SAN-3042-2
Distribution Category UC-63e

AMORPHOUS SILICON SOLAR CELLS BY HYDROGEN IMPLANTATION

QUARTERLY REPORT NO. 2
FOR THE PERIOD
1 APRIL - 30 JUNE 1979

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August 1979

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Prepared for the

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

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SECTION 1
INTRODUCTION

Ion implantation is a technique which provides the ability to produce major alterations of composition and structure in the region of the surface of an existing material substrate. Implantation allows broadly selectable modifications to be easily, reproducibly and uniformly controlled over a depth range in silicon of the order of a micron. As an energetic particle impact process, implantation inherently involves microscopic disordering of substrate atoms in the region affected. This disorder can usually be eliminated by means of annealing or might itself be employed as a useful processing effect. The purpose of this program for investigation of "Amorphous Silicon Solar Cells by Hydrogen Implantation" is to examine whether implantation can be effectively utilized in the preparation of amorphous silicon materials and amorphous silicon solar cell devices.

Because the depth which can be reached in silicon by normal implantation is approximately equal to the necessary thickness of an amorphous film for a photovoltaic device, implantation might be used for one or more of several possible purposes, including:

(i) hydrogenation
(ii) amorphization
(iii) material doping
(iv) device element formation
(v) formation of beneficial atomic complexes

The mass of a silicon film for an amorphous device cannot be deposited by ion implantation. It is likely, however, that implantation can be used to modify an existing nonamorphous silicon film to achieve the material characteristics and device structure required for an amorphous cell. This specific possibility is to be examined under the subject program of this report. Cell devices are to be fabricated of CVD polysilicon deposited upon isolated substrates. Implantation is to be employed to amorphize and hydrogenate the active material of the already functional devices.

Two ion implantation machines being used for investigation under this program can provide the ions of immediate interest, $^{1}H^{+}$, $^{11}B^{+}$, $^{16}O^{+}$, $^{19}F^{+}$, $^{28}Si^{+}$, $^{31}P^{+}$, $^{40}Ar^{+}$, at energies from 10 through 200 keV and at beam currents of a few hundred microamperes or more. Some of the ions, hydrogen in particular, may be utilized in very high level doses. The available implanters are adequate for study purposes. Much higher current machines would be needed for cost effective production processing. Such machines are already feasible by use of designs based upon existing technology.

Investigations under this program are to emphasize the use of cell devices to provide information regarding application of ion implantation to amorphous silicon cells. Special ion implantation procedures and analyses are required. During the period of this report, developmental activities involved preparation of implantation capabilities and procedures, preparation of processing routines for a test cell device and preliminary evaluation of the effects of hydrogen implantation upon operation of devices.

SECTION 2
PROGRAM DISCUSSION

2.1 PROGRAM PLAN

The first 12 months of the technical program which began in January 1979 involve 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

Work during the subject period of this report, months 4 through 6, activities included (i) completion of necessary facilities, procedures and analyses for special implantations, (ii) completion of basic process development for amorphous silicon cell device and material test structures, and (iii) preliminary examination of the effects of implantation and annealing upon cell device structures. Program activities and progress were in accordance with the technical plan.

2.2 DEVELOPMENT OF SPECIAL IMPLANTATION/ANNEALING CAPABILITIES AND PROCEDURES

Facilities, sources and fixtures to allow selected implants of $^{1}H^{+}$, $^{11}B^{+}$, $^{16}O^{+}$, $^{19}F^{+}$, $^{28}Si^{+}$, $^{31}P^{+}$, or $^{40}Ar^{+}$ to be correctly and effectively performed on groups of up to twelve 2 x 2 cm samples were previously prepared. Limits of ion stopping distributions achievable with the implanters to be employed were previously examined. During the period of this report, considerations were directed toward selection of specific conditions to be actually utilized.

Figure 1 shows anticipated distribution of hydrogen deposited in silicon by a 50 keV proton implant to 3×10^{17} ions/cm^2. If the hydrogen were to be uniformly distributed to a depth of 1 μm, a 3×10^{17} cm^{-2} implant could provide approximately 6 atomic percent of hydrogen in the silicon. However, Gaussian stopping from a single condition implant will result in a concentration profile in which the hydrogen is not acceptably distributed. In the case of Figure 1, hydrogen concentration would exceed 20 atomic percent at a depth of 0.5 μm but would be several orders of magnitude lower in the immediate vicinity of the surface. Figure 2 suggests the degree of improvement which can be accomplished by simply combining implants at 2 energies to cover the range of interest. Figure 3 shows an example of an expected distribution from a set of implants at 3 energies. It is possible to compose a resonable approximation to almost any desired distribution by combination of simple stopping theory profiles for a few sets of available implant conditions. Actual profiles should be approximately consistent with these predictions. Some profile composition will be necessary and will be experimentally employed for proton implant investigations of this program.

Implanted ion profile composition may also be necessary for some of the other ion applications to be considered. This is not the case for implants to produce a local element of a device structure, for example, a shallow junction layer. On the other hand, creation of an amorphous zone in an initially polycrystalline silicon film by means of lattice destruction using silicon or argon ions will need multiple condition composition in order to be effective.

Figure 4 shows individual profiles of 4 sets of $^{28}Si^+$ implants used to amorphize an initially crystalline or polycrystalline silicon layer to a depth of approximately 0.5 m. For amorphization purposes, designation of ion energies and fluences is not sufficient to insure the desired result. First samples prepared using conditions as in Figure 4 involved relatively high ion beam current densities ($\sim$100 μA/cm^2). Helium ion backscattering analysis showed the implanted material to be polycrystalline near the surface and amorphous below. Surface region recrystallization was able to occur because of transient heating by high input energy densities of the nondiffuse ion beams. Correction has been made by reducing beam current densities of high energy ions to approximately 10 μA/cm^2.

