameter, 1:0:0 Orientation, 7° Angle Implants

3.1.3 Laser Anneal

Laser annealing work was carried out using a variety of ruby, Nd:YAG, and frequency doubled Nd:YAG lasers. Initial work was performed with a conventionally pulsed Raytheon Model SS500 YAG laser and a Q-switched Korad Model KI500 ruby laser.

In evaluating the YAG laser, various combinations of energies, pulse durations, energy densities, and pulse repetition rates were used. It became apparent that at high pulse energies and durations (40 joules/5 msec and 20 joules/2 msec) annealing was feasible. The calculated spot size (illuminated area on the wafer) for power density of 7.75×10^4 watts/cm² at 40 joules was approximately .363 cm in diameter, whereas for the 20 joules pulse the spot size was .406 cm in diameter.

Visual evaluation of the annealed region indicated that the size of the annealed spot was only about 60% of the calculated size. This is understandable in view of the Gaussian energy distribution of the beam. The effective spot size was therefore .22 cm in diameter for the 40 joule pulse and .25 cm in diameter for the 20 joule pulse. This in turn converts to a power density of 2.5×10^5 watts/cm². The usefulness of annealing at these settings was considerably reduced since frequent shattering of the silicon substrate was experienced.

Tests were repeated at low output energies (4-5 joules/.6 msec) to ascertain whether cell damage can be prevented. It was found that at approximately 4.8 joules, effective spot size of .13 cm diameter, and power density of 6.06×10^5 watts/cm², annealing was attained without damage to the wafer. As was the case with high energy settings, when scanning the substrate with the laser, pulse repetition rates had to be kept fairly low (5 pps) to avoid surface damage. To ensure complete annealing during substrate scan, sufficient overlap had to be utilized. A 50%-60% overlap was found to be adequate for this operation.

With a 50%-60% overlap and the small spot size, annealing operation utilizing a conventionally pulsed YAG laser is certainly not an attractive cost-effective technique since it would take hours (due to the slow pulse rate) to anneal a 3-inch diameter wafer. The investigation was also complicated by the fact that in a conventionally pulsed system, the output energy is tied to the duration of the pulse, consequently, the range over which the energy output is varied while the duration is kept constant is limited. This condition precluded evaluation of utilizing high energy pulses (40 joules) at low durations (.6 msec) for the required annealing operation.

It was decided at this time to temporarily suspend the investigations of the conventional pulsed YAG laser and proceed with the Q-switched Korad ruby laser. The ruby laser investigation was performed at the Korad Applications Laboratory on February 24, 1978. The K1500 laser utilized is rated at 15 joules; however, all tests were conducted with 5 joule beam energies at 20 nsec pulse durations. To defocus the beam to the required spot size, a diffuser plate was placed between the laser and the specimen. An extra added advantage of the diffuser plate was its ability to partially transform the Gaussian energy beam to a more homogeneous intensity profile. It was found that when the diffuser plate was placed 1.3 cm from the specimen, an area approximately 1 cm in diameter was annealed. Thermal and four point probe measurements showed that the annealed region was N-type indicating ion activation and V/I readings were 19-20, similar to those obtained with furnace annealed samples.

The annealed specimens consisted of texture etched and flash etched wafers which were implanted with phosphorus ions at a fluence of 1×10^{15} ions/cm² and 125 KeV and 75 KeV, respectively. As seen in Figures 3 through 8, some melting/slumping of the silicon surface was experienced as a result of the annealing operation. The slumping is very evident on the texture etched specimens (Figures 7 and 8) where the pyramidal surface structures were slightly modified. This condition will be evaluated and analyzed based on both calculated and experimental data and parameters.

Figure 3. "Flash" Etched Wafer ^{31}P Ion Implanted
Prior to Laser Annealing. 2000 X 60°

Figure 4. "Flash" Etched Wafer ^{31}P Ion Implanted
After Ruby Laser Anneal at 5 Joules
With Diffuser Plate 1.3 cm from
Sample. 2000 X 60°

Figure 5. "Flash" Etched Wafer ^{11}B Ion
Implanted Prior to Laser Annealing.
2000 X 60°

Figure 6. Texturize Etched Wafer ^{31}P Ion
Implanted Prior to Laser Annealing.
2000 X 60°

Figure 7. Texturize Etched Cell Surface, ^{31}P Ion Implanted After Ruby Laser Anneal With Diffuser Plate 2.54 cm From Sample. 2000 X 60°

Figure 8. Same as Figure 7 Except: Diffuser Plate 1.3 cm From Sample. 2000 X 60°

Small cells fabricated from the ruby annealed samples described above proved unsatisfactory. Figure 9 shows the wafer processed with several .5 x .5 cm cells. Output measurements confirmed poor cell performance. The melt-slumped texture etch pyramidal structures could have contributed to junction structure disorientation. Nevertheless, some useful information was derived from this first experiment and is as follows:

- o Improved homogeneity of the laser beam using a diffuser plate
- o Reflectance of the textured surface as examined by the International Rectifier in-process tester, was 2-3 times greater than the non-remelt state, but still lower by $<1/2$ of flash etched cells.

