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

Quarterly Report No. 1

By
J. S. Katzeff
M. Lopez

July 1980

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

Lockheed Missiles & Space Company, Inc.
Sunnyvale, California

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

QUARTERLY REPORT NO. 1

JULY 1980

Prepared By

J. S. Katzeff
Principal Investigator

M. Lopez
Project Leader

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

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.

ABSTRACT

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

A Q-switched Nd:Glass laser system is used operating in the 1064 (regular) and 532 (with frequency doubler) nm wavelengths. The laser output is in excess of 30 joules with a 20-50 ns pulse duration.

Material used in this investigation is 3-inch diameter CZ silicon, P-type, 0.014 inches thick, 10 Ω-cm resistivity, <100> orientation. Three wafer surface conditions are being evaluated in this pulse annealing investigation: chem-polished, texture etched, and flash etched.

Annealing was performed with and without beam homogenization. Both modes showed excellent lattice recovery from the implant-induced damage as analyzed using Rutherford Backscattering techniques. Homogenization of the beam was performed using a fused silica rod configured with a 90° bend. The unhomogenized annealing was performed using a plano-concave lens.

Fabrication of laser annealed cells using both modes is forthcoming.

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SECTION 1

SUMMARY

This report describes the first quarter results on a contract to evaluate large spot size pulsed laser annealing of ion implanted silicon wafers for junction formation on solar cells. A second objective is to determine the feasibility and requirements for a laser system to anneal 3-inch dia. wafers at a rate of 1 wafer per second.

The laser used in this contract is a Q-switched Nd:Glass laser, >30 joule output, with a 20-50 ns pulse duration. The laser is equipped with a frequency doubler, and is capable of delivering a spot size in excess of 25mm diameter in the energy densities of interest.

Materials utilized in this investigation consist of 3-inch diameter, CZ silicon wafers, boron doped, 0.014 inches thick, with a nominal base resistivity of 10 Ω-cm and a <100> orientation. Three wafer surface conditions (chem polished, flash etched, and texture etched) are being evaluated to determine laser annealing effects and quality of solar cells produced. Implant dosages are 2.5 and 4 x 10^{15} ions/cm^2 at 5 and 10 KeV levels. Process variables to be evaluated in this contract are as follows:

- o Anneal with $\lambda = 1064nm$
- o Anneal with $\lambda = 532$ nm
- o Anneal with a mixture of λ = 1064nm
532nm
- o Implant level 10 KeV
- o Implant level 5 KeV
- o Single pulse anneal
- o Multi-pulse anneal
- o Raw beam anneal
- o Homogenized beam anneal

Annealing evaluations were performed with the laser operating in a TEM_{oo} output mode. To homogenize the output, the laser beam was passed through a light guide diffuser which consisted of a fused silica rod with a ground input face configured with a 90° bend. To evaluate "raw" beam effects on the silicon wafer, the homogenizer was removed and a plano-concave lens was inserted in the path of the laser beam. This was done to spread out the beam for obtainment of the required energy density.

Initial analysis of annealed surfaces was performed with Rutherford Backscattering Techniques. Tests revealed excellent lattice recovery from the implant-induced damage for both homogenized and raw beam annealing modes. Fabrication of laser annealed solar cells is forthcoming.

SECTION 2

INTRODUCTION

This is the first quarterly report on a process development contract to evaluate the merits of large spot size pulsed laser annealing of phosphorus implanted CZ silicon wafers. Projections will also be made to determine the feasibility and requirements for a laser system to anneal 3-inch diameter wafers at a rate of 1 wafer/sec to meet the high thruput goals of the 1986 LOW COST SOLAR ARRAY PROGRAM.

The contract has an effectivity date of 5 March 1980 and is of a 12 month duration.

The general plan is to purchase CZ silicon P-type wafers from Applied Solar Energy Corporation (ASEC). This will be followed by phosphorus ion implantation by SPIRE Corporation. Ohmic contacting of the cells will be performed by vacuum deposition of titanium, palladium and silver, concluding with a multi-layer anti-reflective coating. Some cells will be processed with a boron ion implanted, electron beam annealed, back surface field. Also, wafer surface conditions consisting of polished, texture etched and flash etched will be evaluated with respect to the quality of cells produced using laser annealing.

Control cells will be fabricated for comparison with laser annealed cells. These control cells will be similar to the evaluation cells except for the substitution of furnace annealing instead of laser. Some control cells will also be made with $POCL_3$ diffused junctions.

The laser system used on this contract is a >30 joule Q-switched Nd-glass laser equipped with a frequency doubler. The pulse duration is 20-50 nsec with a repetition rate of 4 pulses per minute (PPM) and a beam diameter of >25 mm. The equipment is shown in Figure 1. The optical path of the beam is shown in Figure 2.