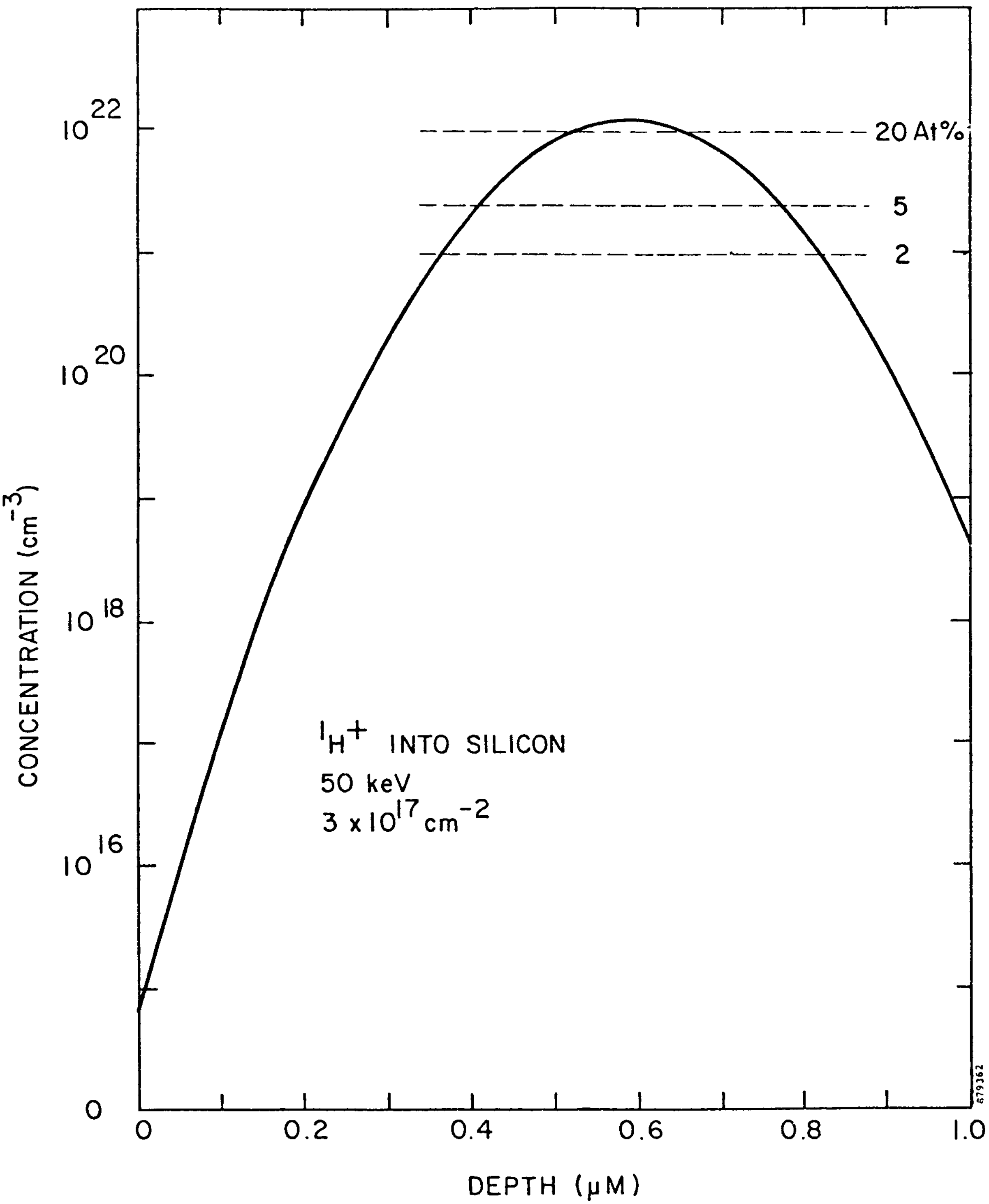

FIGURE 1. ANTICIPATED DISTRIBUTION OF HYDROGEN IN SILICON FROM 50 keV PROTON IMPLANT

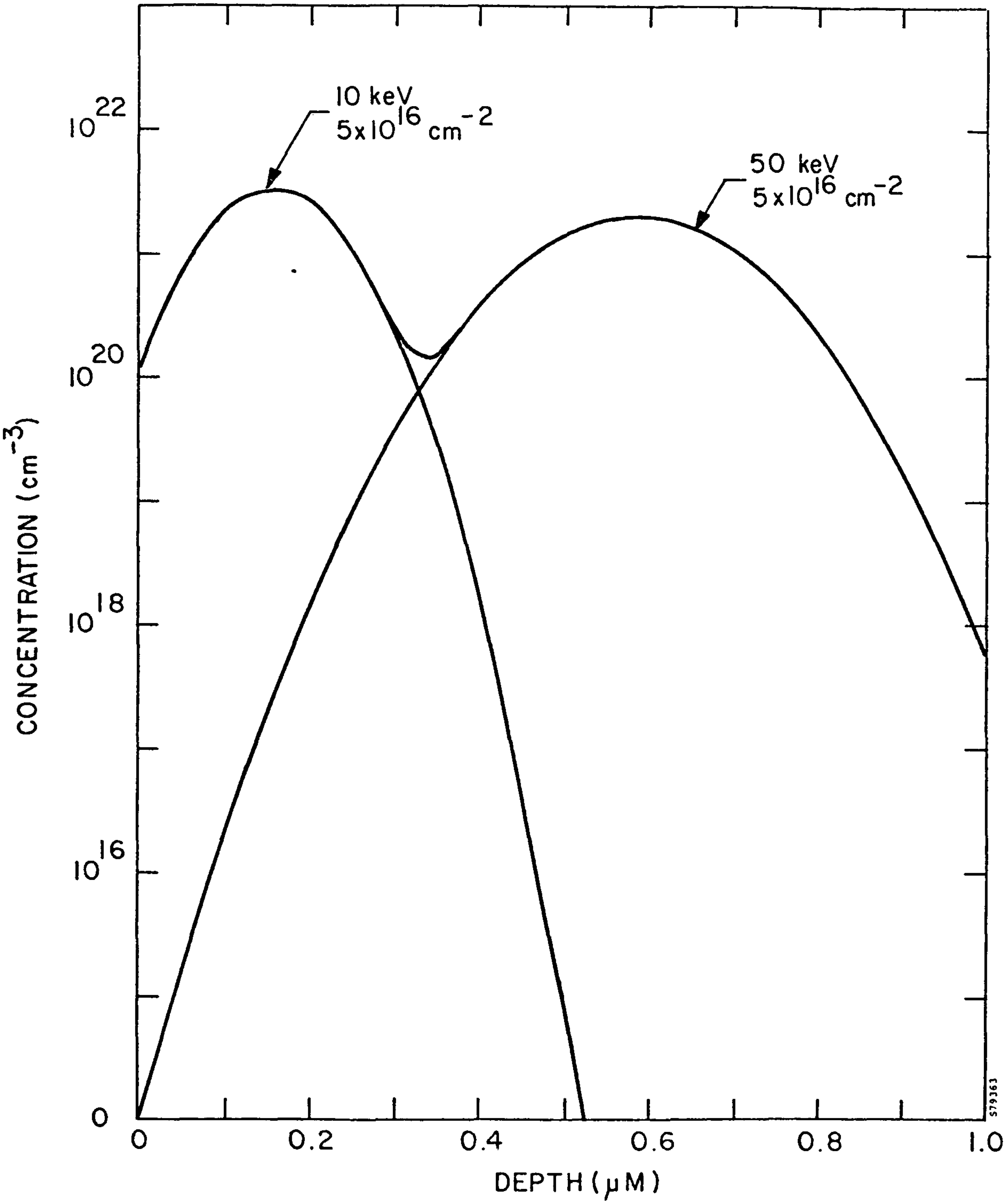

FIGURE 2. ANTICIPATED DISTRIBUTION OF HYDROGEN IN SILICON FROM COMBINED 10 AND 50 keV PROTON IMPLANTS

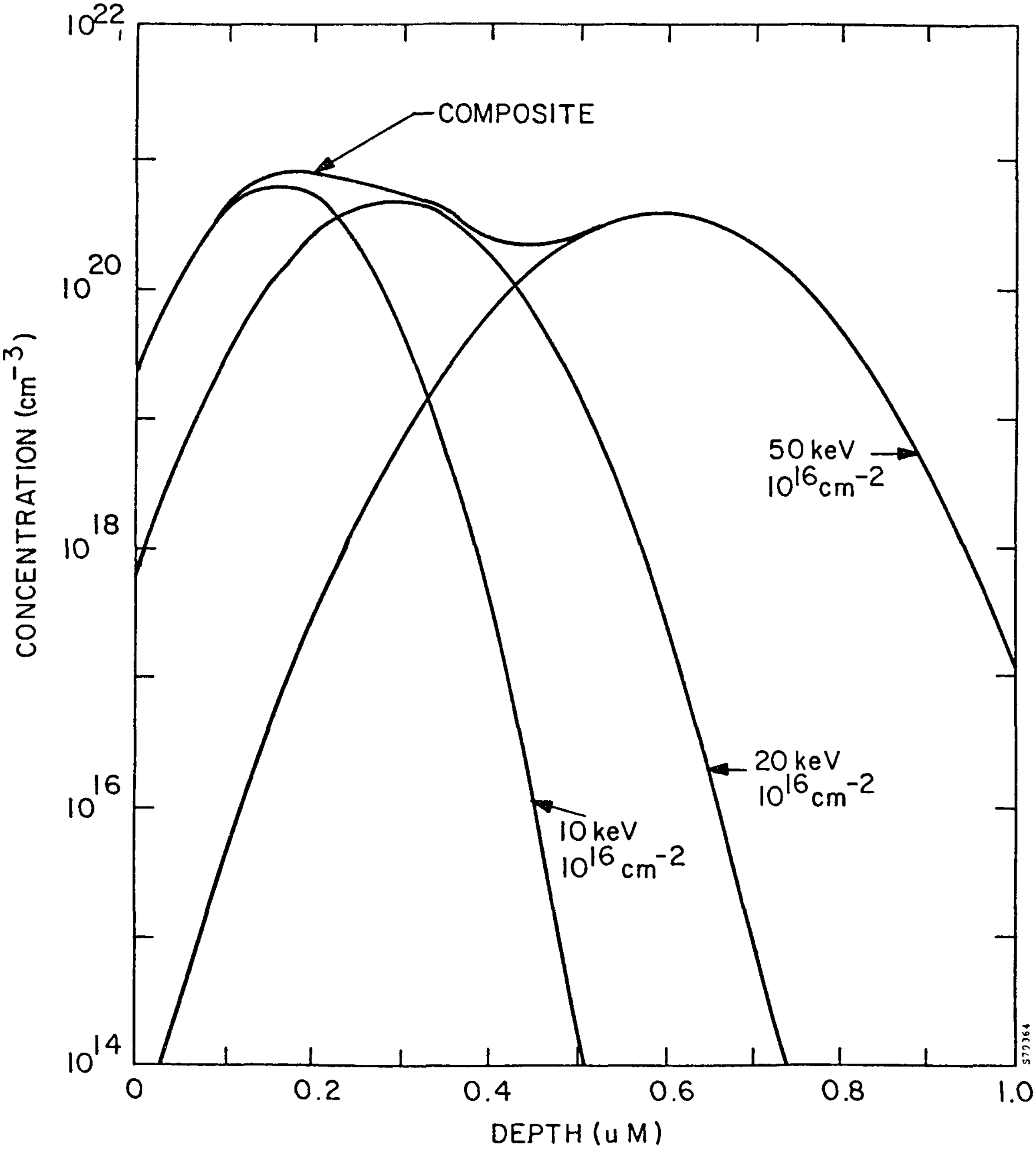

FIGURE 3. ANTICIPATED DISTRIBUTION OF HYDROGEN IN SILICON FROM COMBINED 10, 20 AND 50 keV PROTON IMPLANTS

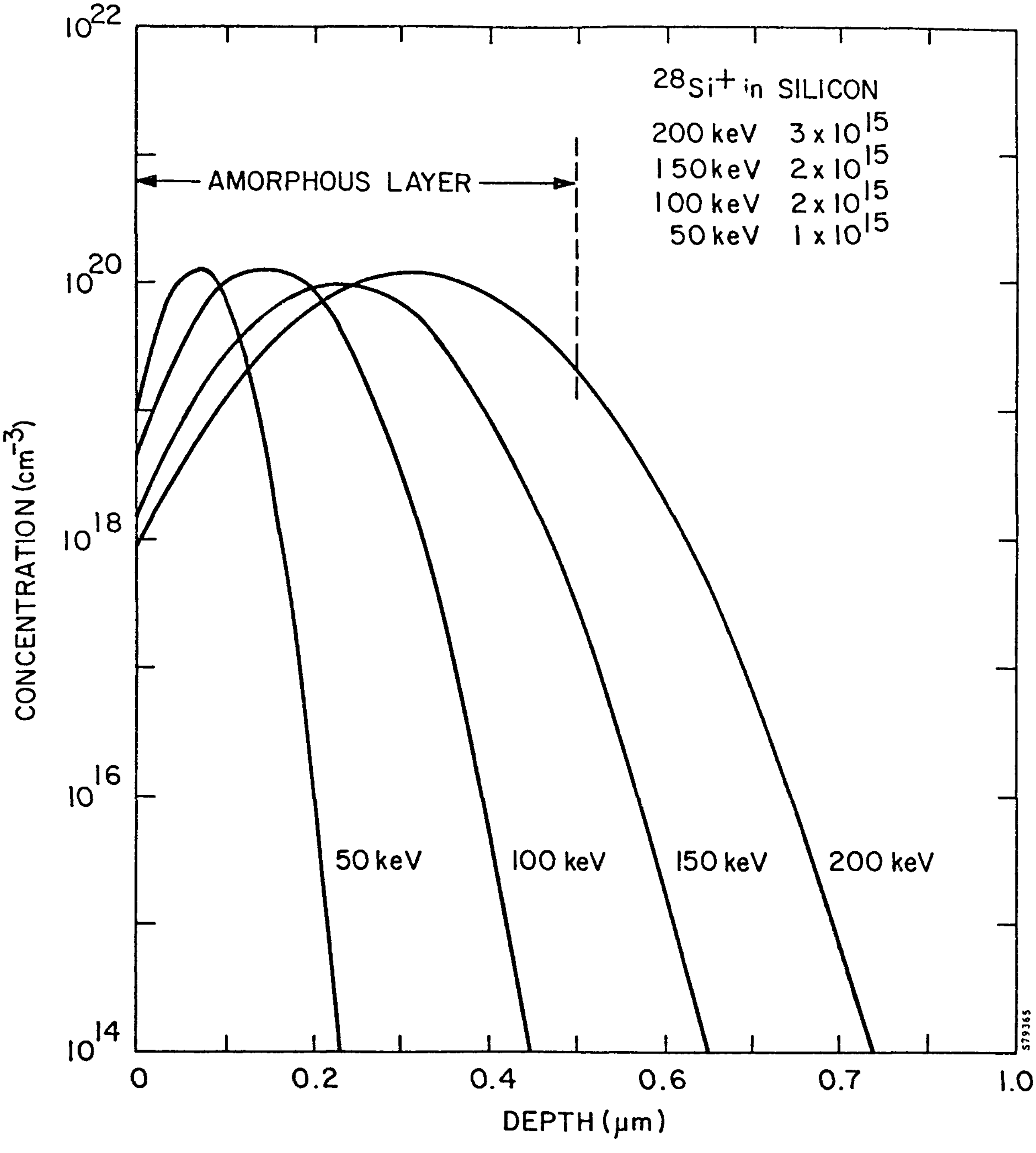

FIGURE 4. $^{28}Si^+$ IMPLANTS USED FOR AMORPHIZATION OF POLYSILICON FILM

Proton implants for hydrogenation purposes involve fluences appreciably higher than those associated with conventional existing applications of implantation. At the same time, little surface sputtering can be produced by protcns impacting upon silicon. Consequently the problem of accumulation of a residue on the proton impact surface because of polymerization of residual atmosphere hydrocarbons of a diffusion pumped vacuum system has been found to be significant. Preliminary experiments involving $10^{17}cm^{-2}$ fluences of 50 keV protons have resulted in buildup upon the silicon surface of several hundreds of angstroms of hydrocarbon film.

Deposition of a nonremovable film of polymerized vacuum pump oil upon the surface of test items undergoing the special implants of this program is not acceptable. Fortunately, for other reasons, one implanter at Spire is to be modified to provide cryogenic pumping of the sample station. This conversion is to be completed during the next quarterly reporting period of this program. The modified implanter will then be used for all high dose proton implants. The surface contamination problem should be eliminated.