The technique of forming small .5 x .5 cm cells will be continued to prove feasibility and establish processing parameters and limitations, prior to scale-up to a full sized cell.

Figure 9. Ion Implanted, Laser Annealed Cells

To broaden the investigation, a theoretical analysis was performed for utilization of frequency doubled Nd:YAG or glass lasers for the required annealing operation. A frequency doubler reduces the wavelength of a YAG laser from 1064 nm to 532 nm. The advantages of this approach are quantitatively analyzed and are as follows.

The equation relating the energy and depth of penetration into an absorber for monochromatic electromagnetic radiation is:

$$(1) \quad E = E_0 e^{-\alpha x} \quad \text{or}$$

$$(2) \quad \frac{E}{E_0} = e^{-\alpha x}$$

Where: E_0 = Beam energy incident on the absorber
 E = Beam energy at distance x from the front surface
 α = The absorption coefficient

Because of the shallow nature of the junction in ion implanted solar cells ($<0.5\mu\text{m}$), it is safe to assume that the maximum required beam penetration depth is $0.5\mu\text{m}$. Replacing x by a $0.5\mu\text{m}$ in equation (2), we obtain for a ruby laser wavelength = $.694\mu\text{m}$, $\alpha \approx 2.2 \times 10^3/\text{cm}$.

$$(3) \quad \frac{E}{E_0} = e^{-(2.2 \times 10^3)(.5 \times 10^{-4})} = .90$$

This indicates that the energy of the beam at a distance of $.5\mu\text{m}$ from the front surface is 90% of the energy incident on the wafer. To paraphrase this, only 10% of the energy is deposited in the first $.5\mu\text{m}$, whereas the rest of it is being wasted in the bulk material where it is not required for our application.

Similarly, performing the same calculations for a frequency doubled YAG or glass system, $= \frac{1.06}{2}\mu\text{m} = .53\mu\text{m}$, $\alpha \approx 1.2 \times 10^4/\text{cm}$ we obtain:

$$(4) \frac{E}{E_0} = e^{-(1.2 \times 10^4) (.5 \times 10^{-4})} = .55$$

This indicates that 45% of the incident energy is deposited in the first .5 μm and only 55% is wasted in the bulk material. The implications of this analysis are obvious. If E_a is the energy required to attain annealing to a .5 μm depth, then from the above calculations, it can be seen that the ruby laser has to provide beam energies equal to 10 E_a , whereas the frequency doubled glass system has to provide only 2.22 E_a , a 4.5 increase in system efficiency.

An analysis of energy requirements to attain laser annealing on a single pulse basis is as follows:

- a. Silicon density (d) = 2.33 gm/cm³
- b. Specific heat capacity (c) = .21 cal/gm = .879 joules/gm
- c. Area (A) of a 3 inch diameter wafer = 45.6 cm²
- d. Volume (V) for wafer depth of .5 μm = (45.6) (.5 $\times 10^{-4}$) = 2.28 $\times 10^{-3}$ cm³
- e. Weight (W) of volume in step (d.) = Vd = (2.28 $\times 10^{-3}$) (2.33) = 5.3 $\times 10^{-3}$ gm

The energy required to raise the temperature of the specimen to approximately 1400°C (predicted annealing temperature) assuming negligible heat loss within a 10-20 nsec period is:

$$(5) E = W c \Delta T$$

Where: ΔT = The difference between required temperature and room temperature

$$(6) E = (5.3 \times 10^{-3}) (.879) (1375) = 6.41 \text{ joules}$$

Since for a ruby wavelength only 10% of the energy is deposited within the required .5 μm , the ruby system must provide $6.41 \times 10 = 64.1$ joules of energy, for 100% absorption, to anneal a 3 inch diameter wafer with a single pulse. A more realistic approximation for absorption is 95%; therefore, the ruby laser would have to provide 67.5 joules of energy.

For a frequency doubled glass system where 45% of the incident energy is deposited in the first .5 μm , the required energy for 95% absorption would be:

$$(7) \quad E = (6.41) (2.22) \left(\frac{100}{95}\right) = 14.98 \text{ joules}$$

The disadvantage of the frequency doubled system is that the conversion efficiency of a doubler is approximately 20%. Consequently, to attain 14.98 joules of energy, the glass laser must be capable of providing $14.98 \times 5 = 74.9$ joules.