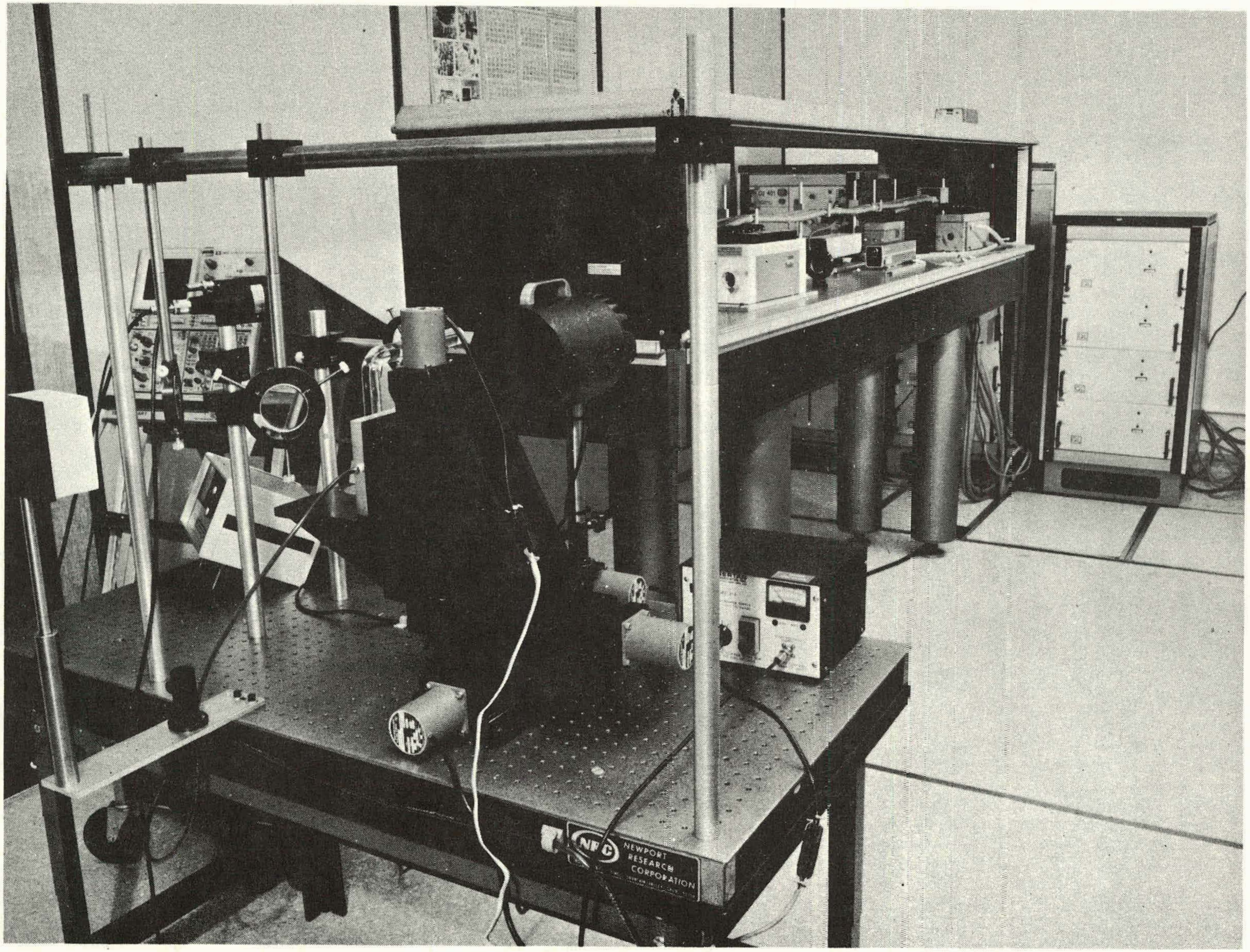


Figure 1 - Laser System

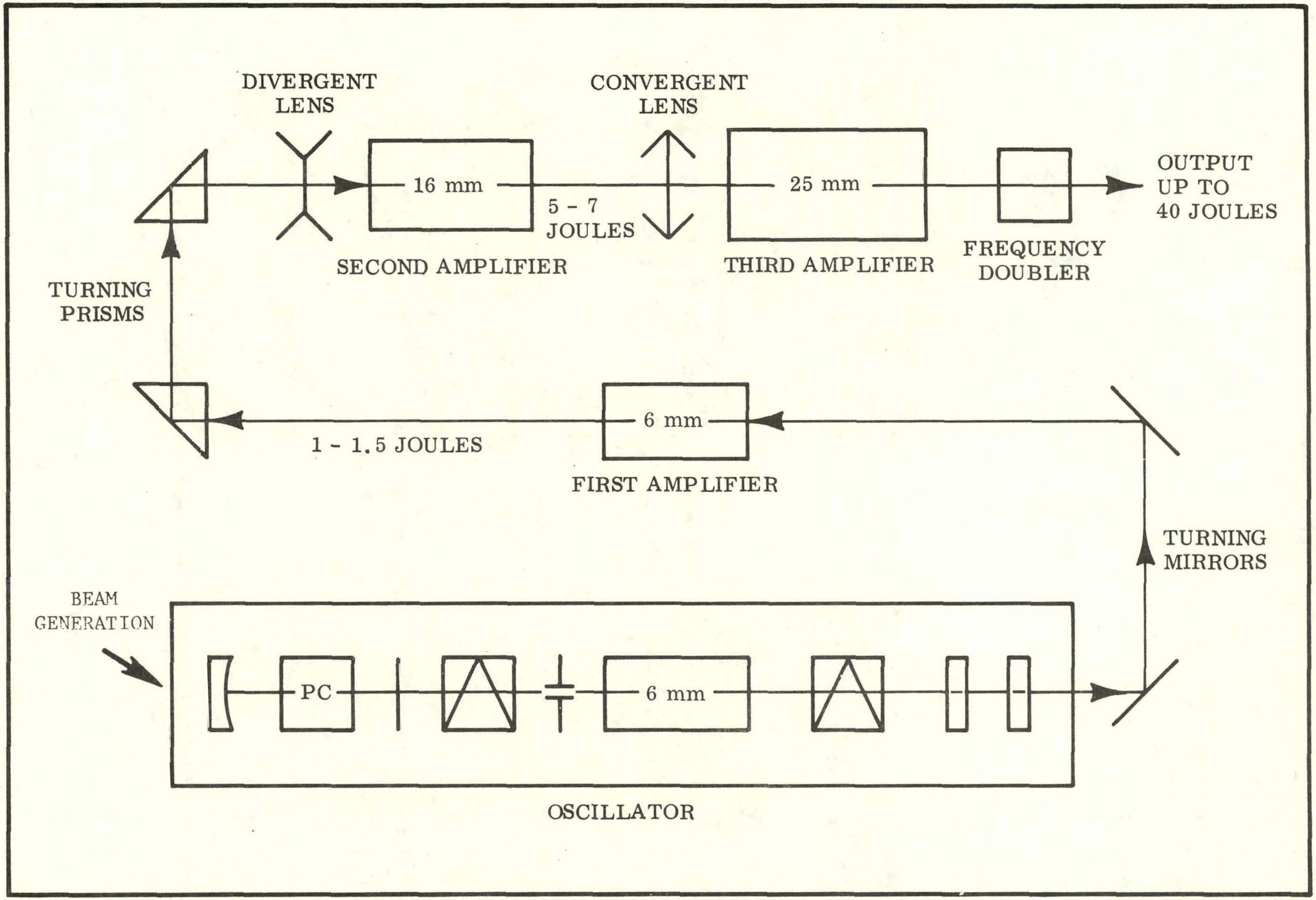


Figure 2 - The Optical Path of the Laser

SECTION 3

TECHNICAL DISCUSSION

3.1 WAFER MATERIAL

The wafers used on this contract are of the following specifications:

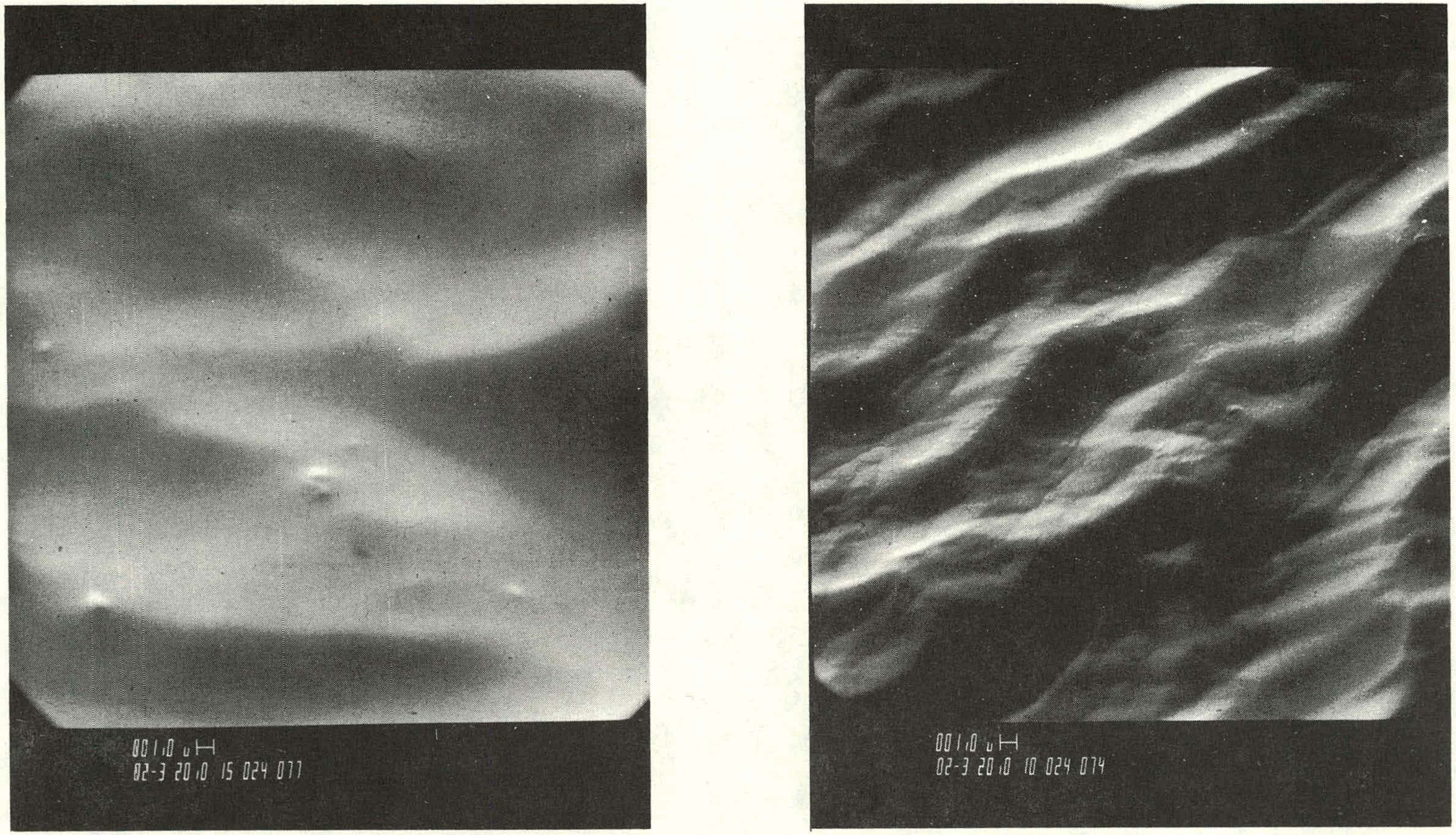
- o 3-inch diameter, boron doped, CZ silicon <100> orientation
- o 0.014 ± .002 inches thick
- o 7-14 Ω-cm resistivity
- o three surface conditions: texture-etched, flash-etched, and chem-polished

The texture etching and polished surface processes are pretty well defined. There is some concern on pulsed laser annealing of texture etched surfaces, since the laser energy causes surface melting and thereby tends to negate the pyramidal structures. Polished surface wafers, on the other hand, might not be cost-effective to satisfy the 1986 LSA goals.

The application of flash etching is only to remove saw damage, and can be achieved using various solutions. The solution recommended was the same as successfully used in our Phase II, Automated Array Assembly Contract.[1] It was supplied by JPL based on work performed by Photowatt (formerly Sensor Technology). The solution consists of a mixture of HAC, HNO_3, HF, in the ratios of 5:3:3, respectively, with immersion of the wafers for 30 seconds, followed by standard rinsing and drying.

