350 2/28/80

DR. 879

SAN-3042-1

AMORPHOUS SILICON SOLAR CELLS BY HYDROGEN IMPLANTATION

Quarterly Report No. 1, January 1—March 31, 1979

By
A. R. Kirkpatrick
A. A. Melas

MASTER

August 1979

Work Performed Under Contract No. AC03-79ET23042

Spire Corporation
Bedford, Massachusetts

U.S. Department of Energy

Solar Energy

SAN-3042-1
Distribution Category UC-63e

AMORPHOUS SILICON SOLAR CELLS BY HYDROGEN IMPLANTATION

QUARTERLY REPORT NO. 1
FOR THE PERIOD
1 JANUARY - 31 MARCH 1979

A.R. Kirkpatrick and A.A. Melas

August 1979

SPIRE CORPORATION
Patriots Park
BEDFORD, MA 01730

Prepared for the

U.S. DEPARTMENT OF ENERGY
SOLAR ENERGY
Under Contract No. 03-79-ET-23042.000

TABLE OF CONTENTS

Section		Page
	ABSTRACT	iv
1	INTRODUCTION	1
2	PROGRAM DISCUSSION	3
	2.1 Program Plan	3
	2.2 Development of Special Implantation Capabilities	4
	2.3 Development of Device and Material Test Structures for Cell Device and Material Evaluations	14
3	SUMMARY	20

LIST OF FIGURES

Number		Page
1	Medium Current 2-200 keV Ion Implanter	5
2	High Current 5-50 keV Ion Implanter	6
3	Predicted Stopping Distributions for 10, 50 and 200 keV $^{1}H^{+}$	7
4	Predicted Stopping Distributions for 10 and keV $^{11}B^{+}$	8
5	Predicted Stopping Distributions for 10 and 200 keV $^{16}O^{+}$	9
6	Predicted Stopping Distributions for 10 and 200 keV $^{19}F^{+}$	10
7	Predicted Stopping Distributions for 10 and 200 keV $^{28}Si^{+}$	11
8	Predicted Stopping Distributions for 10 and 200 keV $^{31}P^{+}$	12
9	Predicted Stopping Distributions for 10 and 200 keV $^{40}Ar^{+}$	13
10	Cooled Sample Holder for Special Implantations	15
11	Wafer Temperature versus Implant Time as Function of Ion Beam Energy Input	16
12	Cell Device Test Structure	18

ABSTRACT

The purpose of this program, "Amorphous Silicon Solar Cells by Hydrogen Ion Implantation", is to investigate applications of ion implantation to preparation of amorphous silicon material and devices. Implantation can be considered for one or more of several purposes including doping, hydrogenation, amorphization and material character adjustment. This program is to be based around examination of the effects of various implantation conditions upon performance of thin film silicon cell devices. Operational devices will fabricated from CVD polysilicon. The device material will be altered to become amorphous and hydrogenated by means of subsequent implantation. Special implantation facilities and procedures and an adequate device structure are required to conduct this study. These were under development during the period of this report.

SECTION 1
INTRODUCTION

This program to investigate "Amorphous Silicon Solar Cells by Hydrogen Implantation" involves examination of a potentially useful approach to fabrication of amorphous silicon cells. In this approach a silicon film to be employed in the cell device would not necessarily have to be initially deposited in an amorphous condition. Nor would the film have to initially contain the hydrogen needed to produce satisfactory material characteristics. Ion implantation of the film after its growth would be utilized to produce amorphization and/or hydrogenation.

Ion implantation is a powerful tool for producing a number of process effects over ranges in silicon of up to a micron from the impact surface. In the case of an amorphous silicon photovoltaic cell, a depth capability of approximately 1 micron allows implantation to be at least considered for constituent species introduction and for material modification purposes over the entire necessary thickness of the device. Present generation high current implanters represent effective research machines for material modification purposes. Future machines which would be designed for such application could involve very high production throughputs at low cost.

In preparation of an amorphous silicon solar cell, implantation might be used for several purposes, including doping, hydrogenation, amorphization and material character adjustment by introduction of special constituents. Little is presently known regarding a number of matters of basic importance involving interactions of deposited atoms with the host structure, types of bonding which will result, effects of radiation damage produced, character of the "amorphous" material that can be generated, etc. A great deal of research could be required to allow preliminary questions to be adequately answered. The work which would be needed is well beyond the resources of this program.

Development to date of present applications of implantation has been first empirical, then analytical. Implantation has been well utilized when it has been treated simply as a process for introducing atoms of interest to selected locations in a host lattice. Devices, including solar cells, have been achieved by implantation before the essential process effects were adequately understood. Understanding then followed.

On the basis of what is now known, it is possible to anticipate the results which can be expected when implantation is utilized for preparation of amorphous silicon cell structures. Assumptions can be made. The purpose of this program is to validate these assumptions or to identify the reasons that they may be invalid. Such a program can best be conducted at the device level.

SECTION 2
PROGRAM DISCUSSION

2.1 PROGRAM PLAN

This program is directed toward using ion implantation for one or more requisite operations to produce amorphous silicon and a cell structure to utilize the material produced. If adequate amorphous hydrogenated silicon can be prepared by implantation of predeposited polycrystalline silicon films, a well controlled and extremely flexible processing approach will become available for amorphous cell devices. Nonconventional implantation and damage annealing procedures will be necessary. The early months of this program involve primarily preparation of the special implantation capabilities and procedures needed to conduct the planned investigations.

Planned efforts of the first 12 months of this program, which began in January 1979, are for the purpose of accomplishing the following:

• Development of Special Implantation/Annealing Facilities and Procedures	Months 1-4
• Development of Amorphous Silicon Cell and Material Test Structures	2-4
• Preliminary Survey of Ion Implantation Effects Upon Device Performance	5-7
• Demonstration of an Amorphous Silicon Cell	6-9
• Investigation to Improve Amorphous Silicon Material	8-10
• Investigation to Improve Amorphous Silicon Cell Performance	8-10
• Fabrication of Best Status Cells	After Month 6

In accordance with the plan, work performed during the subject period of this report involved development of required implantation facilities and procedures and development of test structures to allow initial evaluation of the implantation effects of interest. These activities are described below.

2.2 DEVELOPMENT OF SPECIAL IMPLANTATION CAPABILITIES

For the purposes of this program, ion implantation is treated as a method to introduce any of several component atoms or penetrating ion collision effects into a silicon film. Ions to be considered include at least the following:

$^{11}B^+$, $^{31}P^+$	for doping
$^{1}H^+$	for hydrogenation
$^{28}Si^+$, $^{40}Ar^+$	for amorphization
$^{16}O^+$, $^{19}F^+$	for association with hydrogen

The two ion implanters shown in Figures 1 and 2 are available at Spire to support this project. With these machines all ions listed above are available over the energy range 10-200 keV. Deposition profiles for basic stopping distributions have been generated for the cases of interest. Figures 3 through 9 present examples of 10 and 200 keV profiles for $^{1}H^+$, $^{11}B^+$, $^{16}O^+$, $^{19}F^+$, $^{28}Si^+$, $^{31}P^+$ and $^{40}Ar^+$. The profiles given represent in each case the depth limits available under this study.

The uses of implantation being investigated will require very high ion fluences, 10^{17} ions/cm^2 or more of hydrogen and possibly of the oxygen and fluorine to be introduced for association with the hydrogen. To allow these high dose conditions to be investigated, reasonably effective sources are required for each ion. Source conditions have been identified to provide approximately 500 microamperes of on-target beam of each ion at energies between 10 and 50 keV. Available currents between 50 and 200 keV are typically 50 microamperes or higher.