The main limiting factor in the energy produced by a laser is the size of the rod. Vendor contacts (Korad, Union Carbide) revealed that 7/8-inch diameter appears to be the present practical upper limit for the size of a ruby rod. A ruby laser equipped with a rod of this size will provide approximately 15 joules of energy. This is not sufficient for single pulse annealing of the wafer; however, it is still a practical approach, since annealing can be attained through a step and repeat process requiring approximately 6-8 pulses. This would be accomplished rapidly since a system with a 20 ppm repetition rate can be obtained.

The advantage of the glass laser is that unlike the ruby, glass rods of extremely large size can be manufactured. With these rods, lasers of very high energy outputs can be built. At sufficiently high energy levels, annealing of a 3 inch diameter wafer could possibly be attained by a single laser pulse. In addition, work is currently being done to improve the conversion efficiency of a frequency doubler. This work will be carefully followed by LMSC and I.R.

Subsequent laser annealing work was carried out at the application laboratories of Apollo Lasers, Los Angeles, Ca., Quanta-Ray, Mountain View, Ca., and Quantronix Corporation, Smithtown, New York. A 1 joule ruby laser operating at half power was utilized for most of the work performed at Apollo. Two samples were prepared utilizing a 4 joule ruby laser which was otherwise unavailable for evaluation. At Quanta-Ray, investigations were carried out with an Nd:YAG laser coupled with a frequency doubler or as it is also called, a second harmonic generator (SHG). This accessory reduced the Nd:YAG wavelength from 1064 nm to 532 nm at an energy level of 270 millijoules. Two wafers were sent to Quantronix Corporation where they were annealed with a Model 116 Nd:YAG laser.

Silicon wafers annealed at Apollo (ruby) and Quanta-Ray (Nd:YAG-SHG) covered a broad spectrum of variables. These included wafers that were texture etched, flash etched, and polished. The wafers were implanted at energy levels of 25-125 KeV, 1×10^{15} ions/cm², and at 65 KeV, 3×10^{15} ions/cm², the latter implanted through a 1000Å oxide layer. The two wafers sent to Quantronix (Nd:YAG) were texture etched and implanted at 125 KeV, 1×10^{15} ions/cm².

To attain increased efficiency from the lasers, experiments were carried out where some wafers were heated prior to annealing. At Apollo, a hot plate with a 500°C temperature capability was utilized; however, the exact temperature at the wafer surface could not be ascertained for lack of applicable measurement equipment. A different hot plate was used at Quanta-Ray where it was determined with an Alnor type 4000A Pyrocon that the wafer surface reached a temperature of 360°C.

With the exception of the 4 joule Apollo laser, all other lasers evaluated were of low energy, yielding fairly small spot sizes (annealed areas). The difficulty in performing the required evaluations with these lasers was due to the necessity of going to a lengthy step and repeat process to attain annealed areas of meaningful size. To ensure complete coverage of the surface under investigation, a proper beam overlap has to be utilized in conjunction with

an X-Y positioning table to precisely place the wafer under the laser beam. Since an X-Y positioning table was not available, the wafers had to be moved manually. Often, this led to improper positioning and/or overlap with subsequent creation of unannealed "islands" within the annealed region, coupled with insufficient activation of the implanted impurity ions. This condition caused high surface resistivity as indicated by V/I readings. The latter phenomenon was observed on a good number of wafers which when tested yielded V/I readings that were higher than those obtained with furnace annealed samples.

On wafers where unannealed islands were not observed, V/I readings were comparable to those obtained with furnace annealed samples - typically 20-25. On the wafers that were preheated prior to annealing, a larger heat zone was evident after laser pulsing. This condition generally facilitated attainment of a proper overlap resulting in lower V/I readings as compared to unheated samples. Heating was not required with a 4 joule Apollo ruby laser where a single pulse annealed an area of approximately 1.5 cm in diameter with V/I readings comparable to furnace annealed samples. Table II summarizes some of the work performed at the subject laser facilities.

In reviewing all the work performed by LMSC/IR on laser annealing, it is evident that the best results were obtained using high energy lasers such as the KORAD K1500 or the Apollo lasers. These lasers were used with 5 and 4 joule beam energies, respectively. Both laser systems are currently unavailable for further evaluations. At this time, LMSC is pursuing the necessary overhaul of an in-house ruby laser rated at approximately 3.5 joules. The ruby rod in this laser was previously damaged and has been sent to Union Carbide for polishing. In addition, inquiries are being made with various laser companies for evaluation of high energy frequency doubled YAG lasers.