SEM photomicrographs of the texture etched, chem-polished and flash-etched surfaces are shown in Figures 3 and 4.

Test flash etched wafers were fabricated into functional cells by ASEC preparatory to processing (flash etching) the entire lot of wafers required for this program. Immersion times on different samples were 30 and 90 seconds. Chem-polished wafers were also fabricated for comparison. No BSF was applied to the cells. Output values of the completed cells were quite close, with those chem-polished exhibiting



Wafer Center View

Wafer Edge View

Figure 3 . SEM Photo, Flash Etched Wafer Surface
2000X 60^{o} Tilt

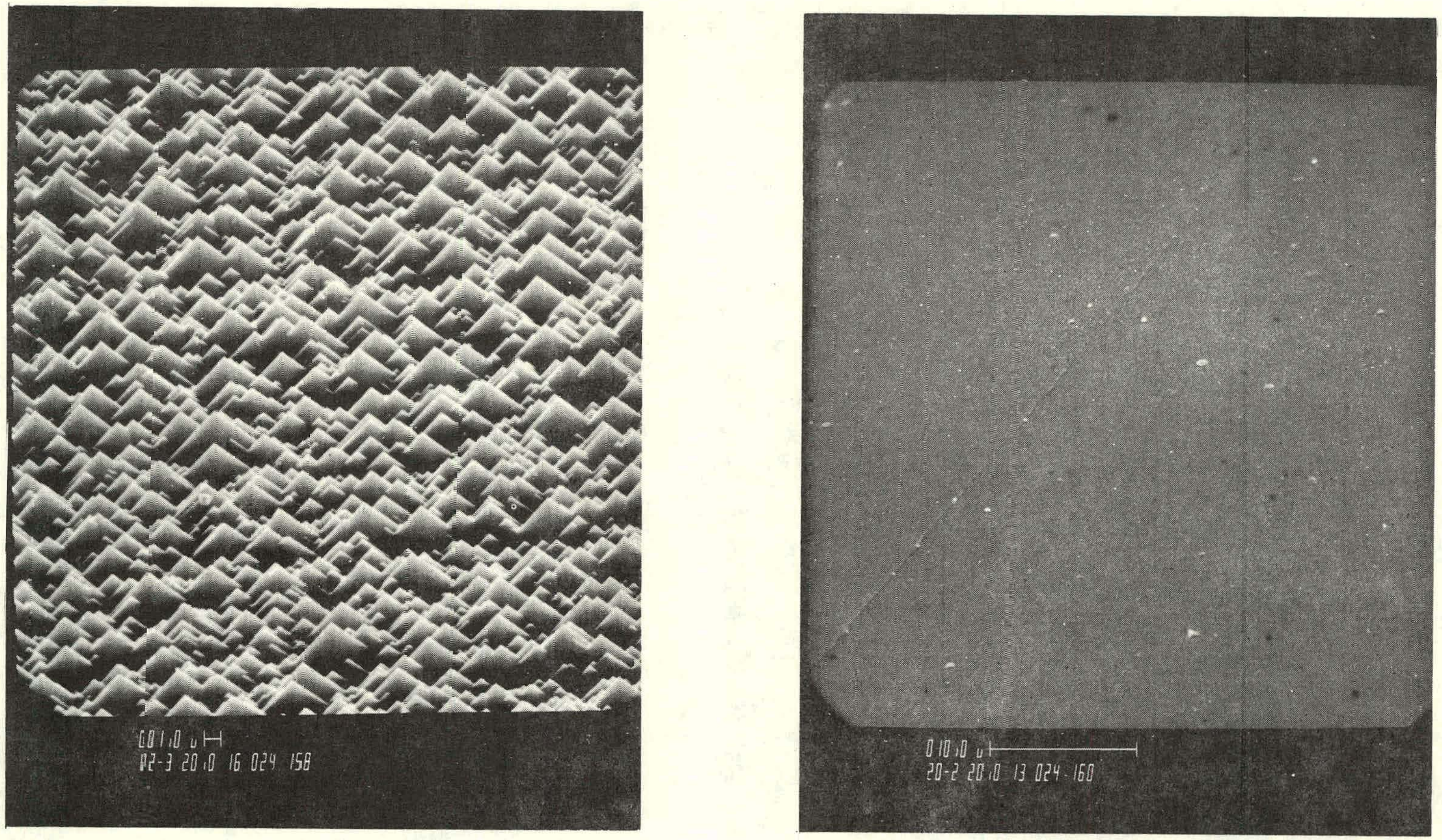


Figure 4. SEM Photos, Texture Etched (left) and Chem Polished (right) Surfaces
2000X 60° Tilt

11% efficiencies, and the flash etched type, 10.9% for both the 30 and 90 second immersion times. Based on these comparable outputs, the flash etching process was deemed acceptable for use and the balance of the wafers were processed.

3.2 ION IMPLANTATION SERVICES

SPIRE Corp. was contracted to perform the ion implantation work for this contract. Table 1 shows the requirements by wafer/surface conditions and front/back implant species and dosages.

The majority of the wafers boron implanted for back surface field will be Pulsed Electron Beam Annealed (PEBA) by SPIRE. A control lot will be furnace annealed for reference, as will others without BSF.

3.3 BEAM HOMOGENEITY

The Nd:Glass laser system obtained by LMSC for performing the laser annealing evaluations is capable of up to 40 joules output in a 20-50 nsec pulse operating in the TEM_{00} mode. Without the use of external optics, the beam diameter is 25mm which converts to 8 joules/cm^2 of delivered energy density.

The problem of annealing with single high power Q-switched laser pulses is that certain limitations are present due to intensity inhomogeneities in the beam. The presence of a mode pattern also yields large intensity variations which can degrade annealing uniformity. In a Gaussian beam distribition associated with TEM_{00} mode operation, unwanted specimen damage may occur in the regions subjected to the central (maximum power) portion of the beam.

To attain satisfactory beam homogenization, an optical system has been developed(2) to eliminate inhomogeneities in high power laser pulses. The system, called a light guide diffuser, consists of a fused silica rod bent approximately 90° in the middle, Figures 5 and 6. The laser output beam is directed to the input face of

TABLE 1

ION IMPLANTATION REQUIREMENTS ON 3-INCH DIA. WAFERS

Wafer Surface Type	PHOSPHORUS - FRONT			BORON - BACK
	5 KeV, 2.5×10^{15}	10 KeV, 2.5×10^{15}	10 KeV, 4×10^{15}	25 KeV, 5×10^{15}
Polished	X			
	X			X
		X		
		X		X
Flash Etched	X			
	X			X
		X		
		X		X
Texture Etched			X	
			X	X

Other implant information: (1) Implant uniformity to be $\pm$ 10%
(2) Implant at 7 to 10° tilt

the rod, which is ground with diamond powder or equivalent. As the beam enters the light guide, it is diffused, although some microscopic intensity inhomogeneities remain. Most of the incident light is scattered close to the forward direction and passes down the guide being subsequently contained by total internal reflection at the guide wall.

A relatively small proportion of the incident light is scattered through large angles at the input face and is lost. As the radiation propagates down the guide, repeated internal reflection further diffuses the beam and speckle components are progressively eliminated. This process is enhanced, especially for near-axis light, by introducing a curve into the guide. A bend of approximately 90^o has been found to be particularly effective in suppressing any remaining speckle while giving rise to minimal light losses. However, such bends introduce caustic patterns into the transmitted light and a further length of guide is required to rehomogenize the beam. The light finally emerges from the guide through an exit face which is normal to the guide axis and highly polished.