A modified ion source was developed to allow 500 microamperes of proton beam current to be produced. The source is fed with hydrogen gas and incorporates a hot filament within a restricted flow gas cavity. Using this source, implants to 10^{17} cm^{-2} fluence over a 4-inch wafer area can be performed in under 1 hour. This is satisfactory for developmental investigation purposes.

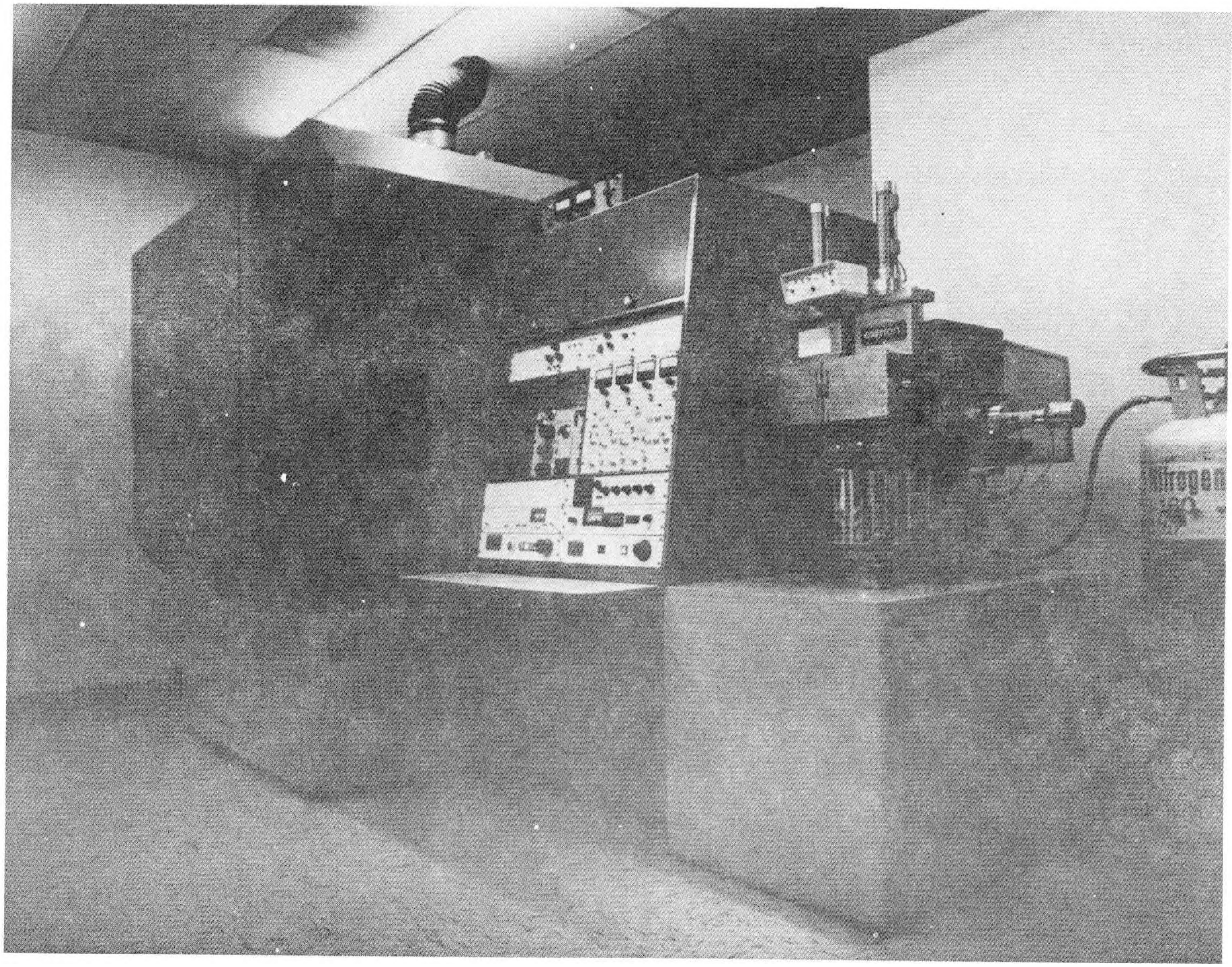

FIGURE 1. MEDIUM CURRENT 2-200 keV ION IMPLANTER

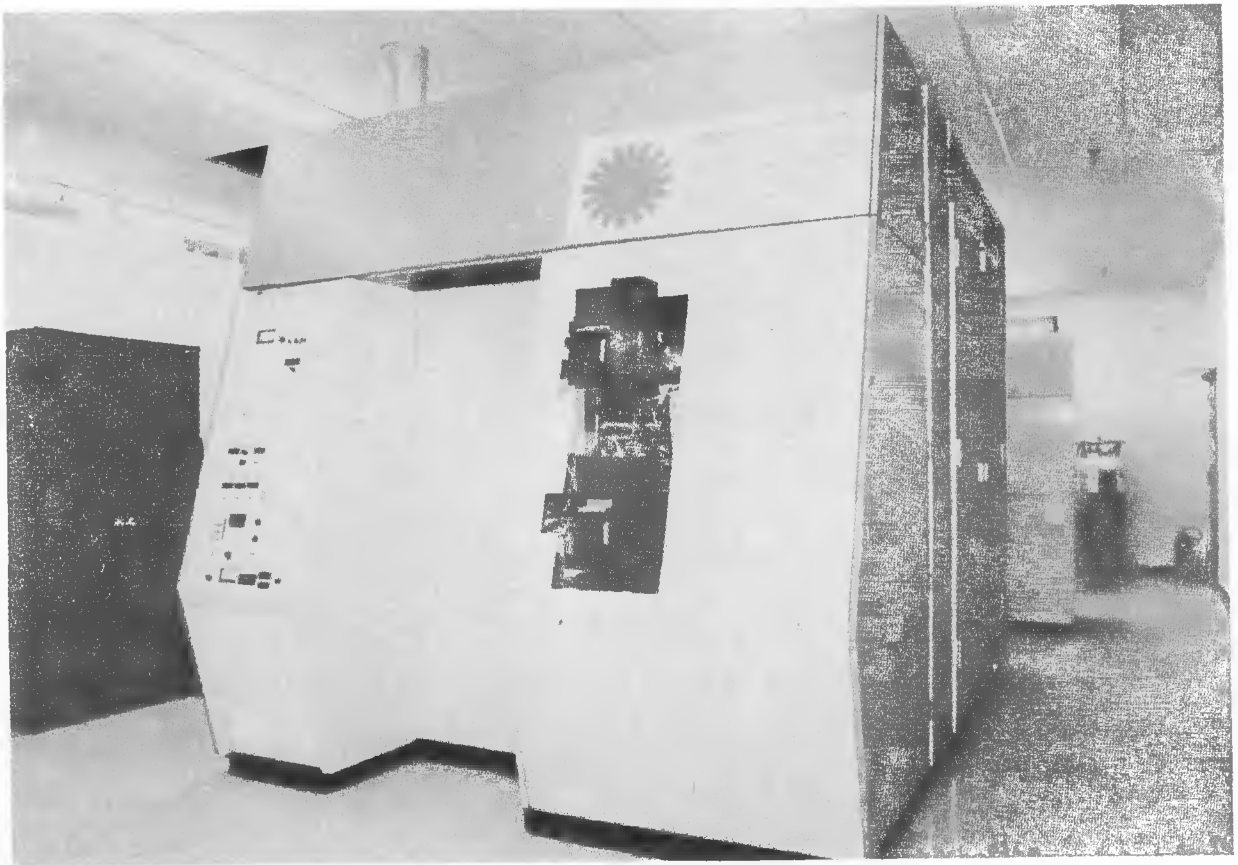