To attain information on distribution of implanted phosphorus ions as a function of depth before and after laser annealing, contacts were made with ARL (Applied Research Laboratories) of Sunland, Ca., and Aerospace Corporation, Los Angeles, Ca. Both firms have the required SIMS and ion microprobe equip-

TABLE II

SUMMARY OF LASER ANNEALING WORK

Wafer Implantation Parameters	Wafer Surface	Laser Type	Hot Plate	V/I		Comments Relative to Laser Annealed V/I Readings
				Laser Annealed	Furnace Annealed	
50 KeV 1×10^{15} ions/cm ² (Run IR 100)	Texture Etched	Quanta-Ray Nd:YAG with SHG	X None	32 40-50	32-33	Narrow annealed region when used without hot plate
25 KeV 1×10^{15} ions/cm ² (Run X-1)	Texture Etched	↓	X	38	23-25	Proper overlap was not attained
25 KeV 1×10^{15} ions/cm ² (Run X2)	Flash Etched	↓	None	28-36	21	↓
65 KeV/1000 Å Oxide Film 3×10^{15} ions/cm ² (Run 158)	Flash Etched	Apollo - 4 Joule Ruby	None	25	21-25	Annealing could have been improved with utilization of a diffuser plate to homogenize the beam
125 KeV 1×10^{15} ions/cm ² (Run 154 B)	Texture Etched	↓	None	24-26	Unavail- able	↓
125 KeV 1×10^{15} ions/cm ² (Run 154 B)	Texture Etched	Apollo - 1 Joule Ruby	X	22	Unavail- able	Low V/I obtained at the point of highest melt
125 KeV 1×10^{15} ions/cm ² (Run 153)	Texture Etched	Quantronix Nd:YAG	None	27-40	17.7- 19.0	Presence of unannealed islands

ment which are capable of performing the required analysis. In addition, ARL has a quadrupole mass analyzer which they feel is ideally suited for this application. Sample wafers will be sent to both companies for a feasibility study.

To gain some insight into the changes occurring in the wafer during the laser annealing process, as a function of absorption depth, a theoretical evaluation was performed for a ruby laser and a frequency doubled Nd:YAG laser. Lambert's law (2) again provided the basis for this evaluation.

$$(2) \quad E = E_0 e^{-\alpha x}$$

Where: E_0 = Beam energy incident on the absorber
 E = Beam energy at a distance x from the front surface
 α = The absorption coefficient for a particular wavelength

Equation (2) was modified to yield information on the wafer temperature at a distance x from the front surface at increments of $.05 \mu\text{m}$. The modified equation is as follows:

$$(8) \quad T = \frac{E_0 e^{-\alpha x_n} - E_0 e^{-\alpha x_{n+\kappa}}}{A t d c}$$

Where: T = Temperature ($^{\circ}\text{C}$) of a $.05 \mu\text{m}$ thick section between the distance x_n and $x_{n+\kappa}$ from the front surface
 x_n = Any distance from 0 - wafer thickness
 $x_{n+\kappa} = x_n + .05 \mu\text{m}$
 α = $\sim 2.2 \times 10^3/\text{cm}$ (ruby); $\sim 1.2 \times 10^4/\text{cm}$ (Nd:YAG with SHG)
 A = Area
 t = Thickness = $.05 \mu\text{m}$
 d = Density = 2.33 gm/cm^3
 c = Specific heat capacity = $.879 \text{ joules/gm}$

To simplify the equation, it was assumed that heat losses are negligible within a 10-20 nsec period. Another factor not taken into account due to

lack of such data is the change of the silicon absorption coefficient with increase in temperature. This will be incorporated in future theoretical analysis as soon as the information becomes available.

Data derived from equation (8) is summarized in Figure 10. It is shown that for a ruby wavelength, the laser energy density must be greater than 1.3 joules/cm² to attain some degree of surface melting as indicated by the dotted line at 1410°C (silicon melting point). At 1.5 joules/cm², 1.7 joules/cm², 1.9 joules/cm², melting occurs to a depth of approximately .63 μm, 1.20 μm, and 1.71 μm, respectively. For a frequency doubled Nd:YAG system, considerably higher surface temperatures are reached. This is due to the shorter wavelength of the frequency doubled Nd:YAG system with subsequent deposition of 45% of its energy in the first .5 μm of the silicon wafer as opposed to only 10% for the ruby wavelength. The numbers in parenthesis in Figure 10 represent the energy density levels incident on the silicon wafer after the Nd:YAG wavelength was frequency doubled by a second harmonic generator with a 20% conversion efficiency, i.e., 1.9 joules/cm² at λ = 1064 nm is converted to .57 joules/cm² at 532 nm. The depth of melting of the silicon for converted energy densities of .57 joules/cm², .51 joules/cm², .45 joules/cm², and .39 joules/cm² are .74 μm, .65 μm, .55 μm, and .43 μm, respectively.