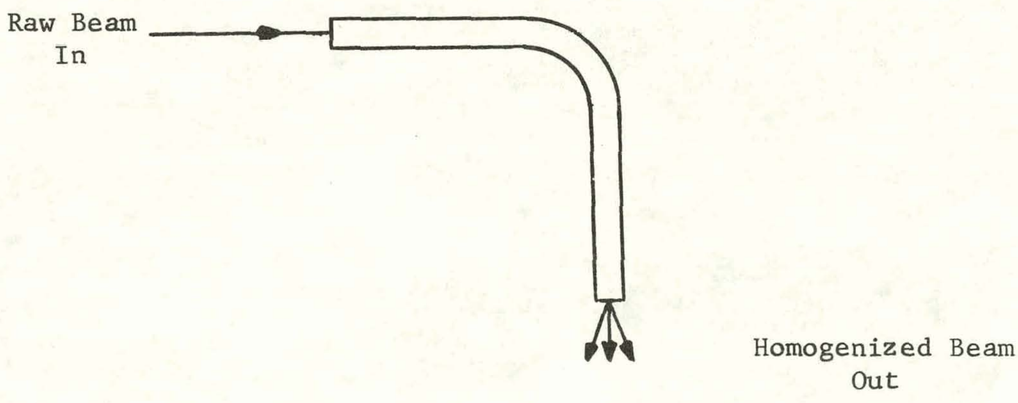


Figure 5 Light Guide Diffuser Schematic

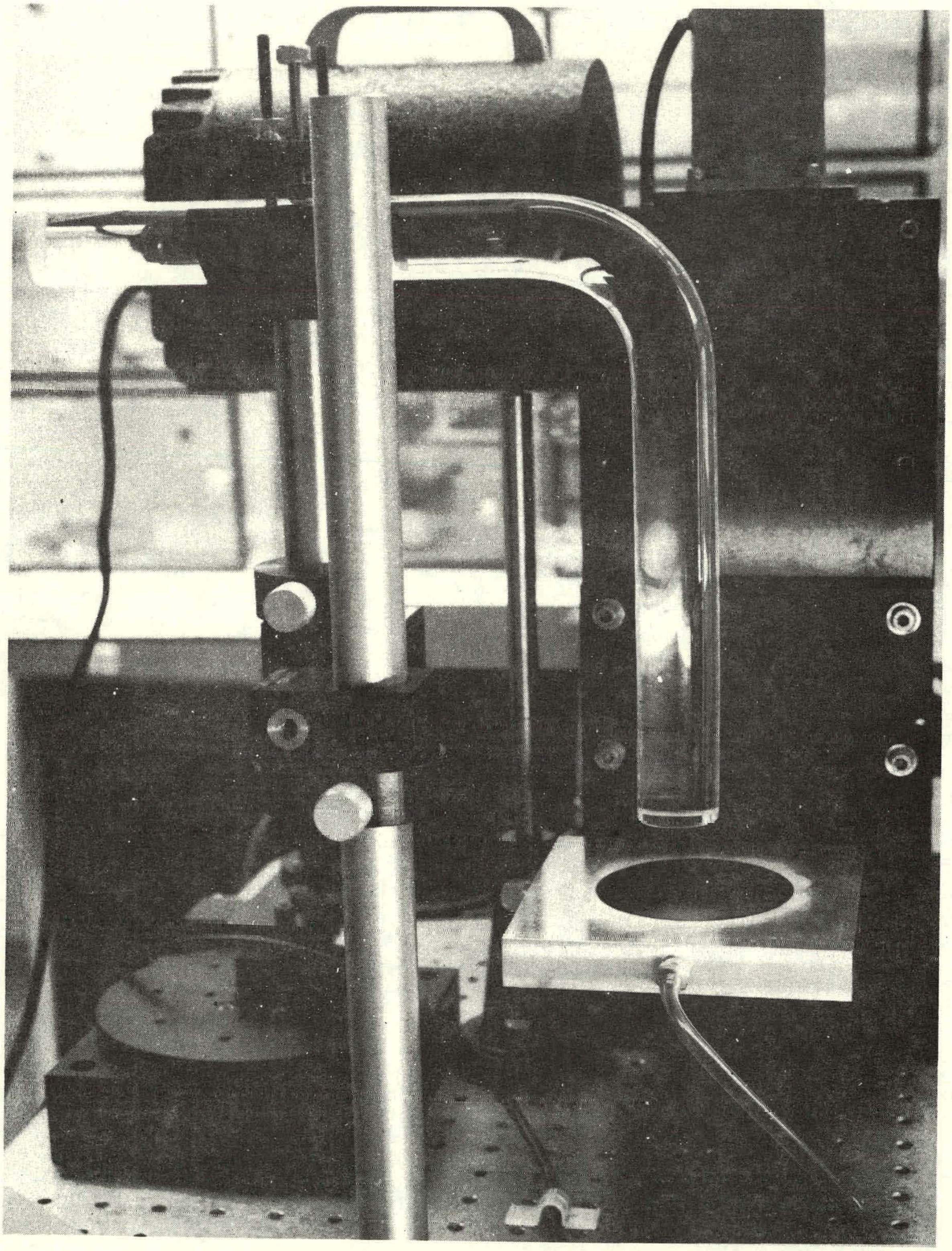


Figure 6 - Light Guide Diffuser

Initial results with a prototype light guide diffuser indicate that very good beam homogenization is obtained. Figure 7 shows laser beam burn spots on photographic paper produced by the "raw" beam in (A) and by the homogenized beam in (B).

(A) (B)

Figure 7. Laser burn spots on photographic paper from a "raw" beam in (A) and homogenized beam in (B) - approximately 1-inch diameter.

The central gray area in the raw laser burn spot corresponds to the maximum beam energy. The progressively darker regions moving radially away from the center are indicative of progressively lower energies typical in a Gaussian beam distribution. The burn spot in (B), however, is of a uniform shade corresponding to a homogeneous energy output obtained with the light guide diffuser.

Figure 8 shows 30mm diameter annealed regions on a 3-inch diameter flash etched wafer. For reference, a 2 x 2cm cell was placed on one of the annealed spots indicating existing capability of single pulse annealing for fabrication of 2 x 2cm solar cells.

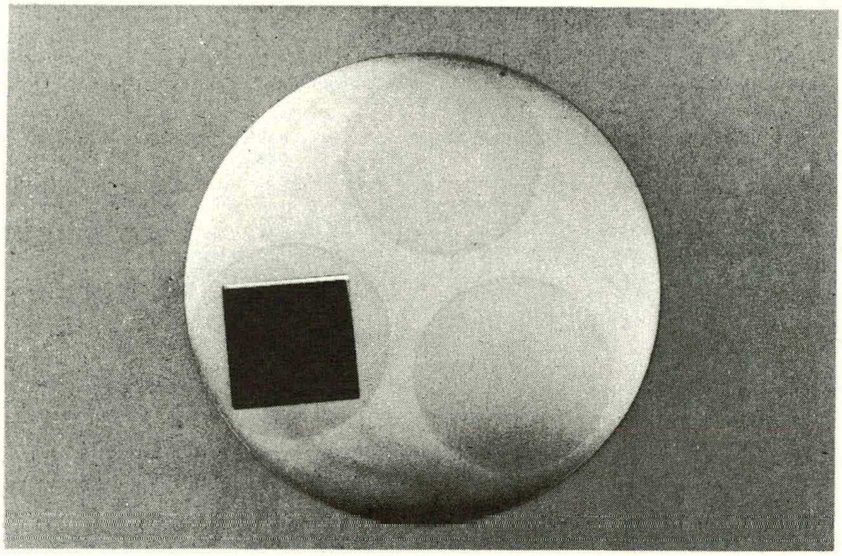


Figure 8. Single pulse 30mm diameter anneal areas on a 3-inch diameter silicon wafer. A 2 x 2cm cell is included for reference.

3.4 LASER BEAM PROJECTION AND EQUIPMENT SET-UP

For evaluating wafers annealed with a raw laser beam, it was planned in our investigations to hold the wafers in a horizontal plane, Figure 9, while reflecting the laser beam 90° onto the sample with the use of special high power laser mirrors. To this end three laser mirrors coated for reflectance at λ=1064nm, λ=532nm, and combination of λ=1064nm, 532nm were purchased from CVI Laser Corporation, one of the leaders in the high power laser coating industry. Post laser radiation exposure evaluations of the mirrors revealed coating degradation from hot spots in the laser beam on mirrors coated for λ=532nm, and combination wavelength. It was concluded by CVI that beam hot spots exceeded the damage threshold of the coatings, and that since these were the highest damage resistant coatings available, no obvious solution was apparent. To alleviate the mirror problem, it was decided that laser annealing could be performed without the aid of the mirrors if the wafers were properly fixtured in a vertical plane. Figure 10 depicts the projection of the beam with the wafer mounted vertically, with the aid of a vacuum fixture. The fixture, Figure 11, made of aluminum offers excellent hold down of the 3-inch diameter wafers, and has been found extremely useful in irradiating test samples. The aluminum reflects the laser energy and is not adversely affected. This set up permits evaluations of sample annealed with a raw beam.