2.3 TEST STRUCTURE DEVELOPMENT

Figure 5 shows a photograph of the cell device structure which is to be used for much of the work of this program. Each device structure consists of nine individual active 0.1 cm^2 cell units on the same silicon film. The silicon film is deposited upon an isolated substrate, at present an oxidized silicon wafer. The device structure of nine already operational photovoltaic cells is to be used to evaluate various implantation effects upon device performance.

The processing sequence for preparation of cell device study structures is essentially as follows:

(i) Deposit 2 - 4 μm of CVD polysilicon film onto isolated substrate.

(ii) Grow thermal oxide on polysilicon film.

(iii) Etch oxide to open active cell areas and back contact region on polysilicon film.

(iv) Implant polysilicon cell junctions through oxide openings.

(v) Anneal implant damage.

(vi) Deposit patterned contact.

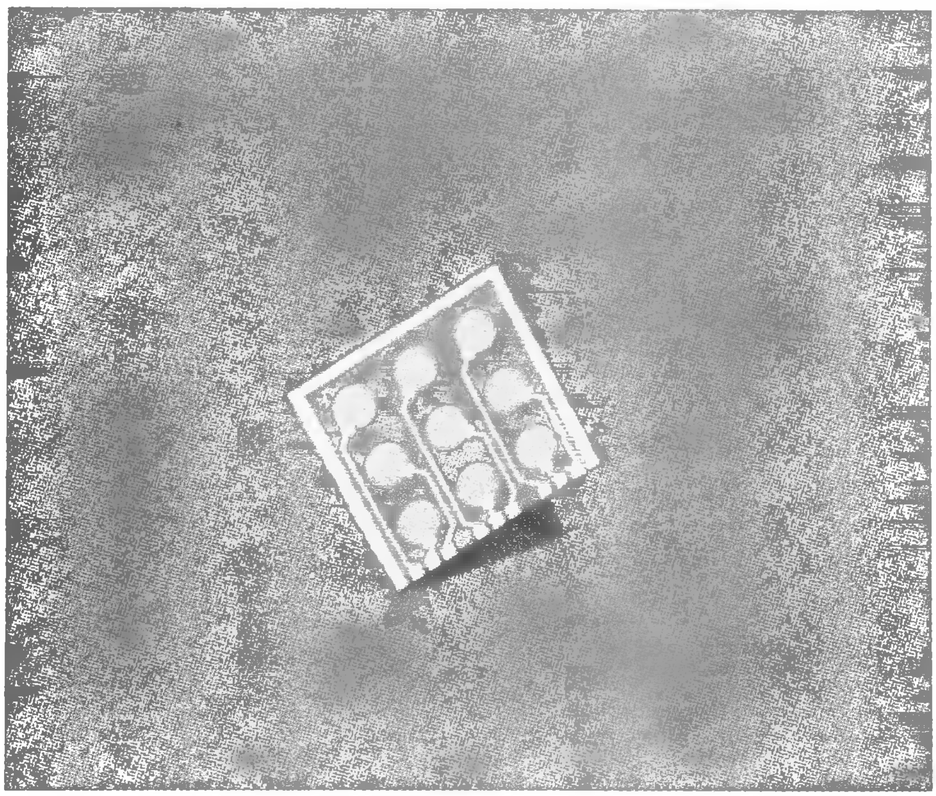

FIGURE 5. CELL DEVICE STRUCTURE

After this processing sequence the device structure is ready to be used as a starting structure for investigation of implantation effects of interest.

The individual cells of the polysilicon film starting device structure must be operational. Figure 6 shows AM0 I-V characteristics of a set of nine cells on one substrate. The cells exhibit the performance to be expected of polycrystalline film devices in which the silicon is too thin to adequately absorb incoming photons and grain size is very small ($\leq 1 \mu m$).

2.4 INVESTIGATION OF IMPLANTATION/ANNEALING EFFECTS

Preliminary investigation of the effects of implantation and annealing upon device structures and upon material samples was initiated during the period of this report. The following were examined:

(i) Effects of candidate annealing conditions upon polysilicon cell device performance

(ii) Basic effect of $^{1}H^{+}$ implantation only upon polysilicon cell device performance

(iii) Basic effect of $^{28}Si^{+}$ implantation only upon polysilicon cell device performance

Combined effect studies are to begin during the next quarter.

Ion implantation produces recoil damage which removes crystallinity and probably short range order as well. High temperature annealing which is conventionally employed to produce recrystallization is not to be needed for amorphous material purposes. However, low temperature annealing will probably be required to establish local interatomic bonding after hydrogenation and amorphization. Device structures must be capable of withstanding the environments involved. Sample structures were subjected to thermal annealing in nitrogen at temperatures up to $300^{o}C$ and also to low fluence $0.1 \; cal/cm^2$ pulsed electron beam annealing. At first some variability was observed; device performance could remain unaffected, could degrade or could improve. Changes which did occur could be related to inadequate procedures in the preparation of the devices. Corrections were made. As-prepared devices are now considered stable under the annealing enironments of interest.

