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Research and Development of High Efficiency Silicon Solar Cells

Third Semiannual
Technical Summary Report

U. S. Army Signal Research
and Development Laboratory
Fort Monmouth, New Jersey

PERIOD COVERED
1 July to 31 December 1960

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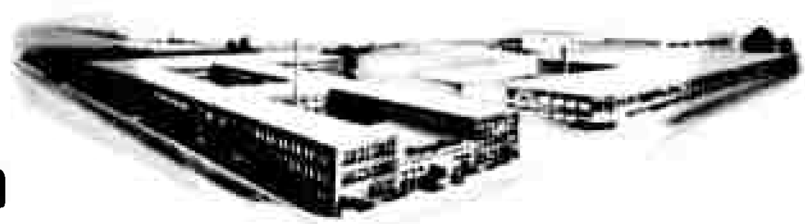

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HIGH EFFICIENCY SILICON SOLAR CELLS

By

Pierre Lamond

Paul Berman

Third Semiannual Summary Report

1 July - 31 December 1960

Objective: An investigation leading to the improvement of the Practical efficiency of silicon solar cells to twelve percent or higher.

CONTRACT No. DA 36-039-SC-85250 TASK No. 3A99-09-001-03

CONTRACT DATE 18 September 1959 PROJECT No. 3A99-09-001

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TRANSITRON ELECTRONIC CORPORATION
Wakefield, Massachusetts

Prepared for U.S. Army Signal Research and Development Laboratory
Fort Monmouth, New Jersey

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ABSTRACT

A summary of the process used at Transitron for the "P on N" solar cells is presented. These have been superceeded by the more radiation resistant "N on P" type cells.

Problems in optimizing the junction depth of solar cells are discussed. The results of diffusion experiments are presented.

The calibration of solar cell standards and artificial light systems for the testing of solar cells is discussed. Special attention is given to the problems encountered in using a tungsten artificial light source to determine the efficiency of solar cells. Experimental results are presented which validate the theoretical discussion.

Results of electron bombardment experiments on "P on N" and "N on P" solar cells are given which show the "N on P" cell structure to be approximately five times more resistant to damage by 2 Mev and 700 Kev electrons. Electron bombardment experiments on "N on P" cells fabricated at Transitron are presented which agree with the results obtained with the Signal Corps "N on P" cells.

The fabrication of Transitron radiation resistant "N on P" solar cells is discussed and the process as developed thus far is given.

PURPOSE

The objective of this contract is to conduct research investigations leading to the improvement of the practical efficiency of silicon solar cells to twelve per cent or higher. This program also includes studies into methods that will result in high yields and techniques that will permit mass production of these more efficient cells at the lowest possible cost for a 1 x 2 cm cell.

NARRATIVE

"P ON N" CELL FABRICATION SUMMARY

The "P on N" cell fabrication process is presented in a simplified form in Table 1. After the silicon crystal has been cut into 1 X 2 X .08 cm^3 slices it is cleaned in a solution of 33 grams of potassium dichromate, 50 c.c. distilled water, and 300 c.c. sulphuric acid, at 70°C rinsed in flowing distilled water for 5 minutes, placed in a 1 normal solution of sodium hydroxide at 120°C for five minutes, and rinsed again in flowing distilled water.

The slices are lapped on one side with 1000 grit powder and rinsed in flowing water for 5-10 minutes. The slices are then etched in an acid composed of 1 part nitric acid and 1 part hydroflluric acid (cold) until the surface is highly etched. The slices are rinsed in water and in alcohol and dried.

The boron diffusion is done by placing boron and 60 silicon slices in a capsule which is evacuated to a pressure of less than 1 micron of mercury. The capsule is then placed in a furnace having a temperature between 1000°C and 1100°C. After a successful diffusion the sheet resistance is about 10 Ω/□. The cells are then cleaned in concentrated hydroflluric acid to remove any oxide which might have accumulated on the cells.

After the SiO anti-reflectant coating has been evaporated onto the top surface of the cells, the aluminum grid configuration is evaporated onto the top surface and alloyed in.

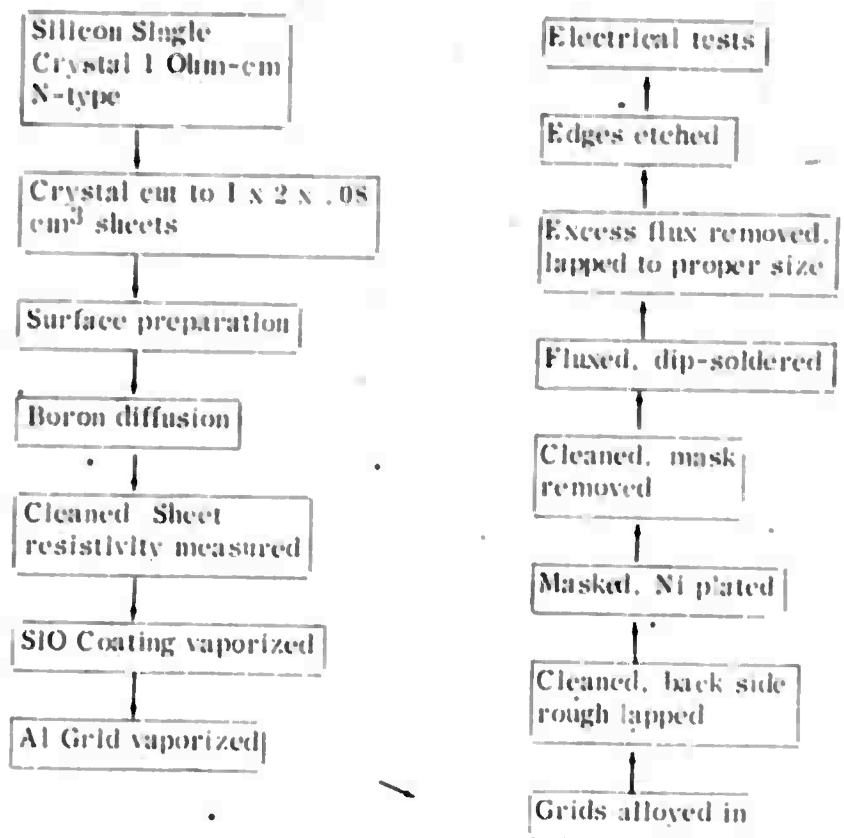
The cells are then cleaned, the back surface rough lapped, and the front surface masked to expose only the grid configuration. The cells are subsequently electroless nickel plated on the grid and the entire rear surface.*