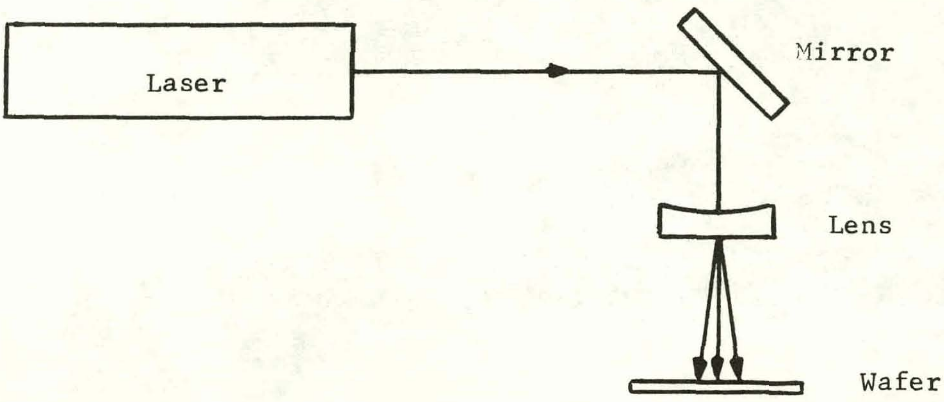


Figure 9. Configuration of optical components for bending the laser beam 90° onto the sample wafer.

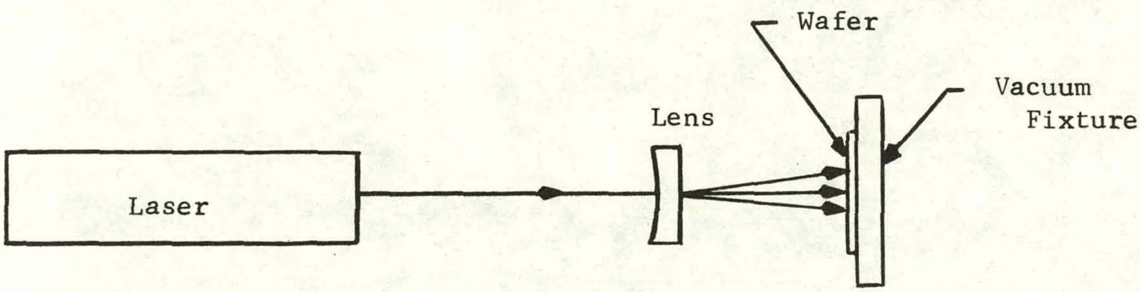


Figure 10. Configuration of components for vertical positioning of sample wafer.

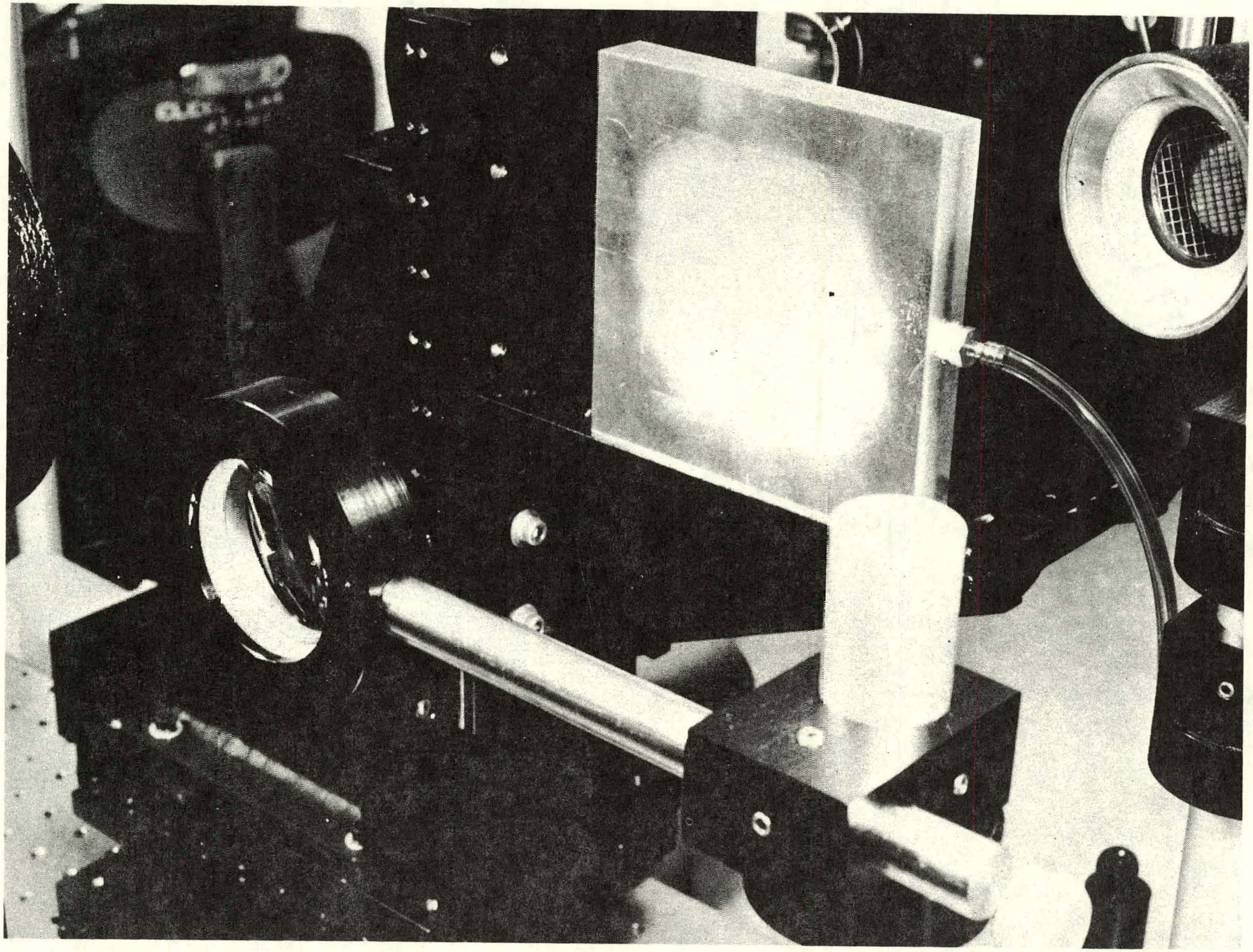


Figure 11. Lens and vacuum fixture set up for holding a wafer in a vertical plane during laser annealing

Preliminary evaluations of laser annealing utilizing the raw laser output were initiated on wafers implanted at 25KeV, 3×10^{15} ions/cm^2 of ^{31}P. These wafers were available from our previous in-house work on laser annealing. To obtain maximum anneal area coverage, a -100mm focal length plano-concave lens was used to diverge the laser beam.

The lens utilized was made from BK7 glass with double peak AR coating. Both the substrate and the coating were damaged by the laser beam, and consequently, it was decided to experiment with uncoated fused silica lenses which have a higher damage threshold than BK7 glass.

Laser exposure tests have shown that the fused silica lenses have excellent stability and damage resistance. However, the tests also revealed two other potential problems. The reflectance of the uncoated lenses is approximately 8%, representing a potential for damage to the laser oscillator from the reflected beam. To alleviate this problem, the lens was tilted at an angle to ensure that the beam would not be reflected back into the system. The second problem was discovered in processing the sample wafers. The annealed area on each wafer exhibited a small circular spot that was untouched by the laser radiation. The presence of this spot is also due to the high reflectance of the uncoated lenses. The laser beam reflected from the concave surface of the lens is focused to a point with sufficient energy density to ionize the air at that spot with the result that the created plasma is opaque to laser radiation. This condition is propagated to the surface of the wafer, as shown in Figure 12.

The condition of having an unannealed area on the wafer presents a problem only in fabricating cells from single pulse annealed silicon with a raw beam. In cases where multiple pulses are utilized, either on the same spot or through step and repeat procedure for large area coverage, this problem is eliminated by rotating the wafer in the case of the former, and using sufficient overlap in the case of the latter.