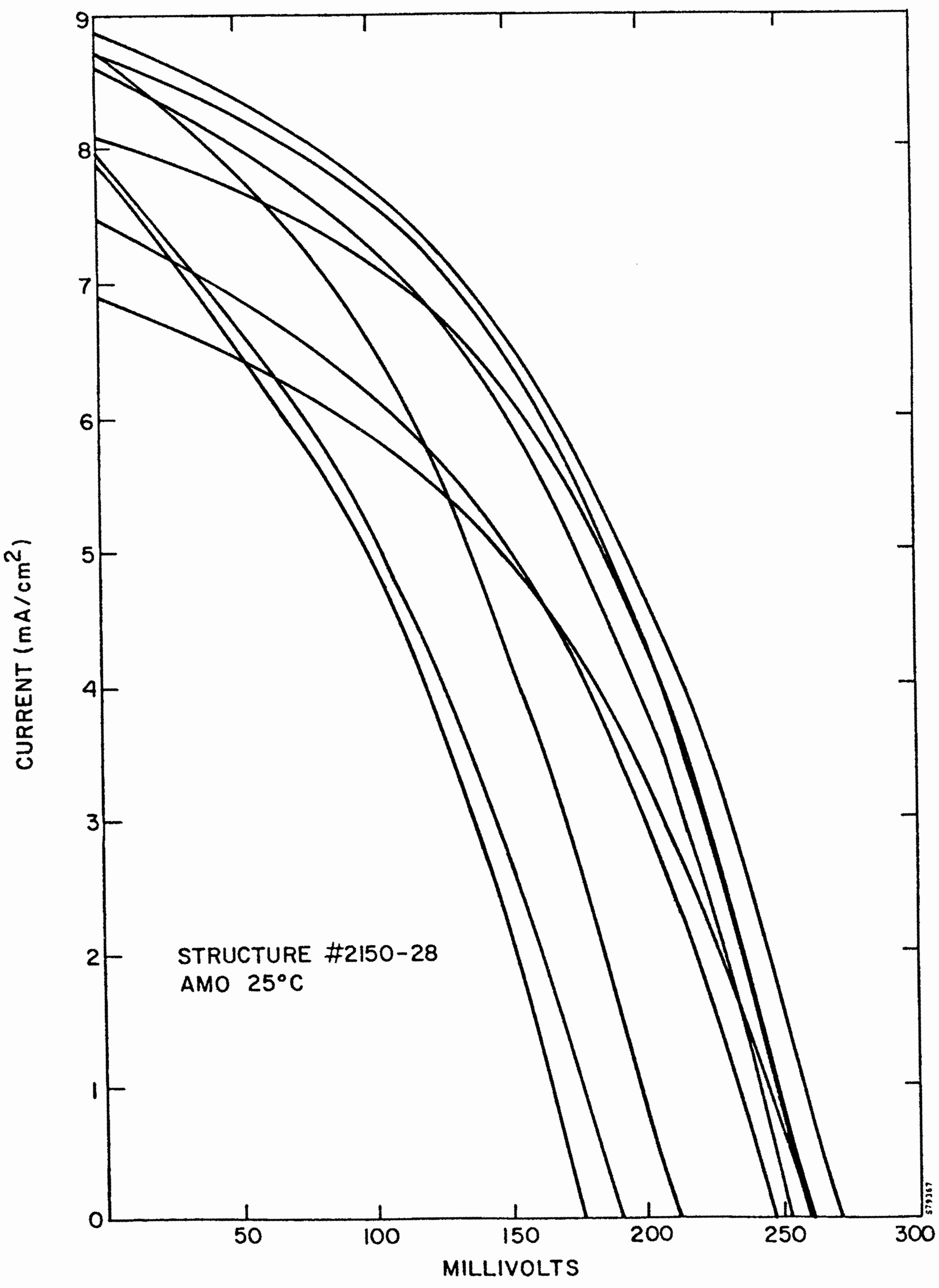

FIGURE 6. ILLUMINATED OUTPUT CHARACTERISTICS OF NINE POLYSILICON CELLS ON ONE SUBSTRATE

Device structures subjected only to high dose implants of protons or to amorphizing silicon ion implants were severely degraded. Figure 7 shows typical effect of $^{1}H^{+}$ implants on a single device. At 3×10^{16} ions/cm^2, photoresponse was virtually eliminated. At higher doses some performance restoration was observed. Additional restoration could be produced by subsequent thermal annealing at 250^{o}C. In the case of silicon ion implants, device output was lost and could not be improved by 250^{o}C annealing. This is consistent with expectation. Figure 8 shows a typical result.

Each device structure is accompanied during implantation studies by a material test unit which consists of a 1.5 μm CVD polysilicon film on a fused silica slide. Figure 9 shows the effects of hydrogen or silicon implantation upon typical total transmittance of material samples.