FIGURE 2. HIGH CURRENT 5-50 keV ION IMPLANTER

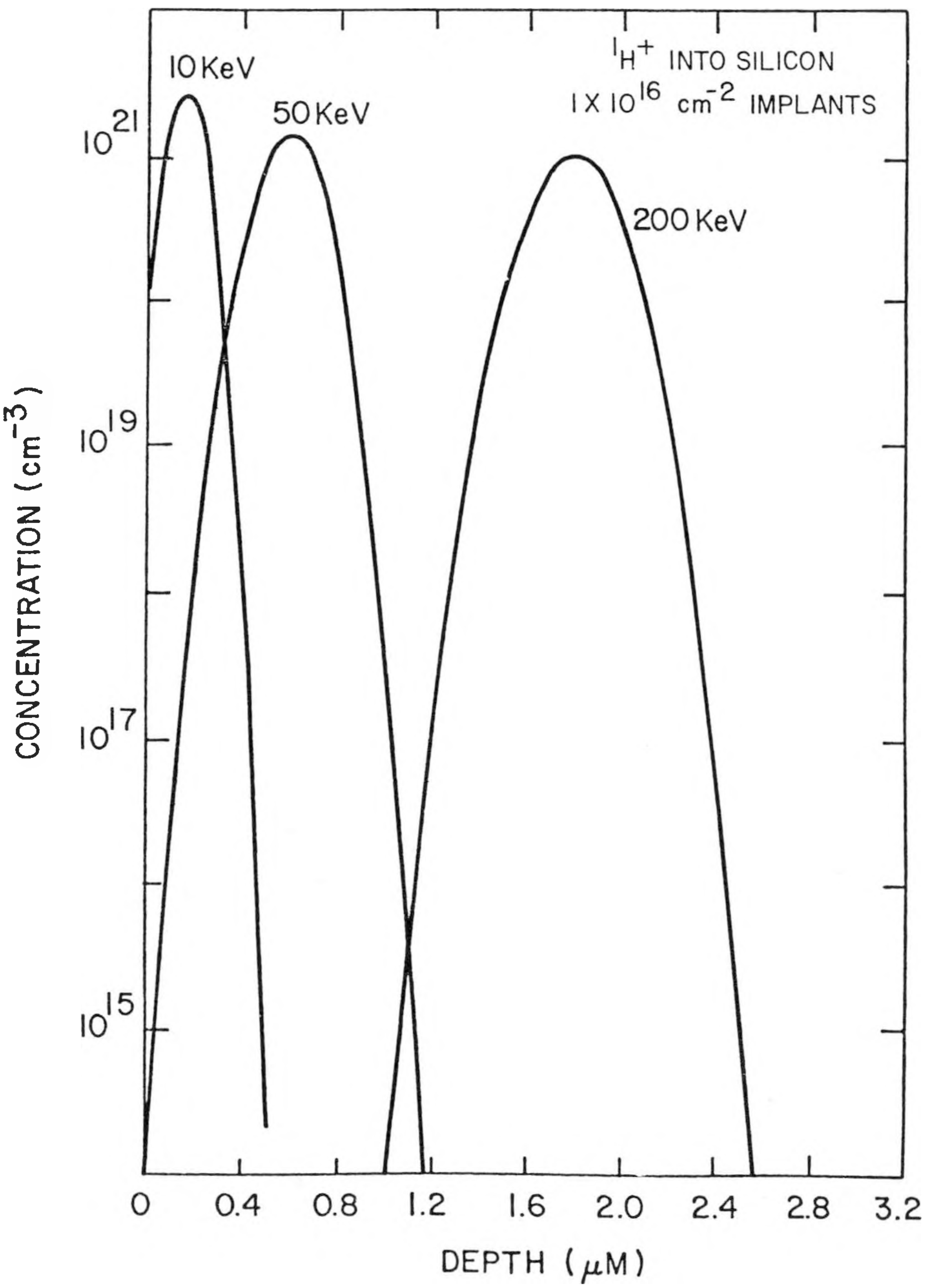

FIGURE 3. PREDICTED STOPPING DISTRIBUTIONS FOR 10, 50 AND 200 keV $^{1}H^{+}$

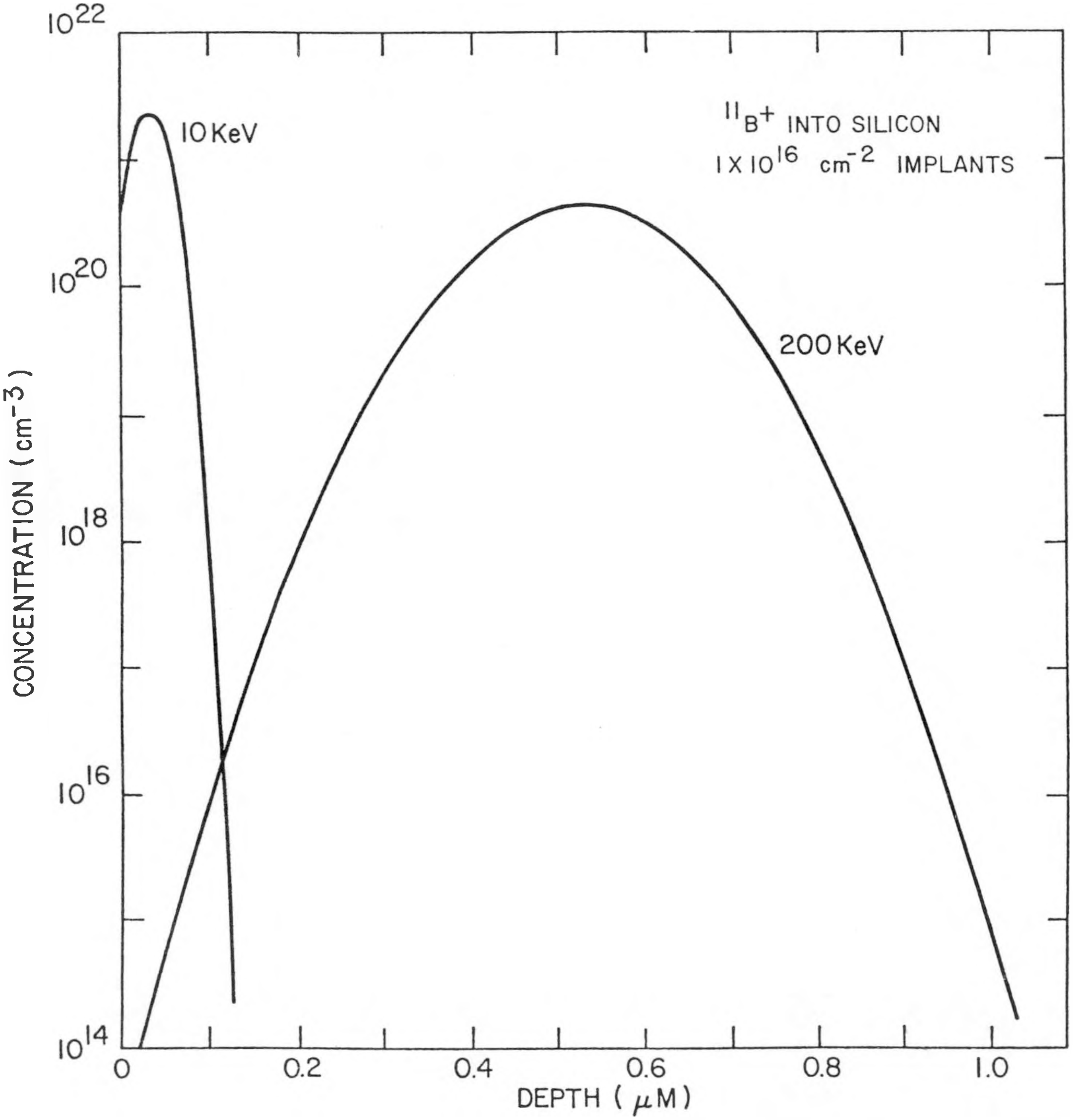

FIGURE 4. PREDICTED STOPPING DISTRIBUTIONS FOR 10 AND 200 keV $^{11}B^{+}$

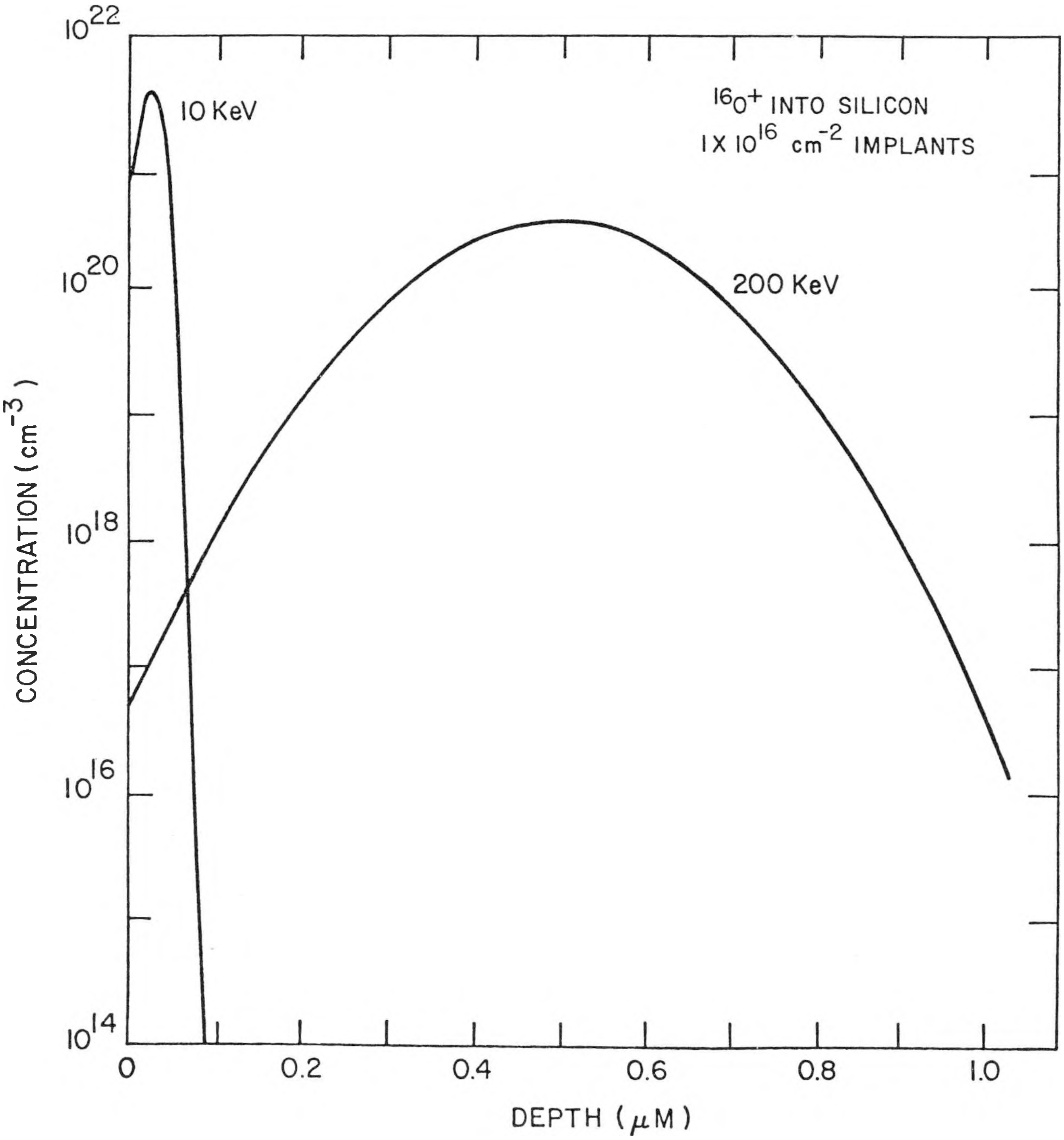

FIGURE 5. PREDICTED STOPPING DISTRIBUTIONS FOR 10 AND 200 keV $^{16}O^{+}$

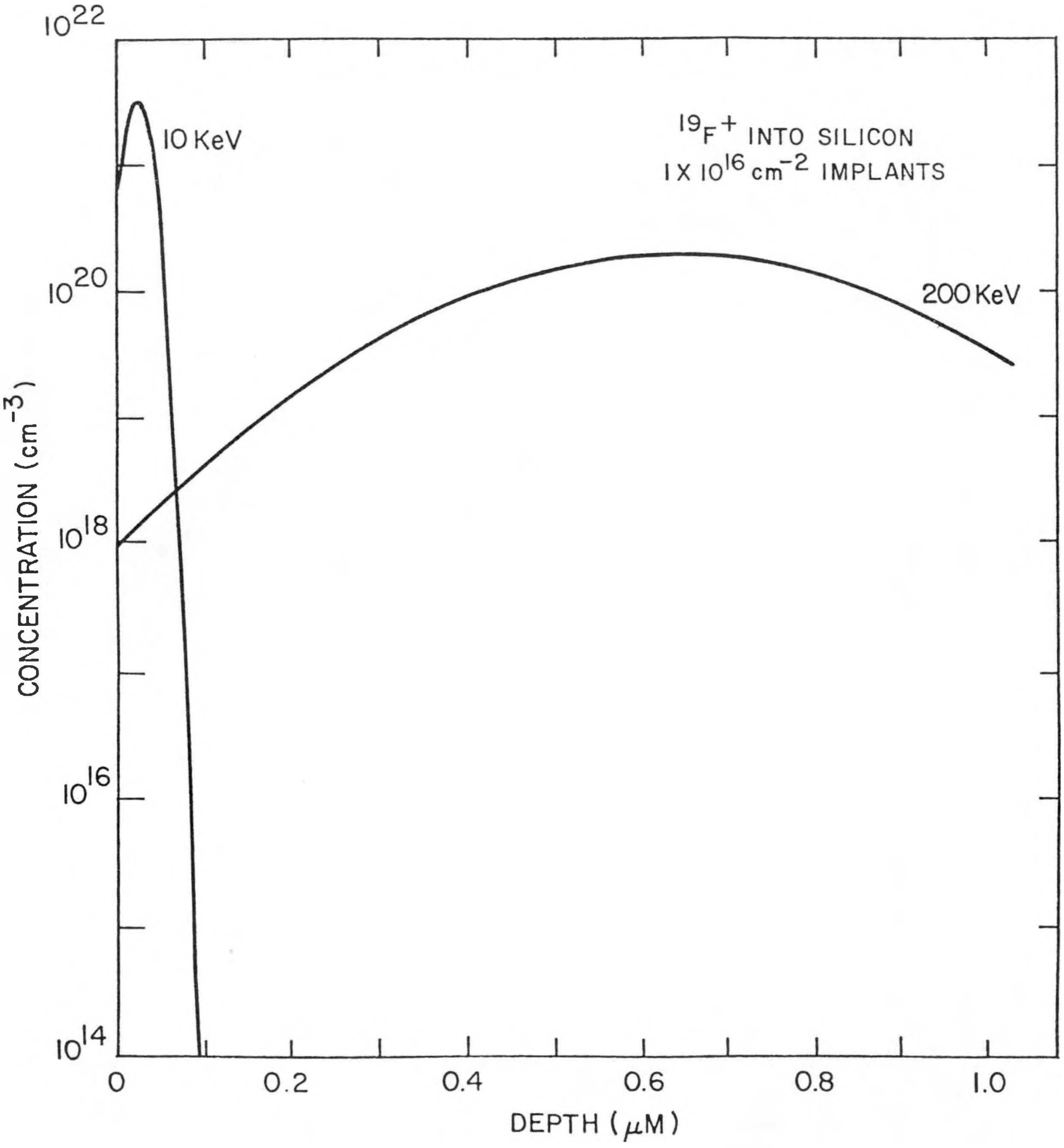

FIGURE 6. PREDICTED STOPPING DISTRIBUTIONS FOR 10 AND 200 keV $^{19}F^{+}$