The cells are fluxed, dip soldered and cleaned in acetone to remove the flux. The edges are scraped, and lapped to remove any traces of solder or nickel plate. The cells are covered with beeswax, the edges stripped of the wax and wiped with alcohol. The cells are then etched in a composition of 1 part 48% hydrofluric acid and 3 parts 70% nitric acid for 30 seconds, rinsed in distilled water and etched again for 30 seconds. This procedure insures clean edges and increases the shunt resistance.

*The electroless nickel plating solution used is described in "Electroless Nickel Plating for Making Ohmic Contacts to Silicon", M. V. Sullivan and J. H. Eigler, Journal of The Electrochemical Society, p. 226, April 1957.

TABLE I

"P^+ ON N" CELL FABRICATION



DIFFUSION STUDIES

The spectral response of a solar cell is quite sensitive to changes in the depth of the junction. For deep junctions the long wavelength response is quite good because long wavelength (1 micron) photons are absorbed well inside the bulk region. Consequently, if the junction is deeper, the probability that the minority carriers created by the long wavelength photons will reach the junction is increased. However, the lifetime of the minority carriers in the diffused region is much smaller than the lifetime of the minority carriers in the bulk region, so that many of the minority carriers created by short wavelength (.5 micron) photons in the diffused region do not reach the junction. By moving the junction closer to the surface of the cell, more of the short wavelength photons are absorbed in the bulk region, creating minority carriers which have a long lifetime and are likely to be collected at the junction. For solar cells which are to be energized by natural sunlight, the small loss in long wavelength response due to the shallow junction configuration is of little concern since the preponderance of photons are emitted in the short wavelength region.

There is , unfortunately, an upper limit to the shallowness of the junction. Thin junctions give rise to high series resistance in the diffused layer, since the cross sectional area is quite small. This situation has been alleviated to a great extent by the use of a conducting grid configuration on the upper surface of the cell. Thin junctions are extremely vulnerable to surface defects which occur either in the processing or in subsequent handling. Small surface scratches will pierce through the diffused layer, resulting in a low shunt resistance or high leakage.

Studies have been made on the relation between efficiency yield and diffusion time (which determines the junction thickness) at a constant temperature. The results are presented below (Table I), and are what one would expect; namely, that with shallower junctions the short circuit current increases due to the improved collection efficiency of the junction, but the open circuit voltage decreases because of lower shunt resistance. The optimum diffusion time seems to be 120 minutes.

TABLE II

DATA ON "P on N" CELLS WITH SHALLOWER DIFFUSIONS

Run No.	No. of Cells in run	ISC (avg.) (ma)	VOC (avg.) (volts)	Diff. Time (Min.)	Approx. Junct. Depth (Mils)	Cell Distribution 9-10 %	10-11 %	11-12 %	12-13 %
490	10	46	.572	120	.06	1	1	5	3
493	9	47	.565	90	.052		2	6	1
492	8	49	.555	60	.042	1	3	2	
494	9	50.4	.550	30	.03	2	5	2	

CALIBRATION OF SOLAR CELLS

One of the most common problems encountered in the testing and calibration of solar cells is the inherent mis-match between the photon-wavelenght distribution of artificial light sources (usually a tungsten source having a color temperature of about 2800^{0} K) and the photon-wavelength distribution of natural sunlight. The tungsten source emits more photons of long wavelength and fewer photons of short wavelength than natural sunlight of equal energy intensity. Therefore, a cell having a particular efficiency under tungsten light of a specific energy intensity will not necessarily have an identical efficiency under natural sunlight of the same energy intensity. For example, if a cell having a weak long wavelength response, but a relatively strong short wavelength response is measured under a tungsten light of a specific energy, it will have a lower efticiency than if it were measured under natural sunlight of the same energy. It would now be appropriate to describe the present method of calibrating a standard and to discuss the disadvantages of this method.

As a matter of convenience cell efficiency measurements are made under light intensity which corresponds to 1.21 gm-cal/cm^2-min natural sunlight energy intensity. The standard cells are measured in natural sunlight by employing a normal incidence Eppley pyrheliometer to obtain the energy intensity of the sun. Since the short circuit current is directly proportional to the light intensity, the value of the short circuit current under 1.21 gm-cal/cm^2-min sun can be calculated by the ratio of 1.21 to the actual energy intensity of the sun (as read from the normal incidence pyrheliometer .) The indoor tungsten source is then calibrated from these cells by adjusting the light intensity so that the short circuit current is the same as the short circuit current (corrected for temperature and for 1.21 gm-cal/cm^2-min sunlight) which the standard exhibited under natural sunlight. It would be convenient to say that now the artificial light source corresponds to natural sunlight of 1.21 gm-cal/cm^2-min, since the short circuit current, which is a measure of the number of minority carriers arriving at the junction, of the standard cell is identical to the 1.21 gm-cal/cm^2-min sunlight value. However, this is only true for this particular standard or for cells having exactly the same spectral response as this standard.