3.1.4 Screen Printing

Screen printing was performed at the LMSC Microelectronics Center using DuPont 7095 Ag paste for the cell front contacts. DuPont 4021 Ag/Al paste for the back was applied on blank wafers. A Precision Systems Co., Model 150, screen printer was used in conjunction with 325 mesh stainless steel screens. Typical machine settings consisted of:

- o Squeegee Speed: 1.25-in/sec
- o Snap-Off: 0.028-in

Figure 10. Temperature vs. Distance (x) from the front surface of a Silicon Wafer for Q-switched Ruby and Frequency Doubled Nd:YAG Lasers at various beam energy densities,

Firing of the screened/baked film was performed in a tube furnace, air atmosphere, for a duration of 45 seconds at a temperature of 650°C. Film thicknesses of 0.5 mils were attained with 10 mil wide grid lines.

Solderability experiments were conducted on the as-fired front contacted cells using 30 ga tinned, stranded hookup wire. Soldering was performed with a 50W temperature controlled solder iron, Sn62 solder (QQ-S-571) and Kester 1544 Flux (Mil-F-14256). Solder wetting was adequate, but requires some refinements for improved processing, such as solder dipping or mild HF etch before soldering.

3.1.5 Sprayed-On AR Coatings

Two other sources for AR coating materials, besides Dow-Corning (ARC material), were established. Owens-Illinois has a glass resin system which, according to the literature, has excellent stability in UV, excellent optical transmission properties, hardness and weatherability. The glass resin system of primary interest is the O-I #650, which is composed of approximately 89% SiO_2 in the final deposited form. Some of the coating applications claimed by O-I for this material include: aircraft acrylic and polycarbonate transparency coatings, plastic windows to increase impact strength, and anti-abrasion coatings. These are desirable properties which might prove useful for cell applications.

Allied Chemicals, Morristown, New Jersey, is the other new source, and they have formulated three different Ta source solutions for our evaluation. They were developed for spin-on, dip, and spray-on applications. The materials are of low viscosity and solids and when cured at approximately 175°C, form essentially Ta_2O_5 . These materials are on order.

Closure was obtained with the Zicon Corporation in determining accessory parts required for spraying the AR coatings using the In-Line Autocoater. Pressure gas for dispensing the spray materials will be N_2 , suitably adapted with appropriate regulation.

3.1.6 Baseline Functional Cells (Control)

Some initial cells were completed this period for use as reference in comparison with other processing steps of our selected sequence. The process steps used were as follows:

- o 3-inch diameter wafer, as-sawn, .5-5 Ω cm
- o Texture Etched with NaOH
- o Ion Implanted, 50 KeV, 1×10^{15} ions/cm² ³¹P, 7° Tilt
- o Thermal Annealed, 900°C/15 minutes, N₂ 2000 cc/min
O₂ 200 cc/min
- o Screened-on Grid Resist
- o Electroless Nickel Plated, Front and Back
- o Resist Removed
- o Edge-etched
- o Solder Dipped

Outputs of cells were measured using a Spectrolab X-25 Solar Simulator. Output values were in the 7% AM0 (9% AM1) efficiency range. Figure 11 shows typical I-V curves on two of these first run cells.

Comments on the Figure 11 cell output curves are as follows:

- a. Isc of 1.28A at AM0 represents a reasonably good response considering the absence of other optimized conditions. Good Isc results may be attributed to retention of high material lifetime surface radiation reflectance.
- b. Low Voc (.5V) can be attributed to a bucking field in the region between the silicon surface and the plane at which the maximum phosphorus concentration exists. It is not expected that the thermal

Figure 11. Output Curves of Two Baseline Cells

annealing would have modified the implanted impurity profile sufficiently to eliminate the profile induced bucking field.

- c. The curve factor on the test cells were below desirable levels. The curve slope indicates higher than desirable series resistance. Contributors to this condition could be:

- (1) Insufficient surface (implant dosage) impurity concentration. An increase over the as-used 1×10^{15} ions/cm² appears to be warranted.
- (2) High contact resistance of the metal grid at the surface because of low cell surface concentration. The curve knee (and dark reverse currents) indicates a possible inadequacy in achieving total annealing.

There are currently other cell runs in process to form baseline, representative acceptable cells. These have been implanted at 25 KeV, 1×10^{15} ions/cm² ³¹P, with evaporated aluminum for back surface field.

3.1.7 Wafer Handling Equipment

As a matter of interest to those involved in the LSSA Project, SILTEC Corporation, Menlo Park, California, has developed wafer handling equipment for their own in-house high volume production of wafers which is now available on the market.