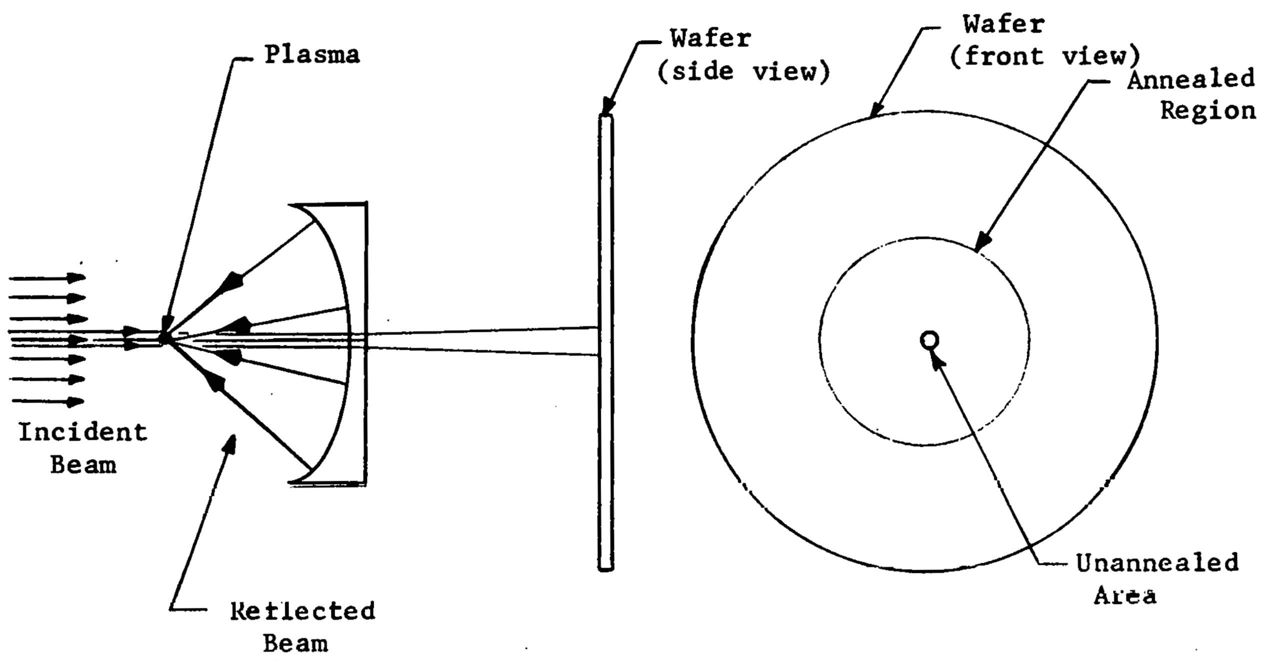


Figure 12. Formation of an unannealed spot on a wafer due to uncoated lens created plasma

The problem can also be eliminated by using lenses with long focal length. A small tilt angle imparted to such a lens places the focal point outside the path of the incident beam, Figure 13, hence eliminating the "blind spot" condition. To this end lenses with -300mm and -500mm focal length were purchased for forthcoming evaluations.

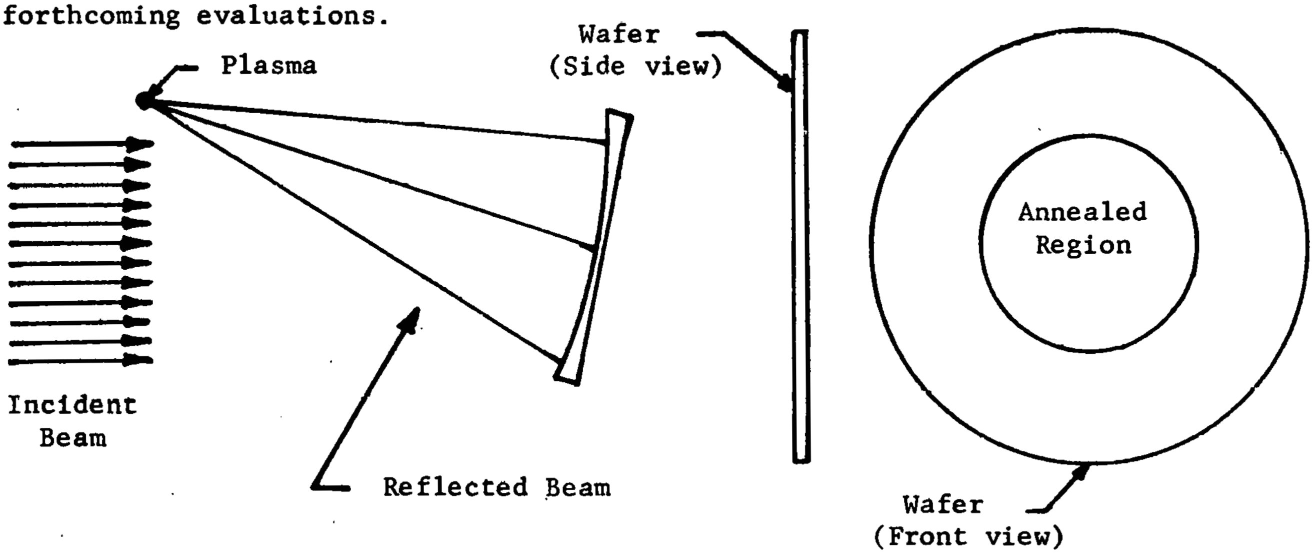


Figure 13. Elimination of an unannealed spot on a silicon wafer by tilting a long focal length plano-concave lens.

3.5 LASER ANNEAL PARAMETER DEVELOPMENT

Investigations this period concentrated on evaluation of the laser anneal quality of ion implanted wafers. The wafers were available from our previous in-house work on laser annealing. The wafers were <100> FZ silicon implanted at 10 KeV and 2.5×10^{15} ions/cm^2 of ^{31}P.

Laser annealing was performed with a combination of parameters which included annealing with a single ($\lambda = 1064$nm) wavelength and mixture of two wavelengths ($\lambda = 1064$nm and 532nm). Typical anneal energy densities were between 1.5 and 2.0 joules/cm^2. Single pulse anneal areas ranged from 25mm in diameter with a homogenizer (light guide diffuser) to approximately 35mm with a plano-concave lens between the sample and the laser beam. Analysis of ion implanted/laser annealed silicon substrates was performed with Rutherford Backscattering techniques. Figure 14 shows $^4He^+$ backscattering and channeling spectra for random aligned, as-implanted, laser annealed and unimplanted (virgin) silicon. The as-implanted spectrum shows a narrow peak which corresponds to the depth of the disordered layer in the silicon introduced by the implanted specimen. Analysis of the laser annealed implant shows a backscattering spectrum that is almost identical to that of virgin silicon, indicating complete lattice recovery from the implant-induced damage.

The illustrated spectrum was obtained from a central section of a sample irradiated simultaneously at both laser wavelengths with the beam spread out through the use of a plano-concave lens. Since the raw laser beam has a gaussian distribution, maximum energy is deposited in the center of the anneal area with the subsequent result that best crystal recovery is obtained at that point. Anneal quality, as shown in Figure 15, is somewhat reduced as a function of distance from the center of the anneal area.

Figure 16 shows a backscattering spectrum from samples annealed as above except the plano-concave lens was replaced with a beam homogenizer. The spectrum is almost identical across the 25mm spot size, indicating very uniform annealing. The spectrum, however, shows a slightly higher scattered particle count than virgin silicon which can imply that 100% recovery of the lattice was not achieved.