Table III shows a series of cells and their short circuit currents under natural sunlight intensity and the ratio of the sunlight Isc reading to the artificial light Isc reading. It is at once obvious that differences in spectral response between cells compared to one another will result in different "equivalent" artificial light "calibration", depending on which cell is used as a standard. Only transfer standards having the same spectral response as the cells to be tested can be used in determining solar cell efficiency under tungsten light.

TABLE III

Cell Designation	α	β	δ	R-2	#2	#2 uc	C	F	G	9X	S
Sunlight Isc (mA) Readings for 1.21 gm cal/cm^2-min Input	47.2	48.7	44.3	31.1	40.9	26.3	39.8	39.1	42.3	37.6	40.0
Readings under artificial (2800°K tungsten) light set at arbitrary fixed intensity. (mA)	47.2	47.3	45.7	30.6	43.8	28.2	43.5	42.7	45.7	38.9	43.7
Sunlight Isc / Artificial Light Isc	1.00	1.03	.97	1.02	.95	.93	.85	.92	.93	.97	.91

RADIATION RESISTANCE

In the Second Semiannual Technical Summary Report the results of several experiments involving electron bombardment of "N on P" and "P on N" were presented. It was shown experimentally that the "N on P" cells, which were furnished to us by Mr. J. Mendelkorn of the Signal Corps Research and Development Laboratories, were far more radiation resistant than the "P on N" cells.

Additional experiments concerning the effects of electron bombardment on "N on P" and "P on N" solar cells have been performed using electrons having an energy of 750 Kev* which corresponds to the energy possessed by the majority of electrons existing in the heart of the inner Van Allen belt.** The relative efficiency of an "N on P" and a "P on N" cell as a function of electron bombardment intensity is shown in figure 1. The "P on N" cell had an initial efficiency of 11.05% while the "N on P" cell had an initial efficiency of 10.7%. However, after the first bombardment (3.1×10^{14} el/cm^2) the efficiency of the "P on N" cell had decreased to 7.15% while the efficiency of the "N on P" cell after this same bombardment had decreased only to 9%.

From spectral response measurements it has been found that in cells of comparable initial efficiency and lifetime of minority carriers in the bulk region, the lifepath in the P region of the "N on P" cell is approximately 6 times larger

* Produced by a Van de Graaff electrostatic accelerator.