Two recently developed items of SILTEC equipment are of particular interest. The first of these is an automatic machine for the etching of wafers while they are held in a cassette. This unit, Model CES 2001 Cassette Etch Station, utilizes a unique transfer assembly with programmed control to immerse a cassette of wafers in temperature controlled etchant followed by rapid transfer to a quench tank and return to start position. An interesting feature of the machine is that the cassette is rotated about an offset longitudinal axis while it is immersed. Wafers are rolled back and forth along their

separating slots in the cassette by the rotation, eliminating any chance for masking of the edges from the etchant. The cassette holding device limits the travel of the wafers within the cassette.

This machine, handling one 25 wafer cassette at a time, is capable of etching a maximum of 4500 wafers per 8 hour shift. While this is, of course, far short of the 1986 production volume requirements, it does suggest that the basic process can be modified as necessary and scaled-up for automatic high volume texture etching of wafers for solar cell manufacture.

The second SILTEC machine development was observed in operation. This was a Model ASP 2630 Automatic Resistivity and Thickness Sorter, the machine is characterized by a modular design similar to that which has been proposed by LMSC for solar cell and array production equipment. SILTEC has developed a cassette loader/unloader module which can be easily bolted to either side of a rail type machine bed. Four of these units, two on each side, are positioned at the lead end of the bed. Wafers are unloaded from these and transferred to a cleated conveyor belt for resistivity and thickness testing at sequential modules mounted to the rear of the bed. A control panel module is mounted in this area at the front of the bed. Tested wafers are sorted into as many as 12 categories and reloaded by category into as many as 24 additional cassette loading modules arranged on either side of the central conveyor belt. The entire process is computer controlled and is capable of processing 2500 wafers per hour. While this testing may become necessary to optimize the cell manufacturing system, the wafer handling system is of greater interest. The advantage here is that the adaptation of this equipment to other processes requires only the development of the appropriate additional modules which can replace the testing modules presently used. It is easy to visualize laser anneal and solar simulation testing using this equipment as a base. The addition of vacuum chambers with interlocks might provide a means for high throughput in ion implantation. The versatility of a modular approach to solar cell and module manufacture is amply demonstrated in this equipment.

3.2 CRITICAL REVIEWS

3.2.1 Texture Etching

The wet chemical process for texture etching using 1%-2% solution of hot sodium hydroxide (NaOH) to anistropically etch 1:0:0 oriented single crystal silicon cells appears by consensus of participants in the LSSA project to be the best suited to meet the 1986 low cost goals.

The present process steps call for an initial alcohol rinse followed immediately by the NaOH etch and then neutralized and washed by immersion in $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ and cascade water baths, respectively. In our process verification phase, it was found that the heretofore accepted flash etch step of $\text{HF}/\text{HNO}_3/\text{CH}_3\text{OOH}$ was not required. The processing of the cells through the etch and rinse steps in cassettes appears adequate to achieve the high throughput requirements.

It is believed that post etch processing could also be simplified. The $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$ and cascade water wash steps could be replaced by a force-flush water wash system. Force flushing could be performed with wafers still in the cassettes using a series of spray nozzles set at different angles to assure 100% flushing action. Recirculation of reclaimed water might offer further benefits. Water spray cleaning equipment for silicon wafers is commercially available.

It is our conclusion, that a hot NaOH texture etch used directly on alcohol wetted, as-sawn wafers, and followed immediately by a series of water spray-rinses would be technically feasible and cost-effective for improving the texture etch process.

Major areas of investigation still requiring significant development in order to meet the 1986 cost goals are:

- o In-process monitoring of etch solution, textured wafer reflectivity, rinse solution pH, etc.

- o Automatic inspection for process uniformity and product quality
- o Etch and rinse solution disposal or reclamation
- o Equipment automation design and integration of monitor feedback loops

3.2.2 Junction Formation by Ion Implantation and Laser Annealing

Present conventional techniques of junction formation such as, POCL, spray or spin-on doping with subsequent redistribution, and solid source diffusion have been evaluated and considered generally deficient due to the materials costs, process complexity, toxic chemical disposal problems, relative high energy consumption and difficulty of automation and monitoring controls.

Ion implantation appears the strongest candidate for the ultimate low-cost, high efficiency doping of solar cells. Present furnace annealing and ion activation requirements have the same high temperature furnace problem of automation as above. However, toxic furnace gases and their associated disposal are eliminated. Use of expensive dopant gases for ion implantation is very low and essentially 100% utilized so disposal poses only a small problem. Also, of crucial importance is the high degree of process and impurity implant control inherent in the ion implant process, which can yield, potentially, the higher efficiency cells than diffusion processes.