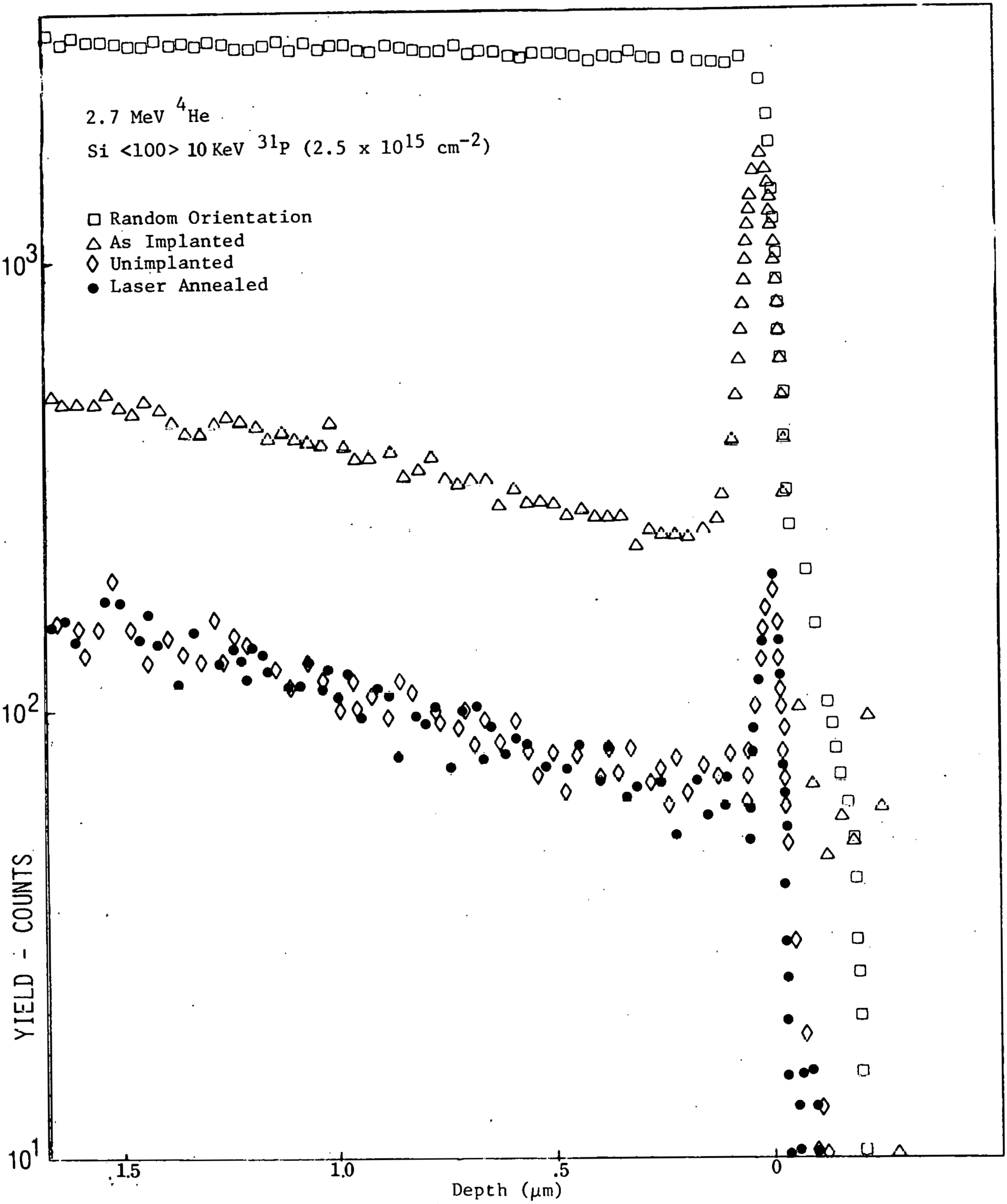


Figure 14. Backscattering spectra of <100> silicon wafers in as-implanted, unimplanted (virgin), and laser anneal states. A random spectrum for the virgin crystal is also shown.

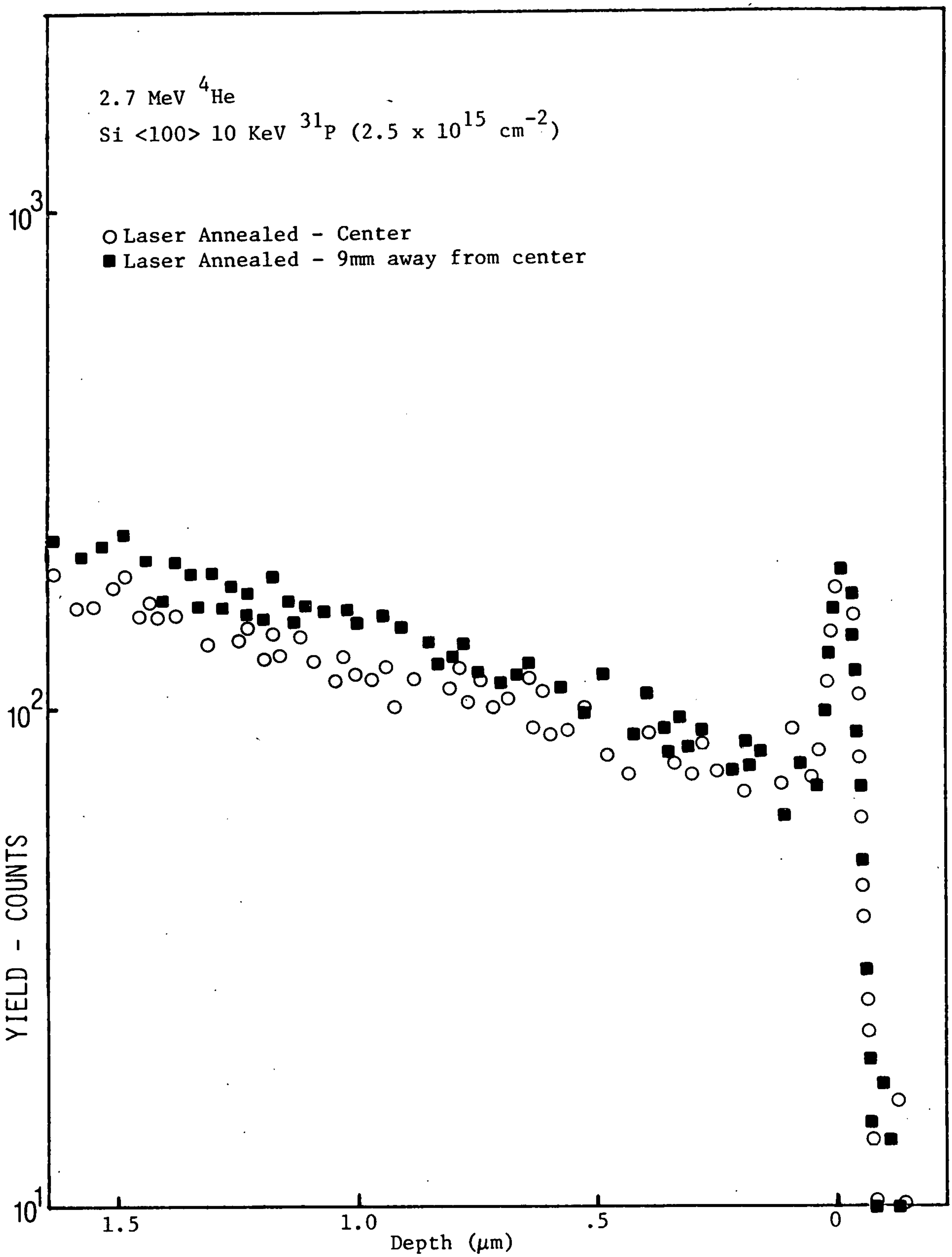


Figure 15. Backscattering spectra of laser annealed <100> silicon wafer illustrating difference in anneal quality as a function of distance from the center of anneal area.

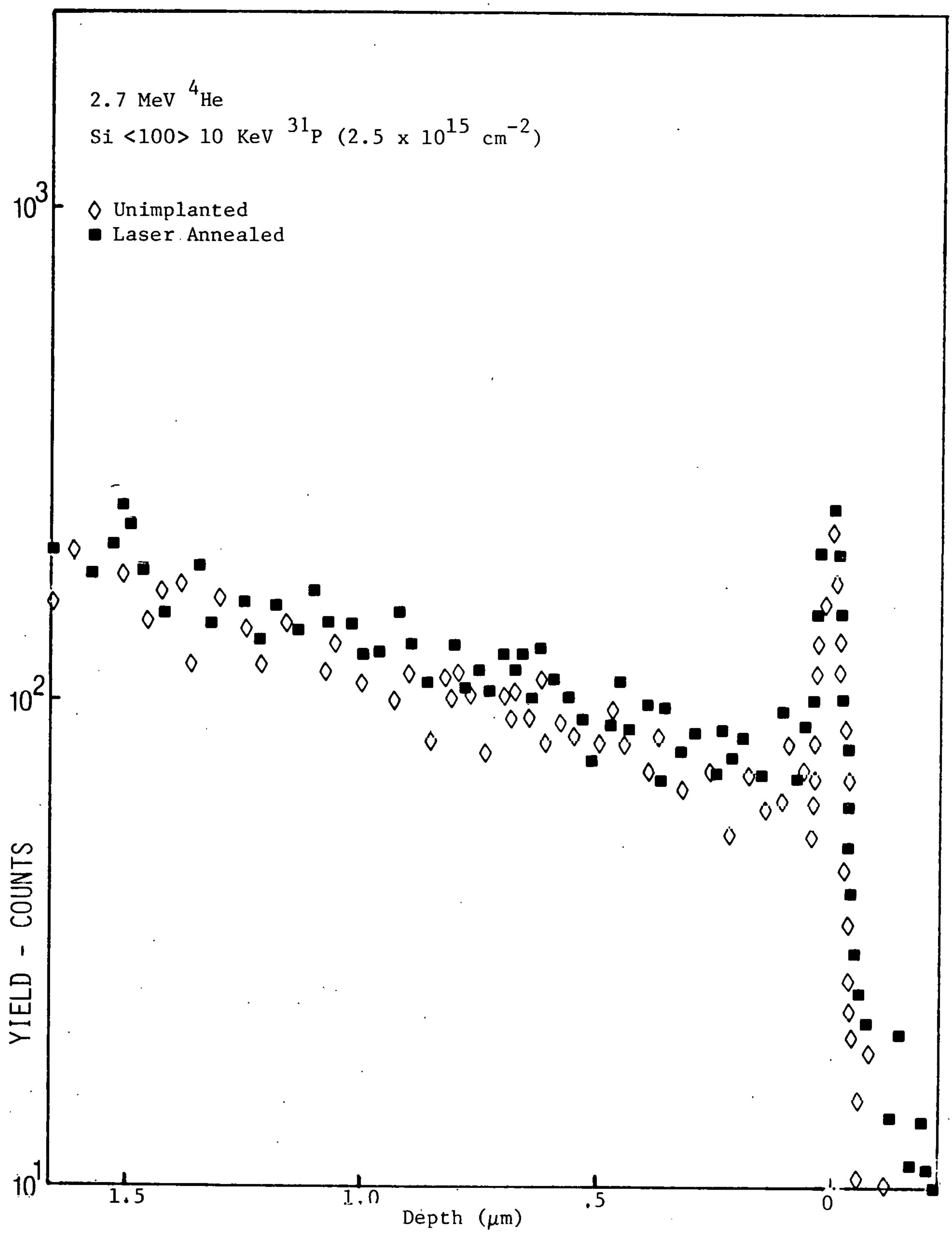


Figure 16. Backscattering spectra of <100> silicon wafers in unimplanted (virgin), and laser anneal states. Laser annealing was performed with a light guide diffuser and combination wavelengths at 1.5 joules/cm^2 -20 nsec pulse.