** THE GEOMAGNETICALLY TRAPPED CORPUSCULAR RADIATION by J. A. Van Allen, J. Geophysical Research, 64, No. 11, Nov. 1959.

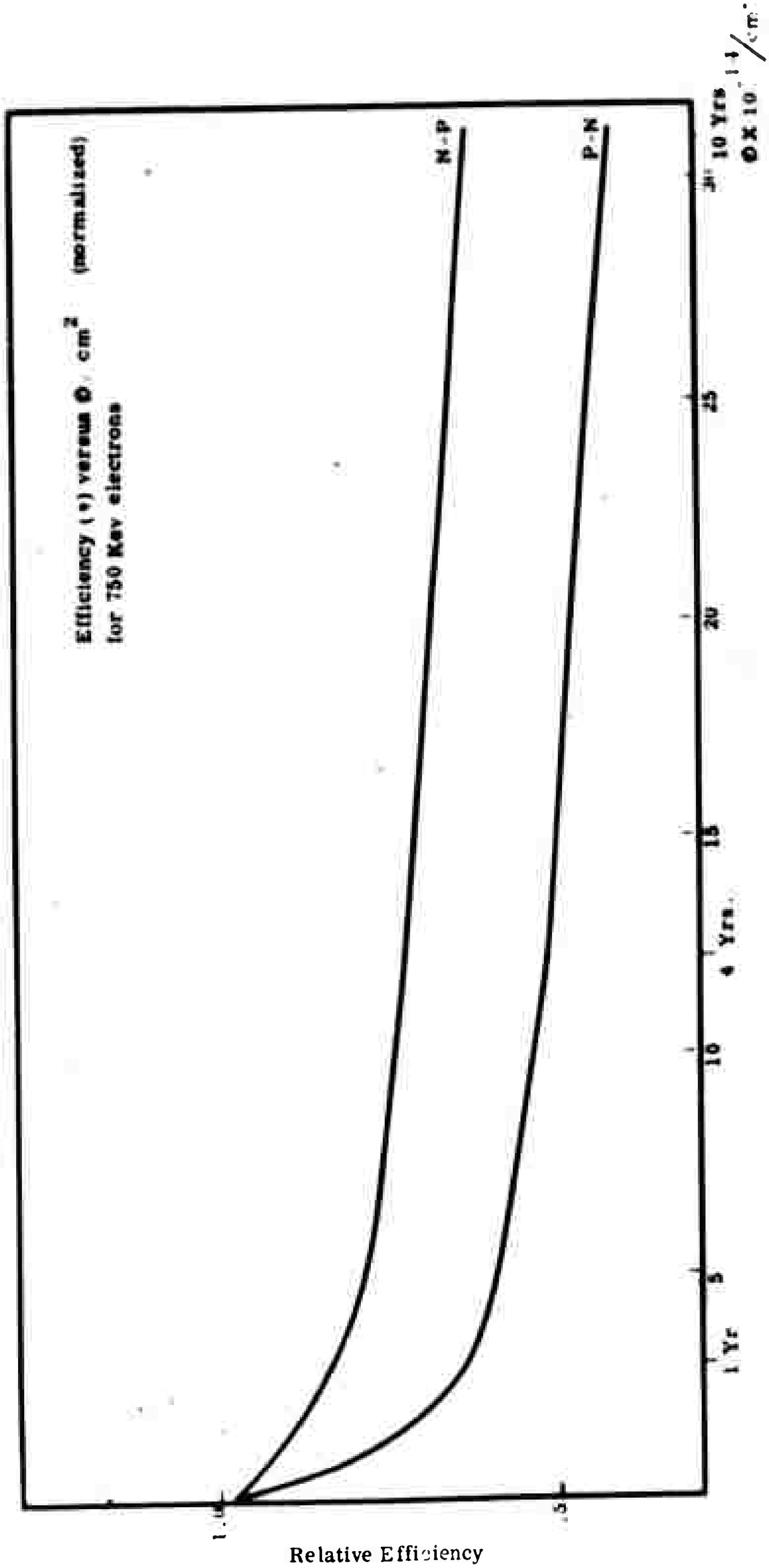

Efficiency (η) versus Φ cm²
(normalized)
for 750 Kev electrons
N-P
P-N
1 Yr
5
10
4 Yrs.
15
20
25
10 Yrs
1.0
.5
Relative Efficiency

FIG. 1

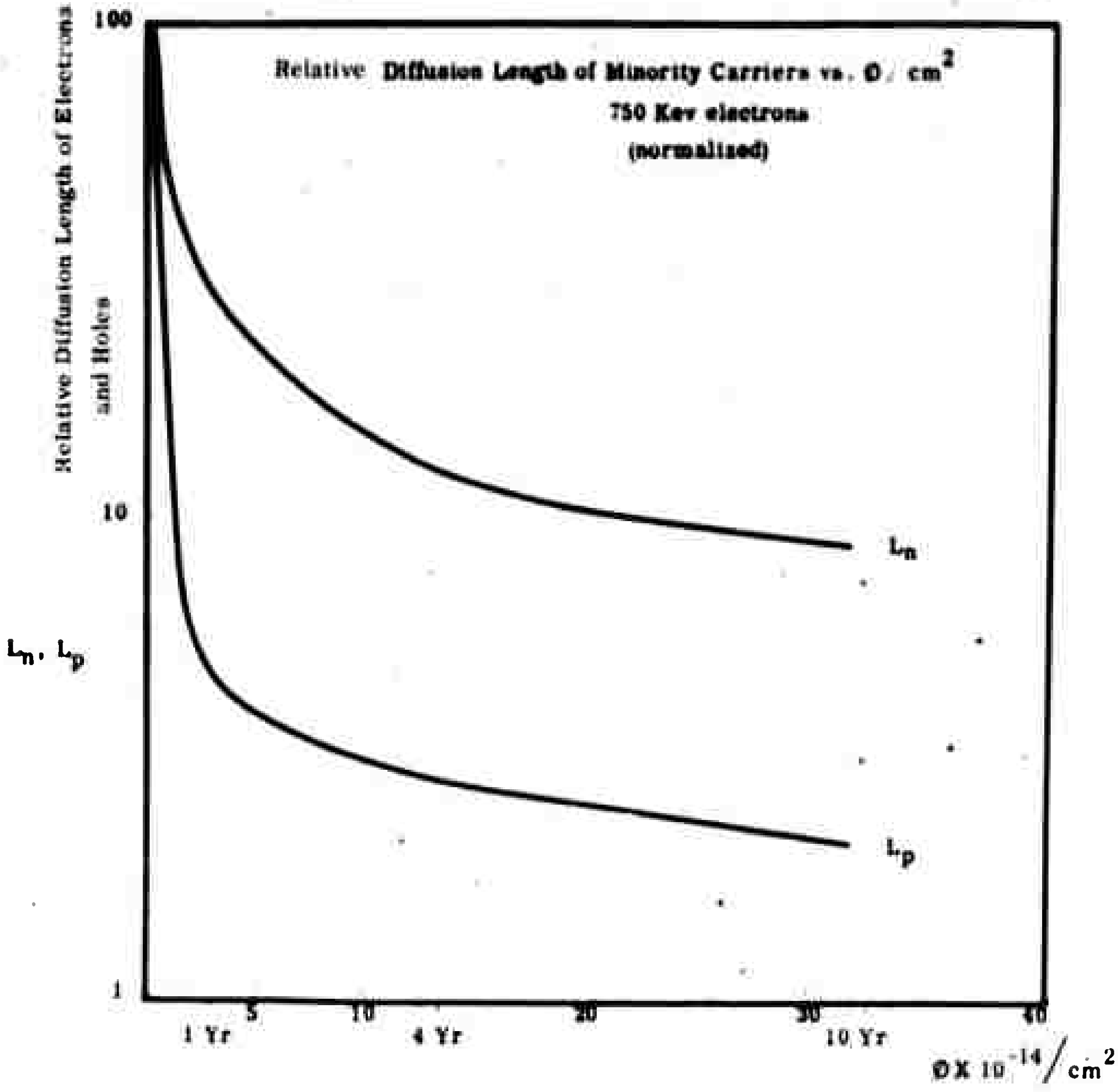
than the lifepath in the N region of the "P on N" cell, after substantial bombardment. A factor of 2.5 can be explained by considering the ratio of the mobility of minority carriers in P and N type materials. The reasons for the additional factor of 2.4 in the lifepath of the minority carriers in the bulk region of the "N on P" cell have not yet been thoroughly explained. It implies a sixfold difference in radiation sensitivity of the lifetime of the minority carriers in the bulk region of two cell structures.

The relative lifepath of the minority carriers in the bulk region of "N on P" and "P on N" cells is shown as a function of electron bombardment intensity in figure 2.

As a result of these experiments a program was instituted to develop radiation resistant "N on P" solar cells, the fabrication of which is described in the following section.