Technology and industry information point to an achievable high beam current, high throughput implanter capable of meeting the required 1986 goal of economy and product quality. Development of a 100 ma system, which is considered feasible within the 1986 time frame, will lead to implantation process times of less than 2 seconds, limited only by wafer handling and thermal shock considerations.

When using beam energies of ~ 10 KeV, a concern of ion implantation is the formation of a bucking drift field which occurs in the region from the silicon

surface down to the region of maximum implanted impurity concentration. This is generally caused by the modified gaussian impurity distribution of the particular species being implanted. Two common techniques to minimize this effect are now in use, namely, implantation through an oxide or nitride, and reduction of acceleration voltage to a level (~ 10 KeV) at which the distribution peak (R_p) occurs at or very near the cell surface. A third method, mentioned in Section 3.1.2, also merits consideration, and has the potential advantages of better energy utilization, higher throughput, and an improved "tailored" doping profile. This method is profile tailoring by time programming of the accelerating voltage while maintaining the current constant.

Reduction of the annealing process time and energy by use of pulsed energy beams (electron beam or laser) appear as distinct possibilities. The laser annealing method of effecting electrical activation of ion implants is beginning to produce practical results of interest in device fabrication. Our work indicates that new approaches to optic design for energy coupling to the irradiated specimen will be necessary in order to optimize energy transfer and achieve process control. A significant advantage of laser annealing over a straight thermal process is the discovery that this method can virtually eliminate lifetime reducing defects introduced in these (diffusion accompanied) processes.

The two principal candidate laser systems, by our estimates, are the TEM₀₀ mode Ruby (694 nm) and the frequency doubled YAG (532 nm); both of these, however, produce radiation patterns that require modification (via optical means) for the attainment of a uniform energy density distribution pattern.

One of the potential limitations of laser annealing was discussed at a recent seminar in Washington, D. C., on laser annealing of silicon and gallium arsenide by Oak Ridge National Labs and Bell Lab investigators. The consensus of opinion was expressed, that to achieve annealing with a Q-switched laser (i.e., laser pulses in the nanosecond range) some melting of the silicon sur-

face has to result. This is in agreement with our previous experimental data (Figures 6, 7, and 8), and will be further evaluated in our ongoing experiments. If verified, some loss of the texturizing AR effect must be anticipated. Also, effects on the junction are not yet known.

In summary, ion implantation and pulsed energy (laser) appear strong candidates to meet the 1986 objectives of high throughput, low materials cost, low energy/peak watt expended, process repeatability and fewest toxic by-products.

Major areas for investigation in ion implantation and laser annealing still required in order to meet the 1986 objectives are:

- o Ion implantation junction profiling by beam energy programming
- o Development and fabrication of a high beam current (50-100 ma), high throughput, dedicated ion implanter
- o Equipment parameter definition for design/development and fabrication of a high power, high throughput dedicated laser system
- o Laser annealing of the silicon wafer while it is still at elevated temperature ($\sim 750^{\circ}\text{C}$) after furnace firing of a back contact (forming both ohmic contact and back surface field) - This would greatly reduce the laser beam energy required for annealing.
- o Process interdependence data of the relationship of wafer surface melting vs. junction movement vs. reflectivity vs. AR coating
- o Laser beam control (optic) to improve beam homogeneity of energy transfer to wafer surface

3.2.3 Screen Printed Contacts

It is our conclusion that the screen printing process, with even presently available printing equipment, can readily meet process cost goals as a production system. Typical of well-designed, high throughput equipment is the Universal Company in-line cassette fed system, engineered to process 1500 wafers/hr, including screening one side and furnace firing. This system is readily adaptable to scale-up for substantially higher rates (as required), well within feasibility for program target objectives.

Printed silver composition contact patterns (a proven ohmic contact system) are obviously more costly as a metallic material than electroless nickel; but as part of a total metallization system, they are attractive for their high throughput potential and low process handling cost.

There is general recognition by principal investigators on the sensitivity of the firing temperatures on Ag penetration into the silicon with the risk of junction shorting. However, through closely controlled processing, high throughput and yields can be achieved. The greatest concern in the use of Ag paste systems is the relative high cost/watt of materials, with estimates ranging from \$.05 to \$.15/watt.

There is also general recognition that other conductive pastes using copper or aluminum would present processing and quality problems due to their high affinity to oxidation. Silver over-printing on aluminum has been performed but not without its drawbacks, such as contact resistance and adhesion problems.