This can be due to insufficient anneal energy density, a hypothesis which will be verified in the near future. Another plausible explanation for the higher particle count is due to the extremely high concentration of ^{31}P atoms implanted in the silicon (10^{21} atoms/cm^3). The phosphorus atoms have a higher scattering cross section than silicon atoms, hence, increasing scattering probability. In addition, phosphorus has a smaller ionic radius than silicon, and in substitutional lattice sites, this leads to a distortion or channel narrowing in the lattice, a condition which also leads to increase in scattering probability with subsequent higher scattered particle count. Additional tests, which will include transmission electron microscopy (TEM) and secondary ion mass spectrometry (SIMS), will be performed. These tests will assist in ascertaining optimum anneal parameters.

Based on the Rutherford backscattering work, there appears some hope that satisfactory annealing can be obtained without the aid of a homogenizing system. The attractiveness of this approach rests in the fact that the light losses incurred are minimum in comparison to those incurred with a light guide diffuser. To further improve upon this approach with subsequent control of spot size and geometry, quartz tubes in 30mm, 35mm, 40mm, and 45mm diameters were ordered. These will be coated with aluminum on the outside for maximum reflection and utilized as illustrated in Figure 17.

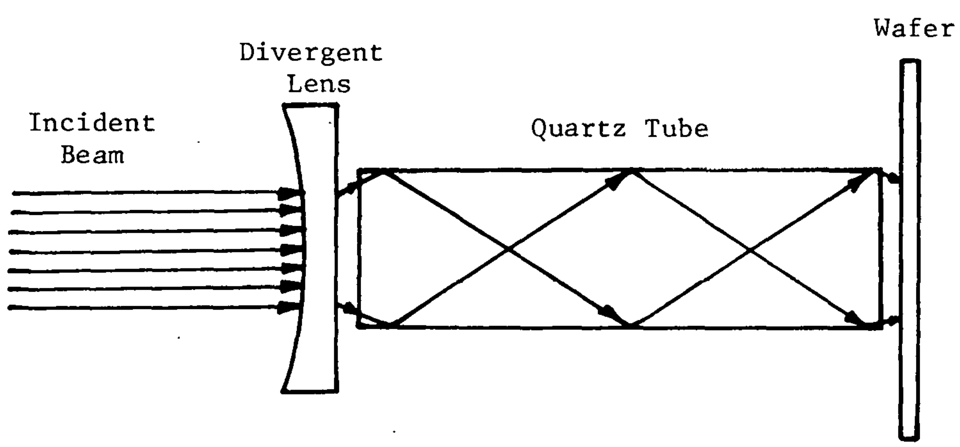


Figure 17. Utilization of a quartz tube for controlling shape and size of anneal area on a wafer.

SECTION 4

CONCLUSIONS

4.1 Good annealing uniformity results were obtained through usage of a fused silica rod with a right angle configuration to homogenize the laser beam.

4.2 Analysis of laser annealed surfaces using Rutherford backscattering techniques showed excellent lattice structure recovery from the implant-induced damage for both homogenized and raw laser beam. Improved annealing uniformity was evident for a homogenized beam mode of operation.

SECTION 5

NEW TECHNOLOGY

No new technology has been developed to completion during this quarter.

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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 SUMIT 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

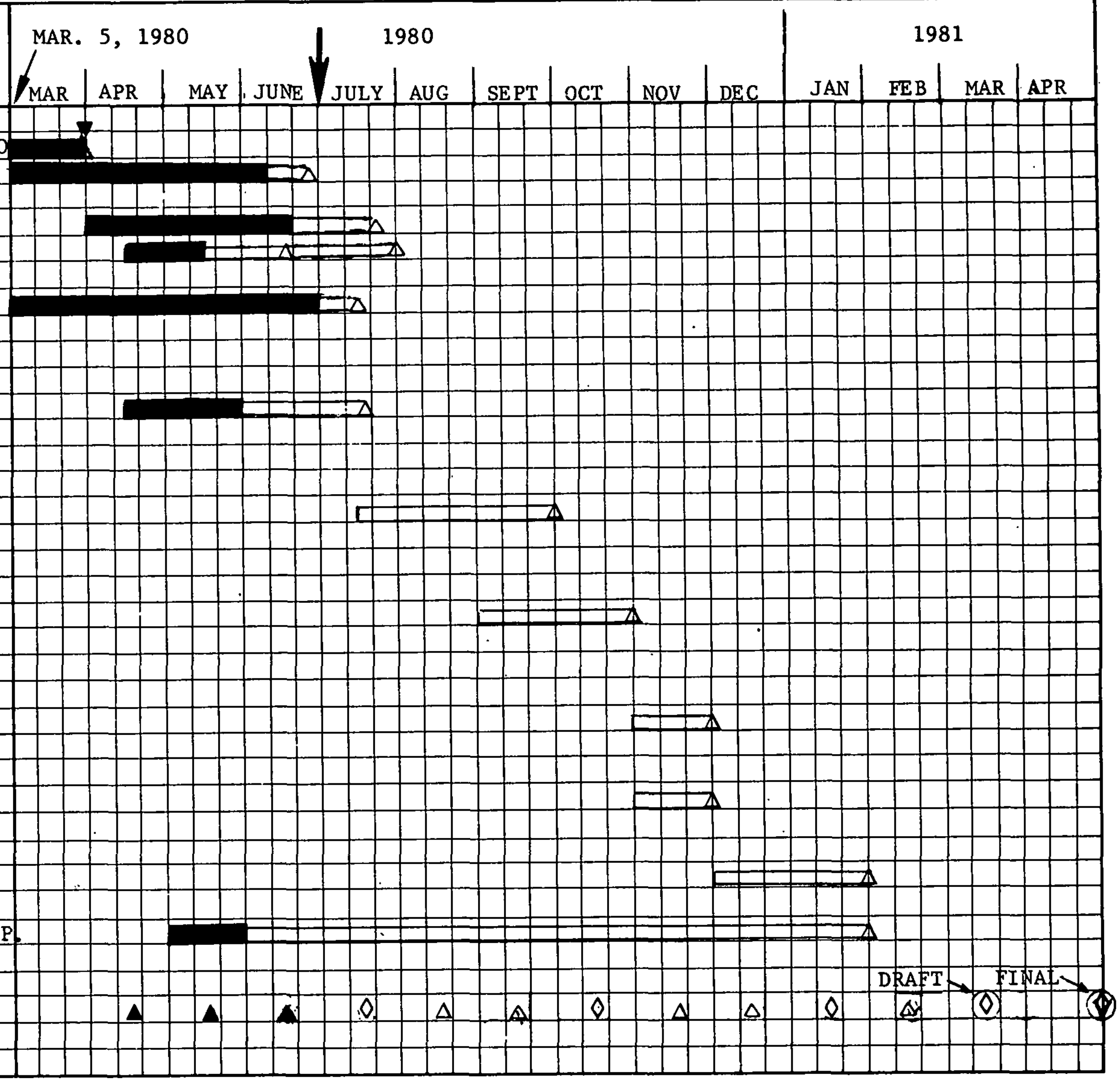
6.0 VERIFY PROCESS-SINGLE/MULTI PULSE BY FAB. SMALL (2x2 cm) CELLS & LARGER.

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.



FORM LMSC 481-3 | *Diazo Reproducible* | ① △ = MONTHLY, ◇ = QTRLY ◎ = FINAL

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