Experiments were performed on the first "N on P" cells developed at Transitron. "N on P" and "P on N" cells underwent incremental bombardments of 2 Mev electrons and the decrease of short circuit current under low level light intensity was observed.* The results of a typical set of experiments is shown in figure 3. Although the short circuit current of the "P on N" cell was initially 14.8 ma, the short circuit current of the "P on N" cell has fallen below that of the "N on P" cell after a bombardment of approximately only 10^{13} electrons per square centimeter. These experiments were made on coated cells. No damage to the coating was observed during these runs.

* Early "N on P" cells were subject to high contact resistance and hence high series resistance. Low level light intensity was used to minimize the effect of series resistance.



Relative Diffusion Length of Minority Carriers vs. Ø / cm^2
750 Kev electrons
(normalized)
Relative Diffusion Length of Electrons and Holes
L_n, L_p
100
10
1
L_n
L_p
5
10
20
30
40
1 Yr
4 Yr
10 Yr
Ø X 10^{-14}/cm^2

FIG. II

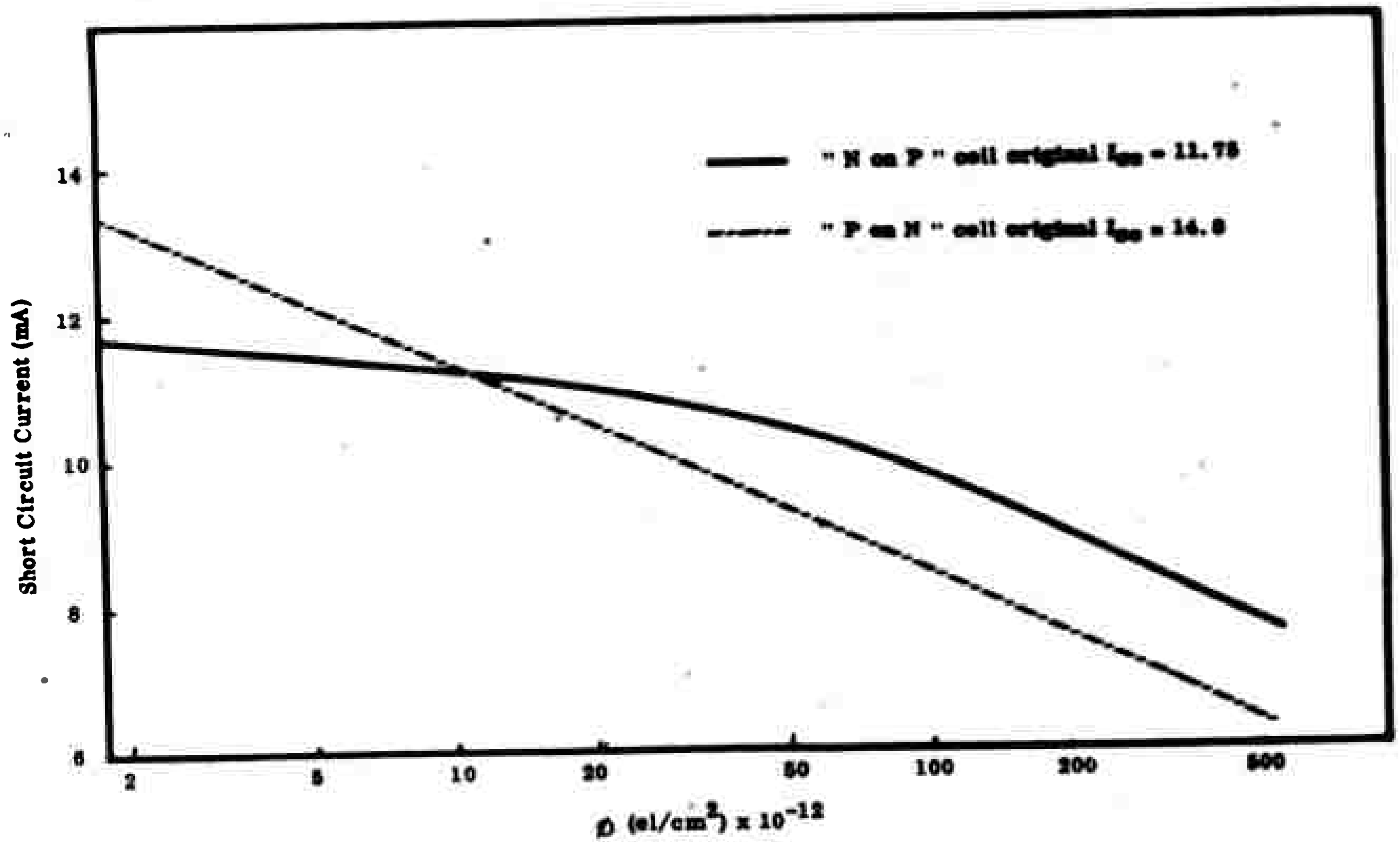


FIGURE 3: SHORT CIRCUIT CURRENT VS ELECTRON BOMBARDMENT FOR 2 MEV ELECTRONS