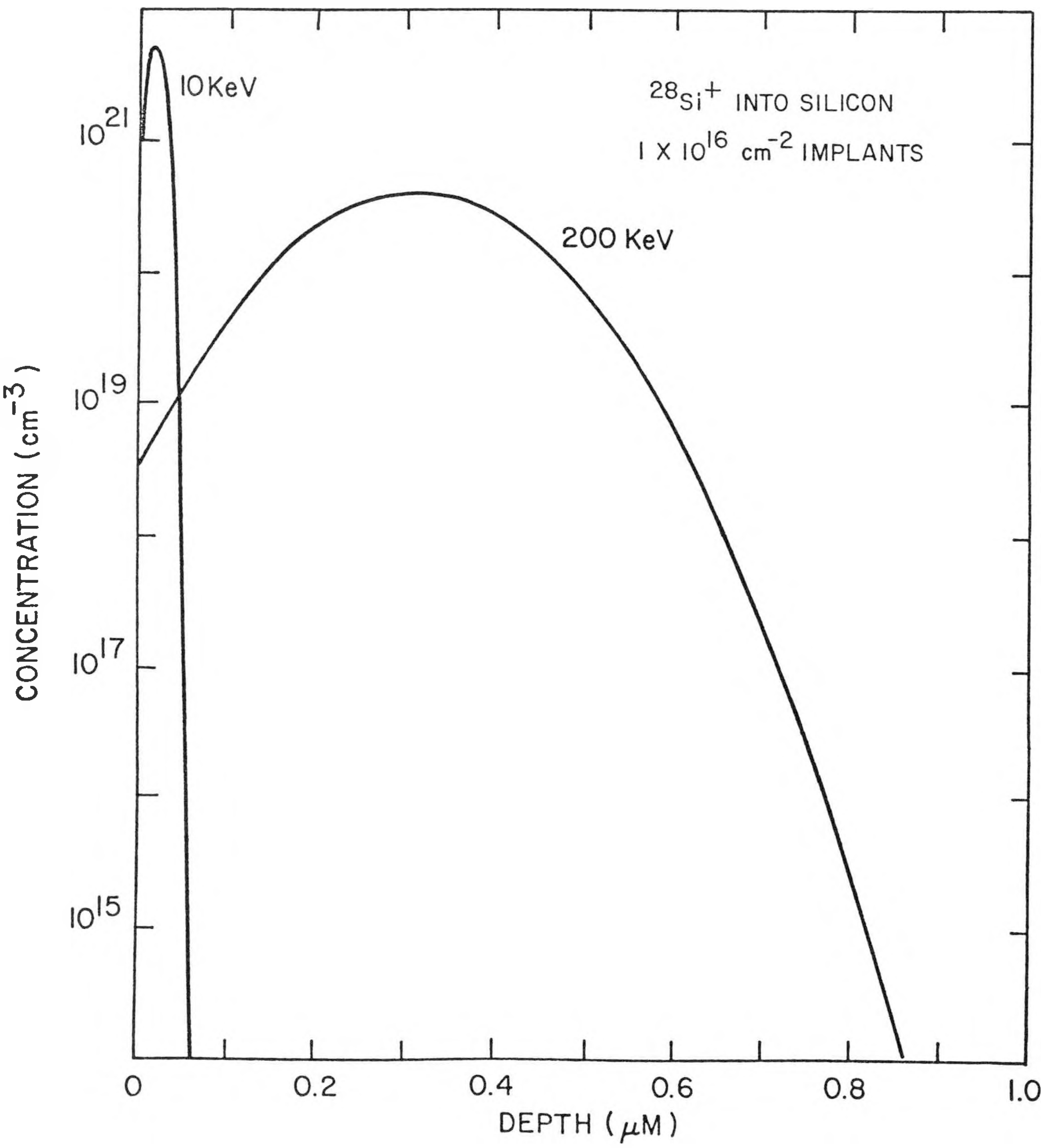

FIGURE 7. PREDICTED STOPPING DISTRIBUTIONS FOR 10 AND 200 keV $^{28}Si^+$

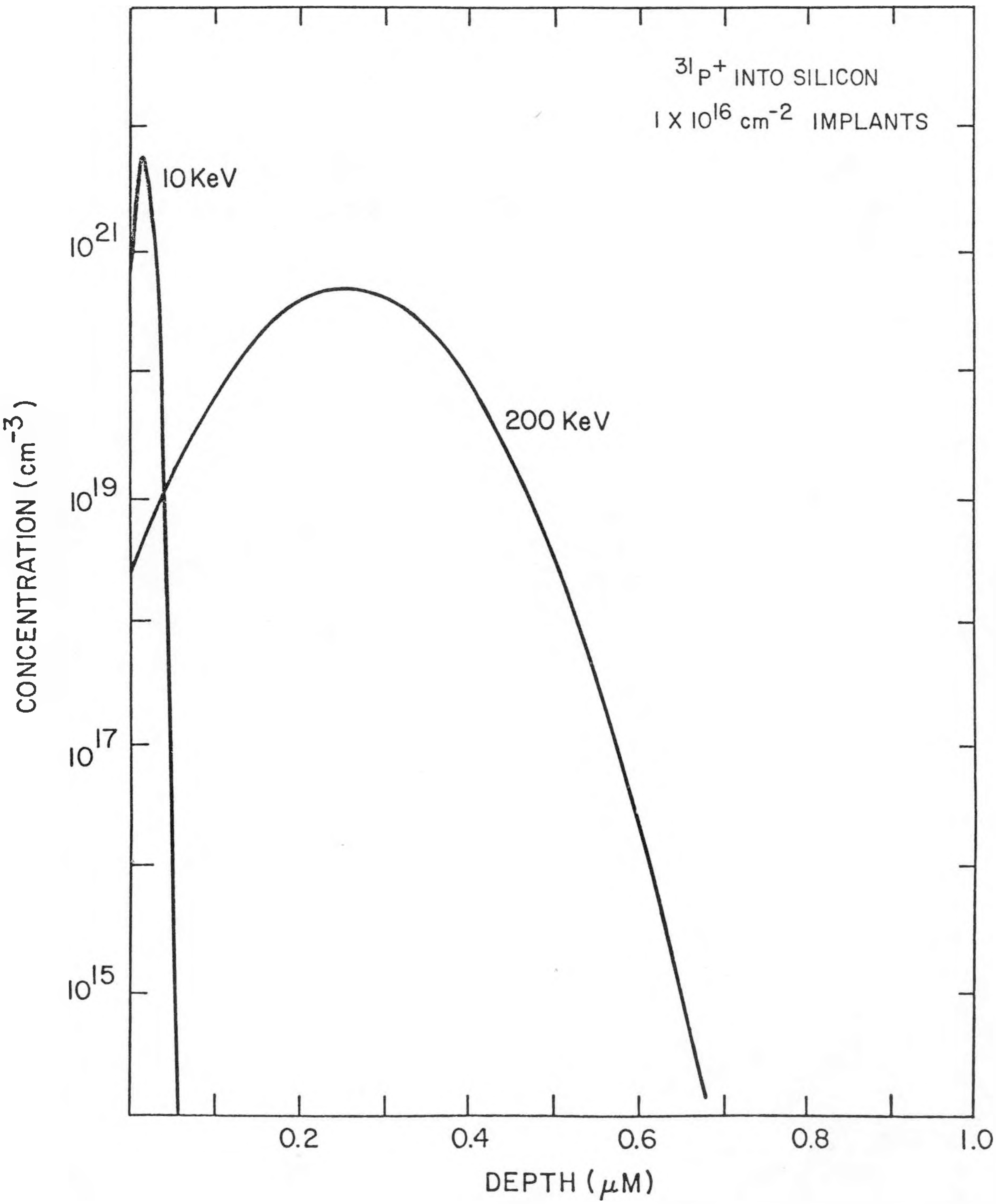

FIGURE 8. PREDICTED STOPPING DISTRIBUTIONS FOR 10 AND 200 keV $^{31}P^{+}$

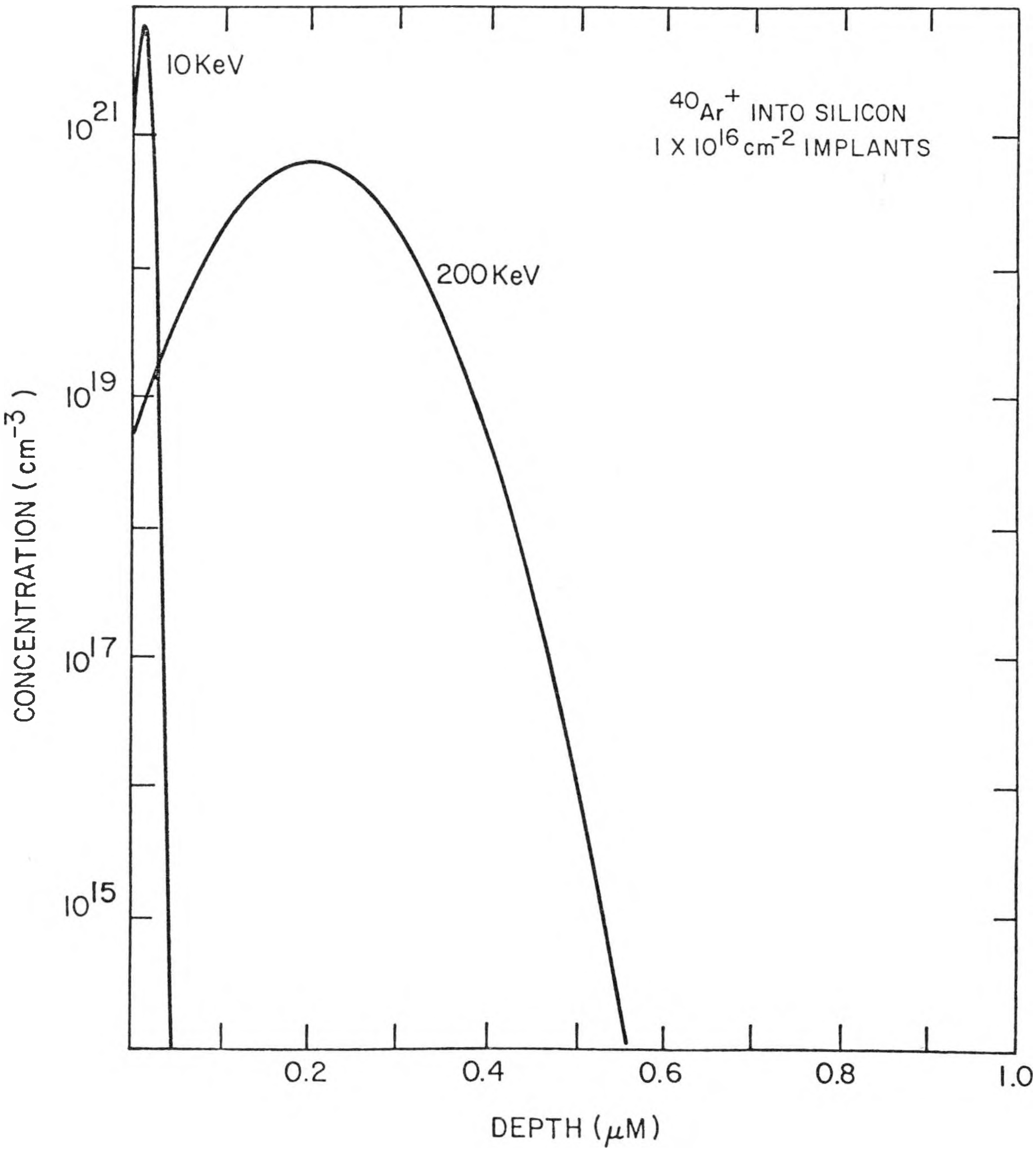

FIGURE 9. PREDICTED STOPPING DISTRIBUTIONS FOR 10 AND 200 keV $^{40}Ar^{+}$

High substrate temperatures during implant could cause loss of implanted hydrogen, uncontrolled partial recrystallization of the radiation damaged silicon material and perhaps other effects to the disadvantage of the investigation being performed. Consequently, substrate temperatures must be carefully limited during implants which could normally involve significant heating. All implants are to be performed under nominal room temperature conditions.

Special fixtures upon which samples are held during implant have been designed and constructed. Figure 10 shows one such holder which is used for implanting twelve 2 x 2 cm substrate items simultaneously. The holder is water cooled and samples are mounted to it so as to provide good thermal contact. Sample temperatures during implant have been monitored by means of small thermocouples bonded to the surface being implanted. Figure 11 shows examples of sample temperatures observed using the holder in Figure 10 under different ion beam energy input conditions. Maximum beam input energy planned to be employed is approximately 25 watts (500 microamperes at 50 keV), and samples need not experience temperatures above $60^{\circ}C$.