Significant development is still required for screen printed contacts in the following areas:

- o Reduction of the amount of silver required for back contacting with special emphasis on reduced thicknesses in combination with a secondary add-on conductor, such as solder

- o Optimized patterning of the copper interconnect and the silver back contacts maintaining high performance efficiencies at reduced costs
- o Improved front screen-on fine-line resolutions ($<0.005''$) to increase cell active area
- o Performance data on long life projections of screened contacts

3.2.4 Spray-On AR Coating

Spray coating of the AR film presently shows promise of an economical way to enhance the cell efficiency with a reduction in material cost and process time over presently used evaporated silicon oxide or silicon nitride coatings. Equipment for spraying is presently available which exhibits the potential for high throughput.

Tantalum Pentoxide (Ta_2O_5) is of special interest under this contract as a candidate for spray-on application. Unfortunately, due to the limited availability of data and responsiveness from suppliers, this cannot be properly assessed during this reporting period. Standard material obtained in powder form is of excessively large particle sizes, 25 to 34 microns, which precludes its use without reducing the size to the $<.1$ micron range. The material is insoluble in the most common solvent systems; an alternative method of application is as a mixture with a suitable binder, such as a glass resin matrix. When spray-dispensed, there is sufficient adhesion to permit low temperature firing. Due to the $1470^\circ C$ melting point of Ta_2O_5 , surface fusion as a final cell process step is totally unacceptable. Efforts are underway with suppliers to identify and obtain appropriately formed material.

Other spray-on coating systems have become known during the course of this investigation which offer good promise for low-cost processing. These are: ARC, an SiO_2 matrix system developed by Dow Corning, and a glass resin system developed by Owens-Illinois. These too will be assessed for their technical and economic adequacies in subsequent reporting periods.

3.2.5 Module Assembly

The LMSC module design, which is, by direction, the baseline configuration for this contract, has been examined critically for its ability to satisfy the LSSA requirements. There is no doubt that the assembly of this module can be almost completely automated. Production rates can be achieved and readily maintained at a reasonable investment in capital equipment. However, the high costs of the primary structural materials, the superstrate glass panel and the aluminum frame, will not meet the 1986 project goals. These materials cannot be appreciably reduced through either economy of scale or technological development. Therefore, it must be concluded that this module design can survive only if the Array Encapsulation Task fails to produce a less expensive combination of materials with satisfactory performance and/or if the LSSA cost objectives are modified.

3.3 PROCESS DESCRIPTIONS

Detailed preliminary, manufacturing process procedures were prepared for texture etching, ion implantation, and thick film printing and firing.

SECTION 4

CONCLUSIONS

- 4.1 Texture etching of 1:0:0 Cz silicon wafers without an initial flash etch step yields acceptably prepared surfaces, thereby simplifying the process.
- 4.2 It is also concluded that the post texture etching hydrogen peroxide solution step can be replaced by a series of H_2O force flushing neutralizing steps.
- 4.3 Surface melting using wavelengths encountered with ruby (694 nm), Nd:YAG (1064 nm) and frequency doubled Nd:YAG (532 nm) must be attained in order to achieve annealing.
- 4.4 Energy densities required to achieve annealing vary depending on the laser wavelength and its relationship to the absorption coefficient of silicon. For example, with ruby lasers ($\lambda = 694$ nm) an energy density on the order of 1.5 joules/cm^2 is required.
- 4.5 Ruby and frequency doubled Nd:YAG lasers rated at 70 joules would provide single pulse annealed spot sizes of 3 inches diameter. However, availability of practical ruby rod sizes is limited to 7/8" diameter, which yields approximately 15 joules energy and would require step-and-repeat annealing to accommodate a 3-inch diameter size wafer.

PROGRAM PLAN STATUS

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

PROGRAM PLAN

Page 1 of 3

PROGRAM PLAN

Page 2 of 3

MODEL	PLAN	TITLE	PREPARED BY:	DATE
ISSUE NO.	REFERENCE	PH 2, AUTOMATED ARRAY ASSEMBLY - Contract 954898	M. Lopez	12-6-77
	CDRL Item 2(a)		APPROVED BY:	DATE

PROGRAM PLAN

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MODEL	PLAN	TITLE	PREPARED BY:	DATE
ISSUE NO.	REFERENCE CDRL Item2(a)	PH 2, AUTOMATED ARRAY ASSEMBLY - Contract 954898	M. Lopez	12-6-77
			APPROVED BY:	DATE

	1977				1978								
	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov
6.0 ARRAY AUTOMATION PLAN													
<u>TECHNICAL DOCUMENTATION</u>													
a. Process dev & program plans		DRAFT	APPROVED										
b. Matls, supply & process specification & procedures													
c. SAMICS													
d. Monthly tech progress report													
e. Quarterly report													
① Abstract													
② Report													
f. Final report													
① Draft													
② Approved final													
g. New technology													
<u>MEETINGS AND WORKSHOPS</u>													
a. Program Review (at LMSC)													
b. Project Integration (at JPL)													
c. Workshop													
d. Verification hardware													