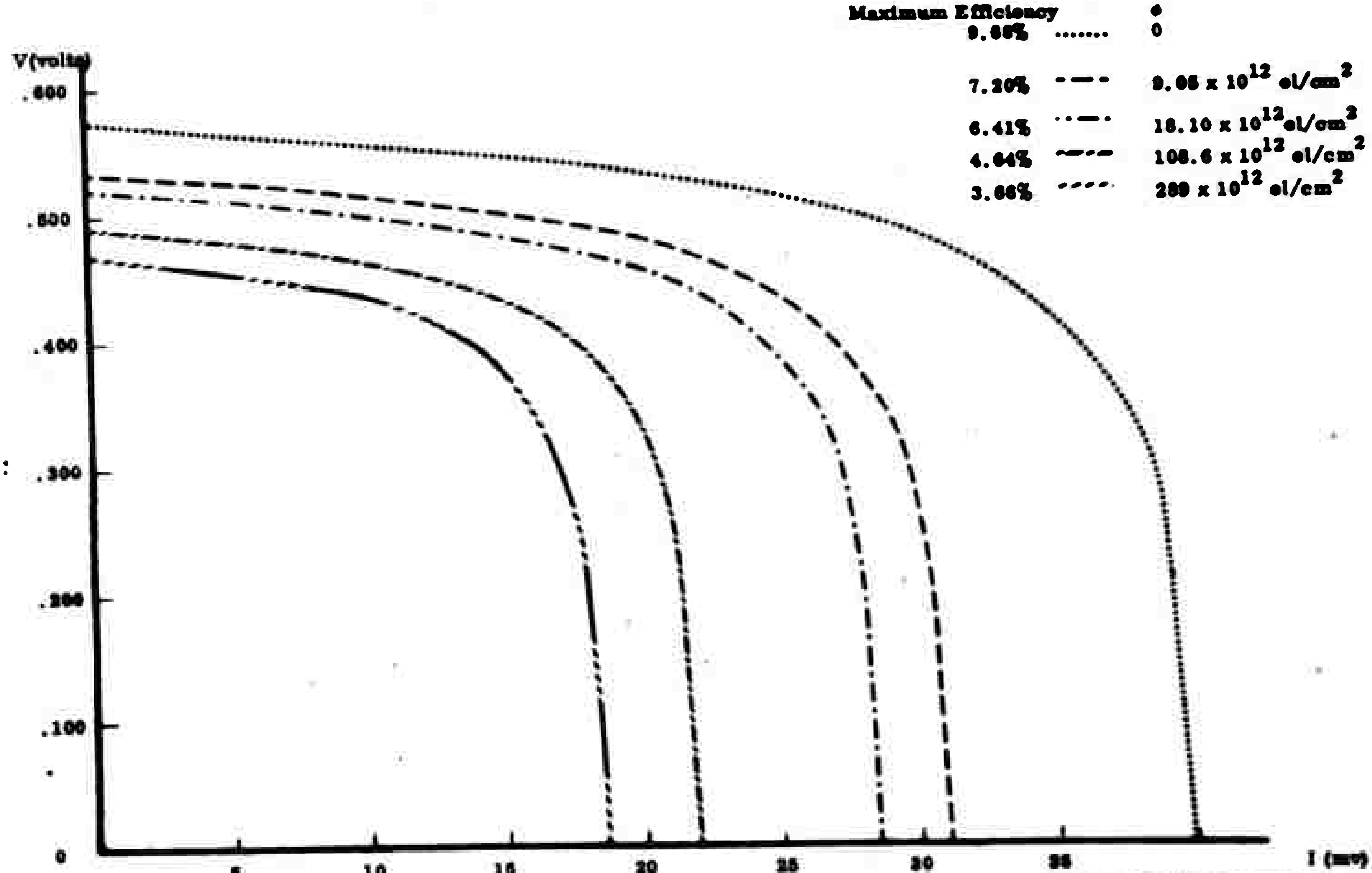
Subsequent experiments were performed at a more advanced stage of "N on P" solar cell development. Three "N on P" and three "P on N" Transitron solar cells were subjected to incremental electron bombardment by 2 Mev electrons. The current-voltage curve of each cell was extracted after each bombardment and the maximum efficiency determined. Current-voltage measurements were made under 2800°K tungsten light having an intensity which corresponds to solar intensity of 1.21 gm-cal/cm^2-min. These measurements are shown in figures 4-9. The decrease in cell efficiency as a function of electron bombardment intensity is shown in figure 9. From the curves of figure 10, it can be seen that a 25% decrease in cell efficiency of the "N on P" cells occurs after approximately five times the radiation which causes the efficiency of the "P on N" cells to decrease by 25%.

The time lag between electron bombardments and cell measurements ranged between 1/2 and 70 hours. However, cells which have been electron bombarded about six months ago, exhibit no noticeable change in efficiency since the last bombardment, indicating that any annealing effects are negligible in the additional six months.