Consideration has been given to instantaneous temperatures on a sample surface caused by individual passes of the ion beam as it is scanned over the holder area. Under this program ion beams will be kept diffuse with densitities much less than 100 A/cm^2 or 5 $watts/cm^2$. Analysis has shown that instantaneous temperature excursions at a silicon surface due to the maximum single pass of a beam during scanning will not be significant.

2.3 DEVELOPMENT OF DEVICE AND MATERIAL TEST STRUCTURES FOR CELL DEVICE AND MATERIAL EVALUATIONS

Implantation might be employed for one or more of several purposes in the fabrication of an amorphous silicon device. Practical utilization could involve optimization of the character of material already deposited in an amorphous and hydrogenated condition. But initially, investigations under this program are to assess whether implantation can be employed to produce rather than modify amorphous silicon properties of interest. Consequently initial work is to be conducted using basic CVD polysilicon films as starting materials.

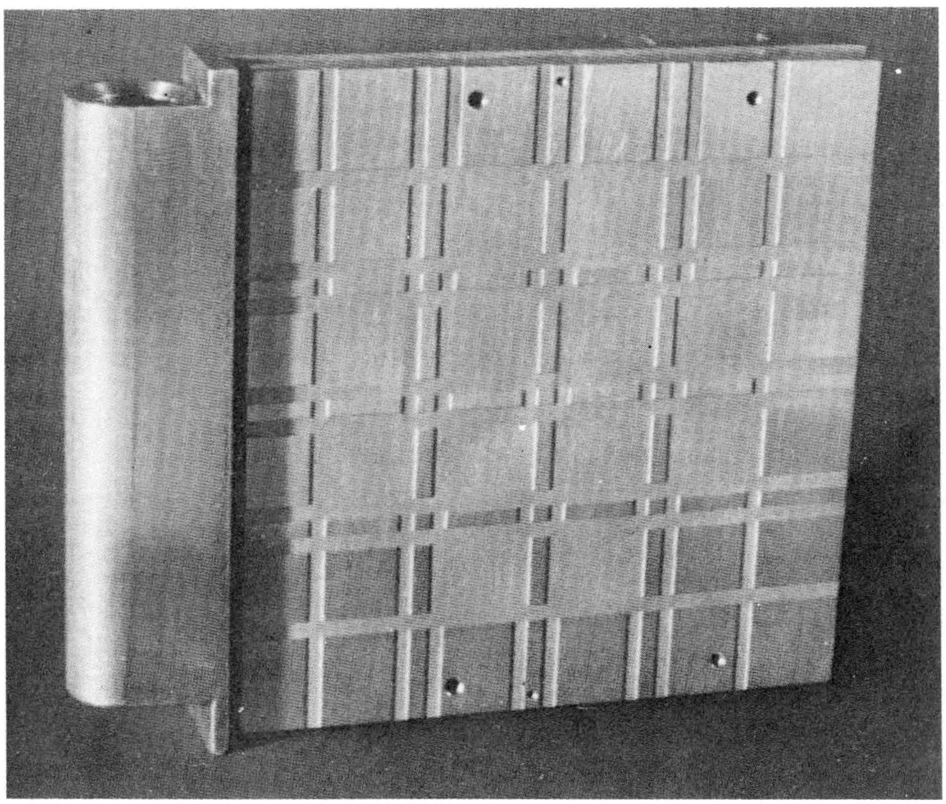

FIGURE 10. COOLED SAMPLE HOLDER FOR SPECIAL IMPLANTATIONS

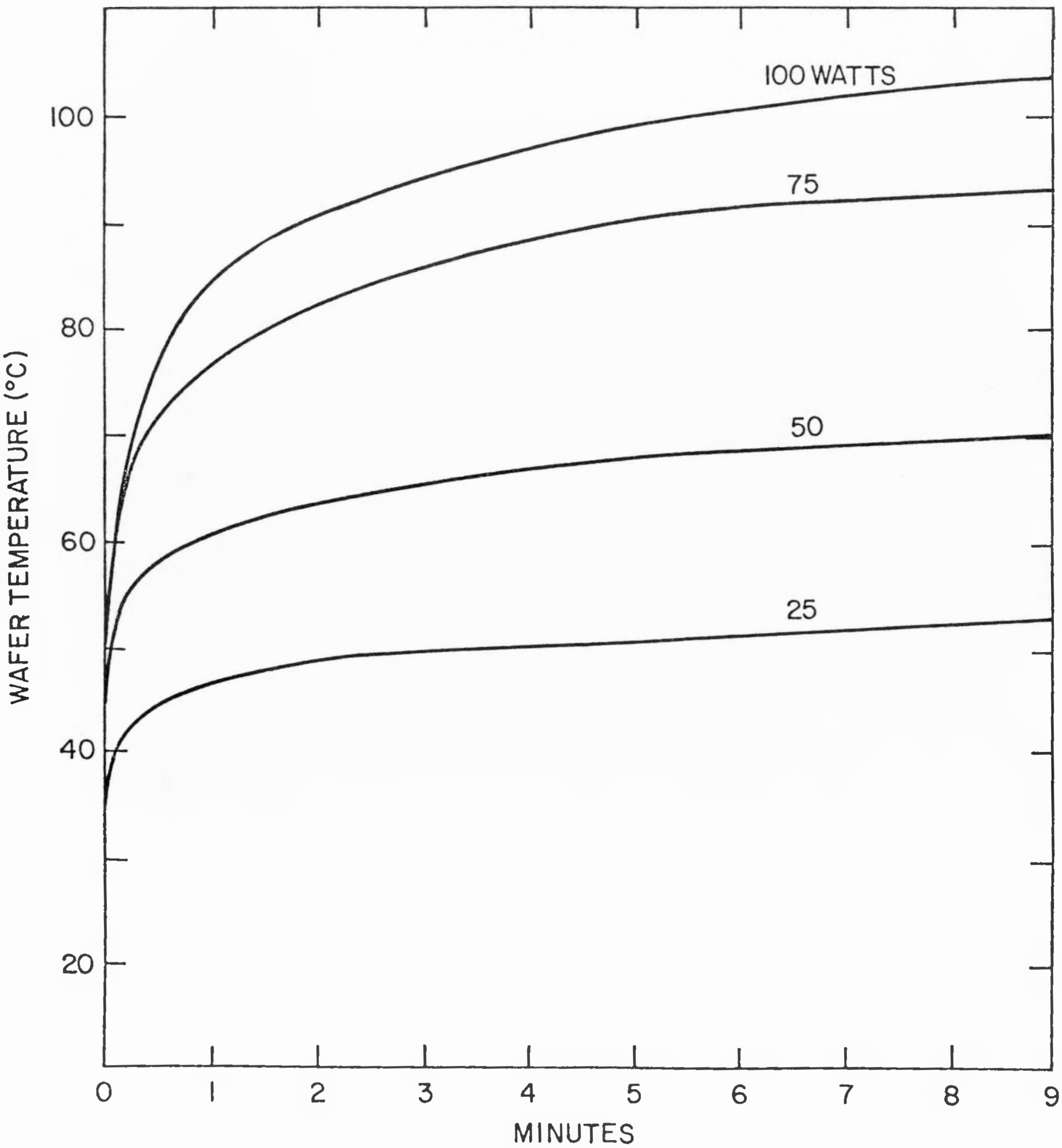

FIGURE 11. WAFER TEMPERATURE VERSUS IMPLANT TIME AS FUNCTION OF ION BEAM ENERGY INPUT

As much as possible investigations are to involve evaluation of effects of ion implantation and associated processing upon the operational characteristics of simple photovoltaic device structures. Cell structures for this type of study should incorporate the following:

(i) Preparation from a polycrystalline silicon film on an inactive substrate.