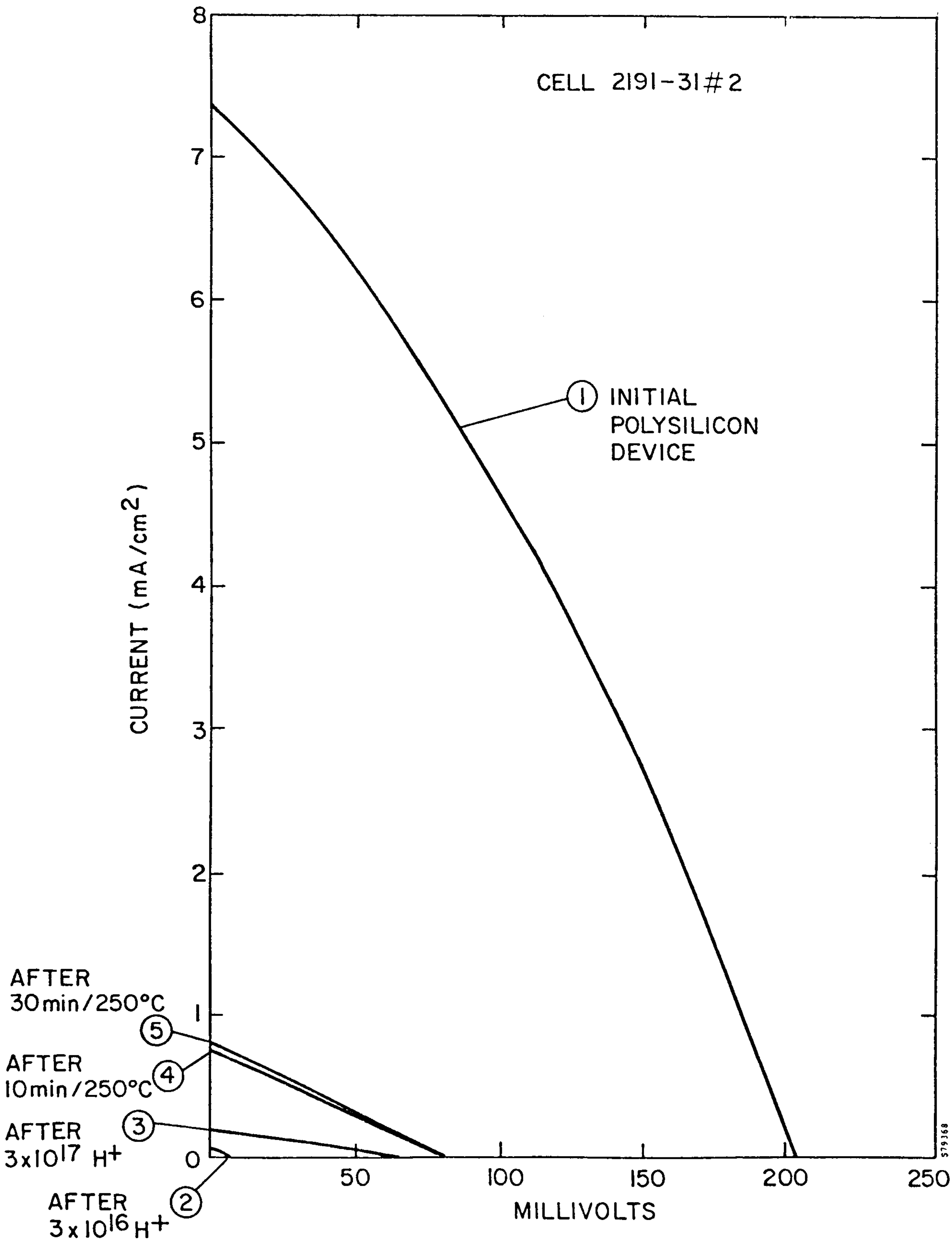

FIGURE 7. EFFECT OF $^{1}H^{+}$ IMPLANT AND SUBSEQUENT 250°C ANNEALING UPON POLYSILICON DEVICE PERFORMANCE

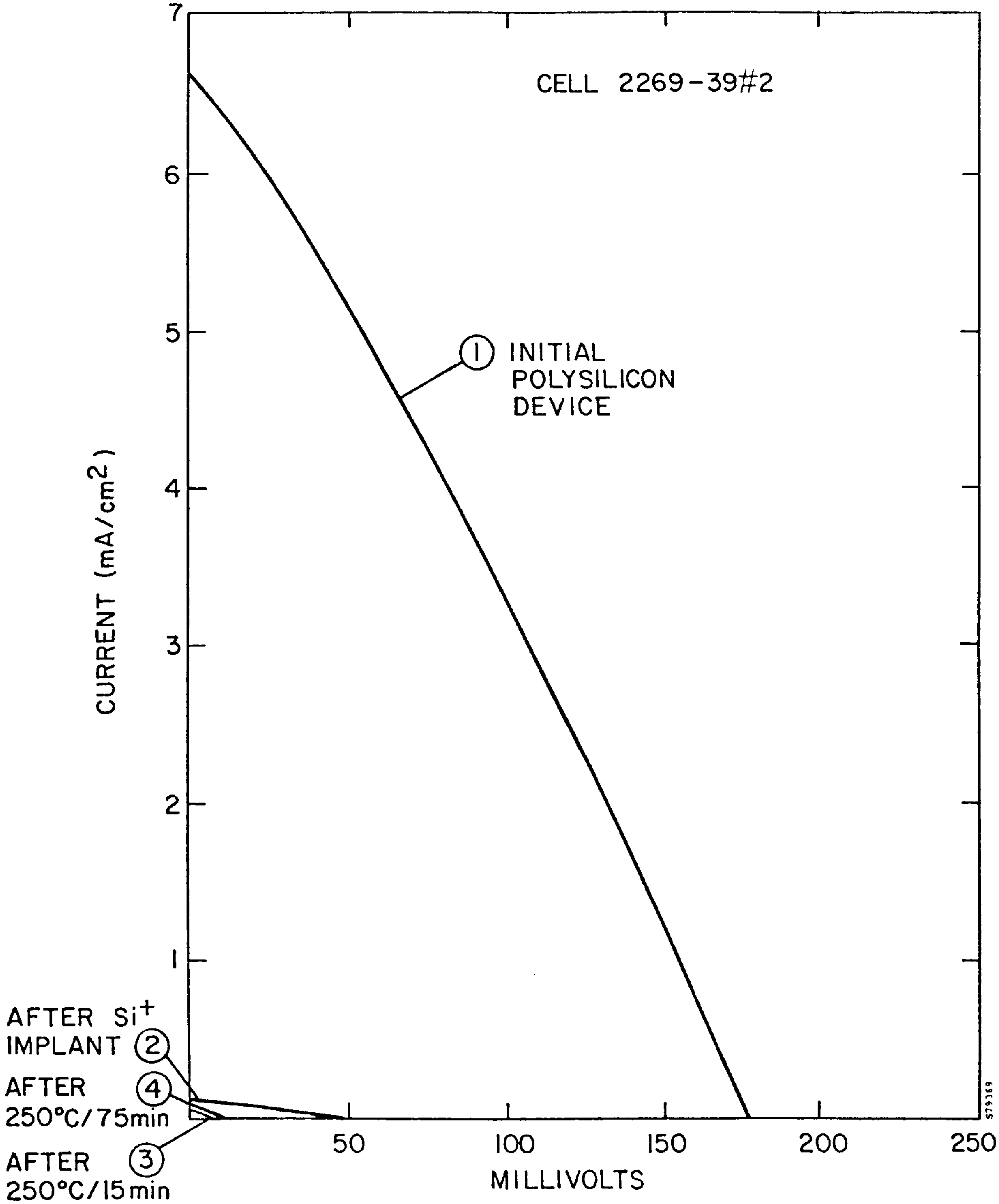

FIGURE 8. EFFECT OF AMORPHIZING $^{28}Si^{+}$ IMPLANT AND SUBSEQUENT 250°C ANNEALING UPON POLYSILICON DEVICE PERFORMANCE

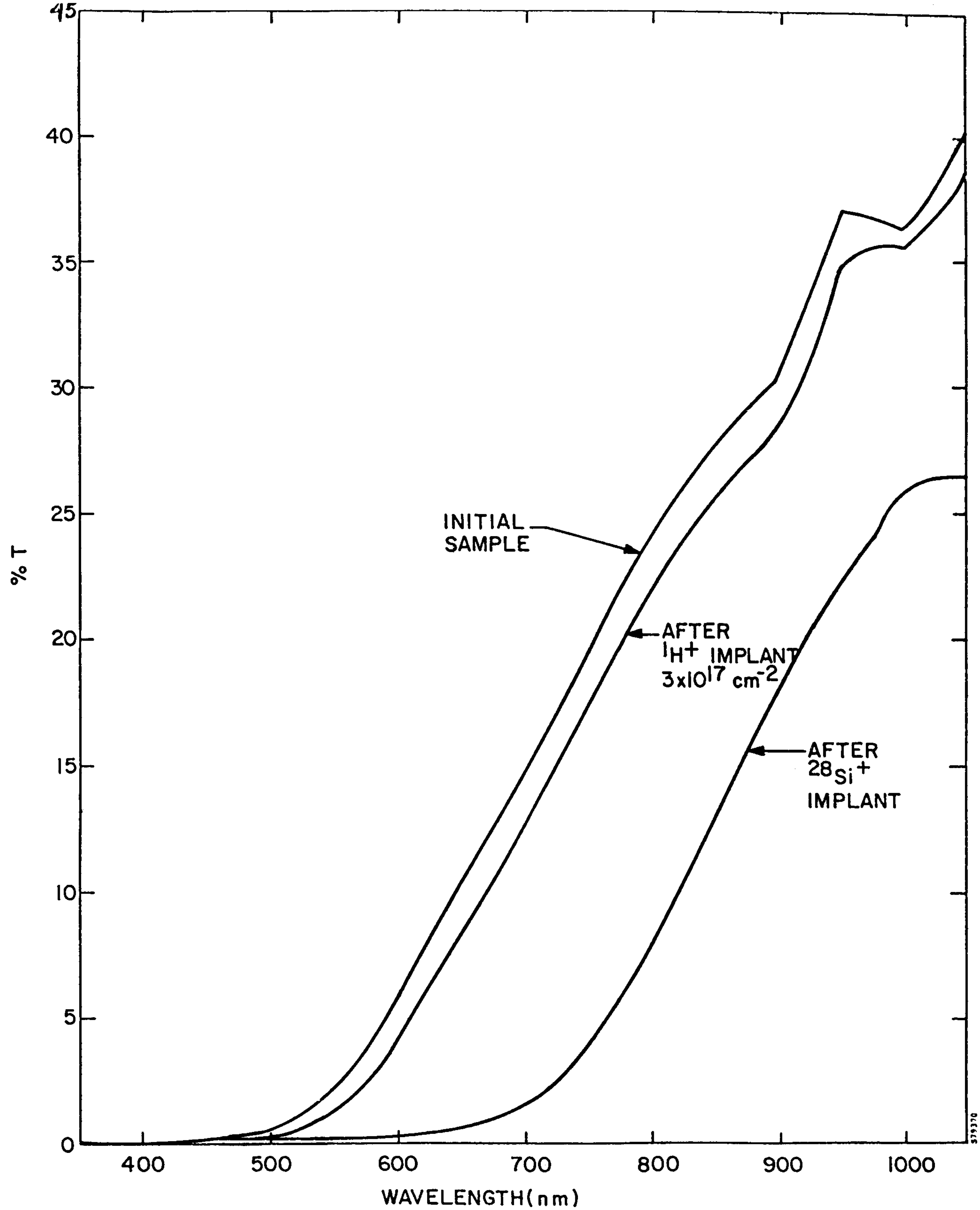

FIGURE 9. EFFECT OF $^{1}H^{+}$ AND $^{28}Si^{+}$ IMPLANTS ON TRANSMITTANCE OF SILICON FILM SAMPLES

SECTION 3
SUMMARY

During April through June 1979 the preparatory phase of this program was essentially concluded. Necessary special procedures, sources and fixtures for implantation were available and tested. One problem requiring correction was identified. Films of polymerized hydrocarbon residues originating from vacuum diffusion pump vapors were formed on samples subjected to high dose hydrogen implants. This problem should be eliminated during the next reporting quarter.

Development of a cell device structure to be used for preliminary effects studies was completed. Small area cells are fabricated in groups of nine on single 2 x 2 cm substrates. Starting material for these cells is a small grained polycrystalline silicon film deposited by chemical vapor deposition. Observed efficiencies of the polysilicon film cells are typically on the order of 0.7 percent. Variation in performance of these cells to be produced by ion implantation will be a primary subject of investigation during the next quarter. The cell device structures are themselves compatible with requirements for special implantation processing and are stable under thermal annealing to 300^{o}C or under 0.1 cal/cm^2 electron beam transient annealing.

Implantation effects studies were initiated during the quarter. Consideration was given to selection of actual sets of parameters necessary to produce reasonable special distributions of effects within the film under process. First experiments were performed using $^{1}H^{+}$ and $^{28}Si^{+}$ implantations on cell device structures and material evaluation samples. Results were consistent with expectations.

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