CONCLUSIONS

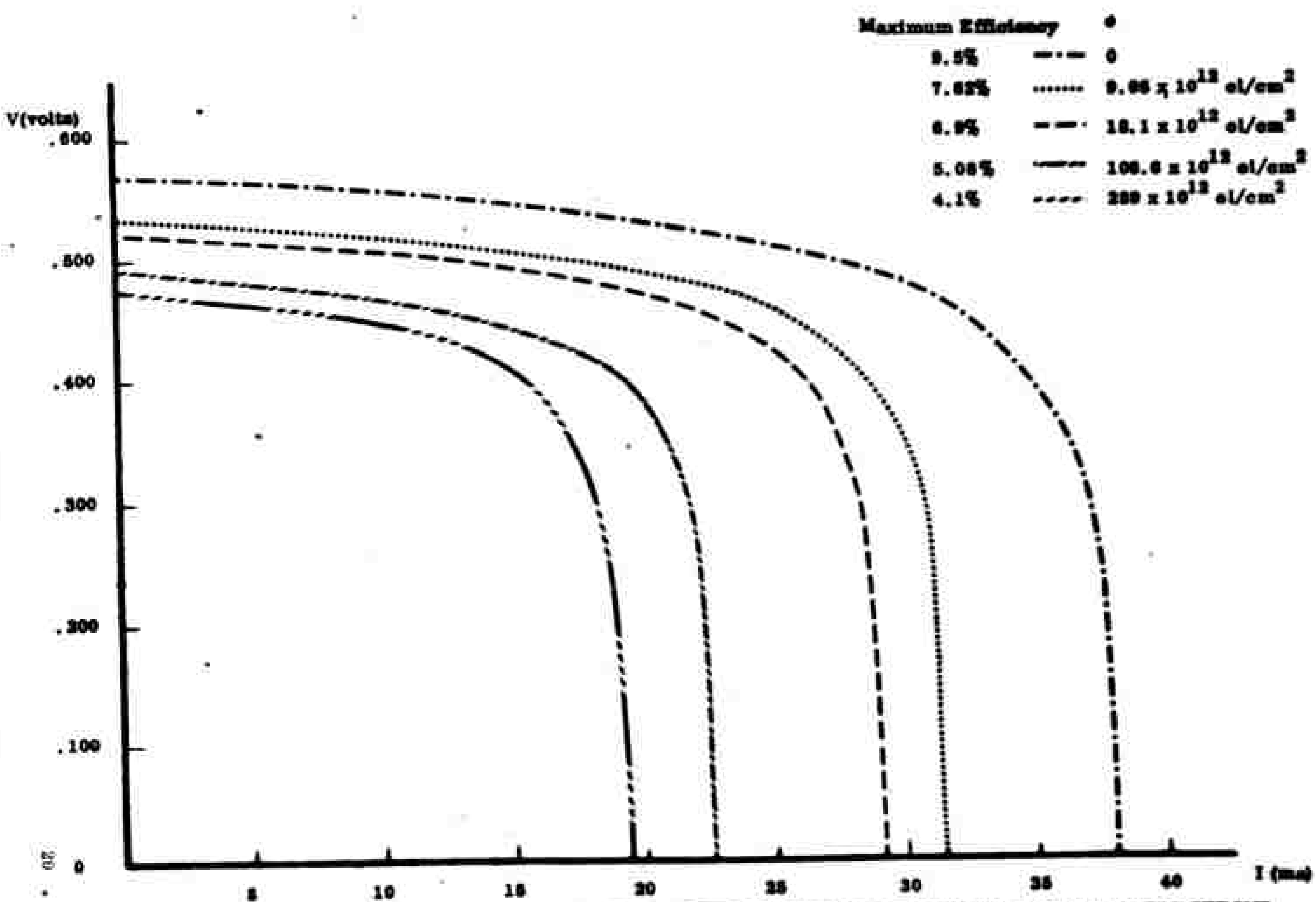
It is clear that further investigation into the mechanisms which are responsible for the increased radiation resistance of the "N on P" solar cell structure is absolutely necessary if theoretical and practical optimization of the mechanisms are to be achieved. Such invesitgations are being initiated at Transitron.

The tremendous value of radiation resistant solar cells cannot be underestimated especially in the field of space technology. The electrical systems of present day satellites will not function when the power output of the solar cell array (which is used to charge a battery) goes below approximately 75% of its initial power. Hence, a decrease of about 25% in the efficiency of the solar cell array results in power failure. The lifetime of the electrical power system depends on the radiation encountered, and the effect this radiation has on the solar cells.