(ii) Device operation before introduction of hydrogen or amorphization by implantation.

(iii) Operational sensitivity to implantation process effects.

(iv) Structural stability under thermal or transient process anneal conditions which might be employed in conjunction with implant processing.

The preliminary test device structure shown in Figure 12 is expected to satisfy these requirements. Processing for this structure is being developed. For convenience, initial units are to be fabricated upon silicon wafer substrates isolated by thick thermal oxide layers.

The cell test structures will consist of nine individual active units, each of area 0.1 cm^2, on the same silicon film. Use of masks during performance measurements will allow the operational characteristics of the nine devices to be separately determined. Information regarding uniformity and reproducibility of observed effects should result. The small active areas of the individual devices upon the same film and substrate will allow problems associated with a practical back contact to be temporarily avoided during preliminary investigations. Single cells on 2 x 2 cm substrates will be produced in a modified configuration later in the program.

Studies to be performed by implanting into already operational polycrystalline film cell devices should provide information regarding general effects of hydrogenation, amorphization, etc., by implantation. It is expected that at any test stage it will be possible to measure dark and illuminated current-voltage characteristics and quantum efficiency versus wavelength of each device. Useful information regarding general effects should result. However, observable performance changes will occur because of complex changes within the material of the device structure. It will be necessary to be able to correlate changes in device operation with associated variations in the material.

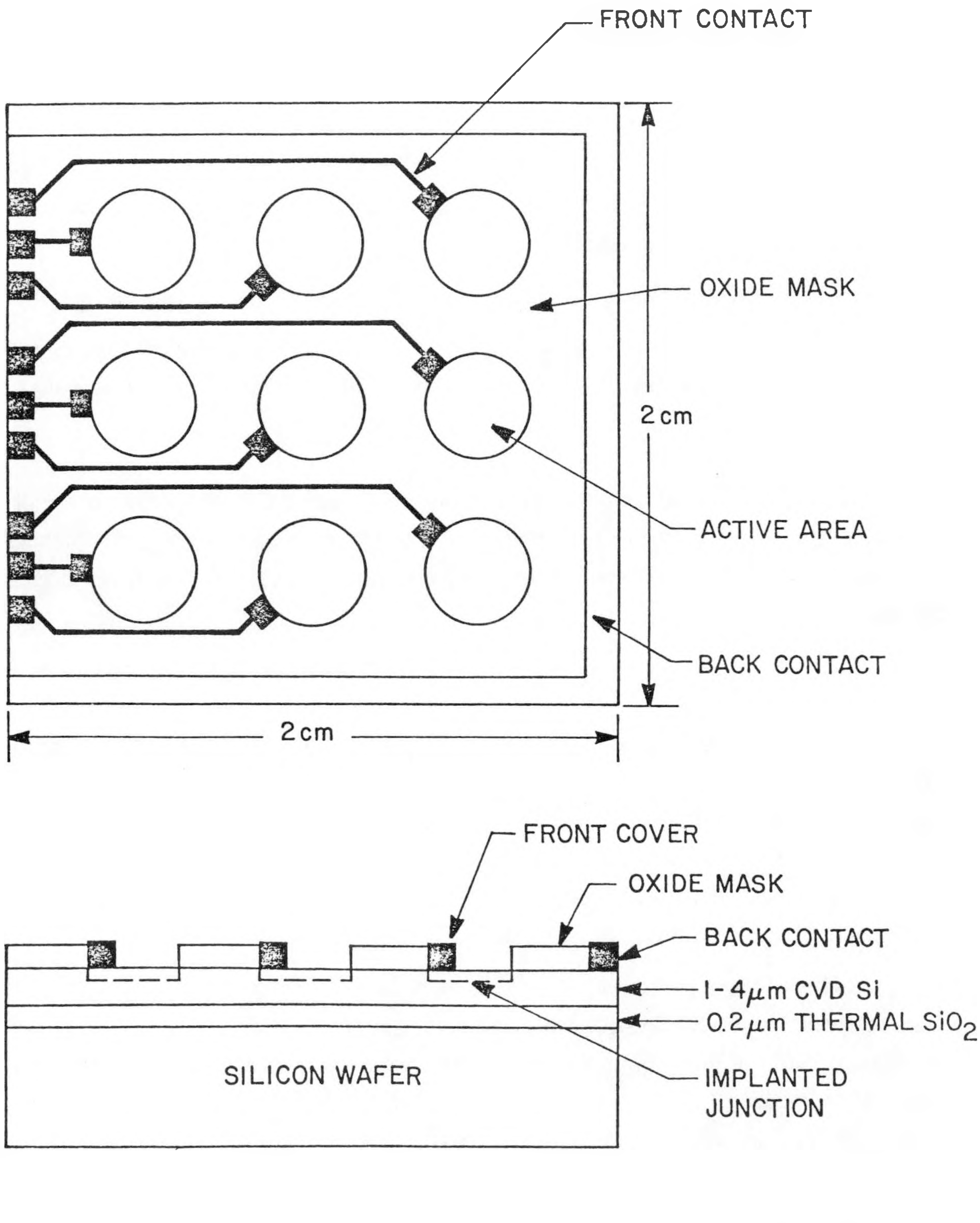

FIGURE 12. CELL DEVICE TEST STRUCTURE

Composition and structure of the silicon film will have to be identifiable. These properties will have strong spatial dependence because of the distribution of implanted ions.

Necessary information regarding the effects of implantation upon the material properties of a silicon film cannot be determined from the device units. Consequently, it is planned that throughout testing, material evaluation samples will be processed along with the device units. These material evaluation samples will be adequate for examination of optical transmittance changes and will be used for property examinations by techniques such as x-ray diffraction, sputter Auger, SIMS or helium ion backscattering.

SECTION 3
SUMMARY

During the period January through March 1979 this program to investigate applications of ion implantation to preparation of amorphous silicon material and cell devices was initiated. Emphasis during the quarter was placed upon establishing a number of special ion implantation capabilities needed in order to conduct the program. Adequate beams of all ions of initial interest were made available over wide ion energy range. Special fixtures to provide active sample cooling and required area masking were produced. Implantation environments were experimentally verified.

Analytical studies were conducted to insure that transient thermal effect problems could be avoided during high rate implantations to be employed. Ranges of available implantation effects for $^{1}H^{+}$, $^{11}B^{+}$, $^{16}O^{+}$, $^{19}F^{+}$, $^{28}Si^{+}$, $^{31}P^{+}$ and $^{40}Ar^{+}$ into silicon were examined. Work was initiated to begin selection of actual implantation parameters required to accomplish specific effect investigations.

A cell device test structure was selected to be employed as a primary investigation vehicle for initial evaluation of implantation effects. The structure is to consist of nine individual 0.1 cm^2 active area cells provided in a silicon thin film on an isolated 2 x 2 cm substrate. The silicon film is to be initially polycrystalline material approximately 2 μm thick deposited by chemical vapor deposition. After operational devices are produced from the polycrystalline material, implantation will be used to alter the film to be amorphous and hydrogenated.

☆U.S. GOVERNMENT PRINTING OFFICE: 1980-640-258-1938