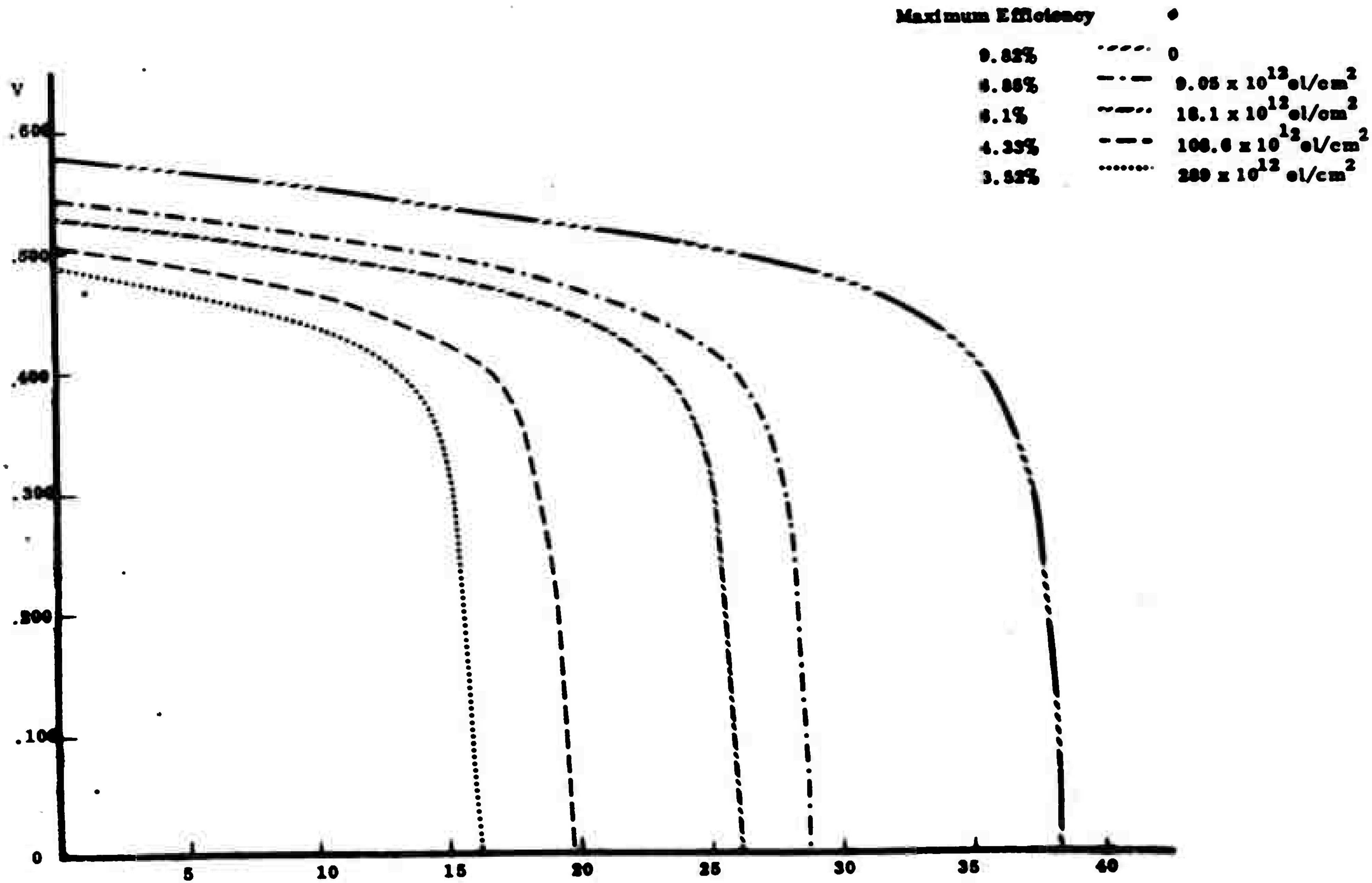


V-I CURVES OF "P ON N" CELL AFTER VARIOUS BOMBARDMENTS BY 2 MEV ELECTRONS

FIGURE 4

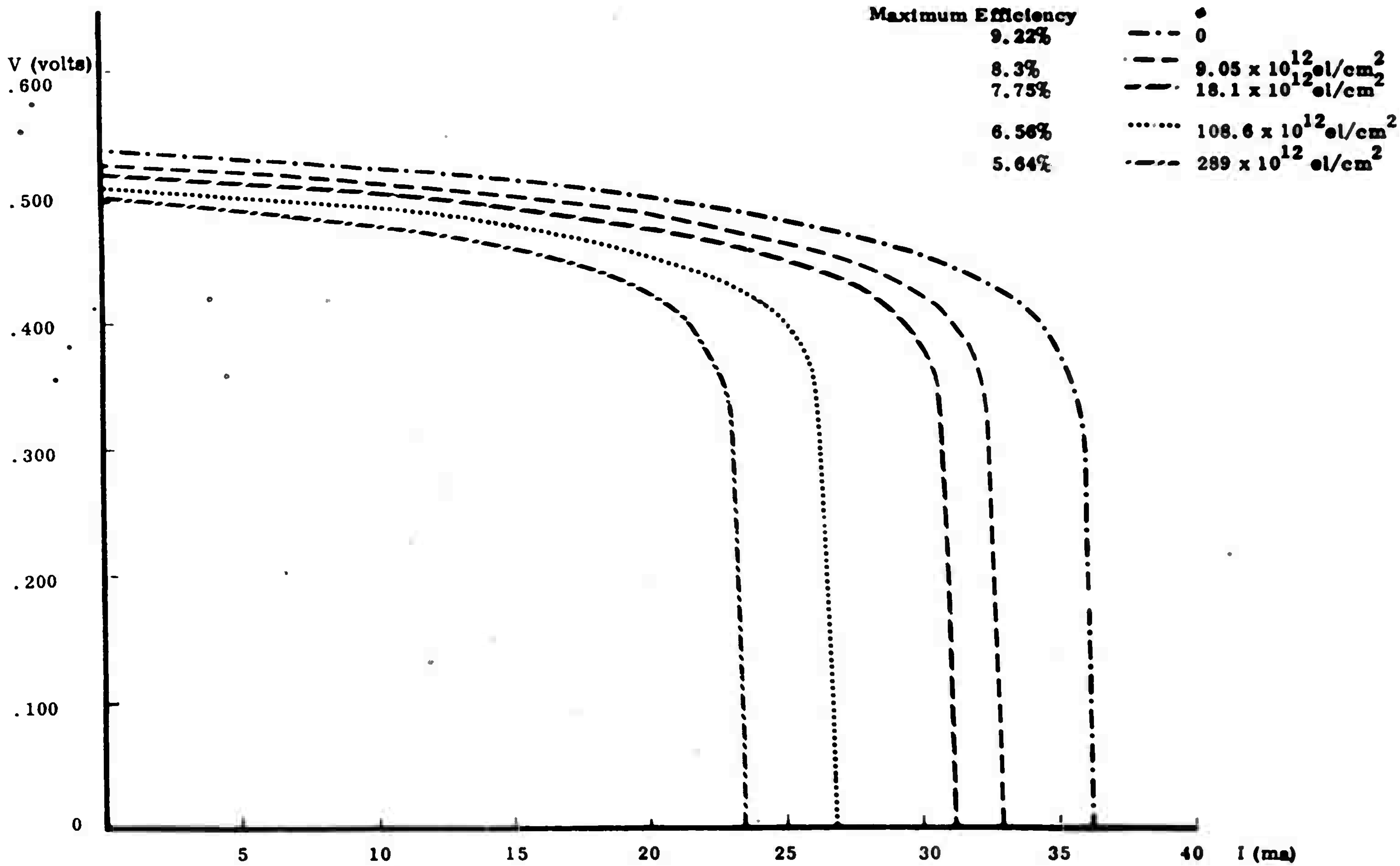


V-I CURVES OF "P ON N" CELL AFTER VARIOUS BOMBARDMENTS BY 1 MEV ELECTRONS
FIGURE 5



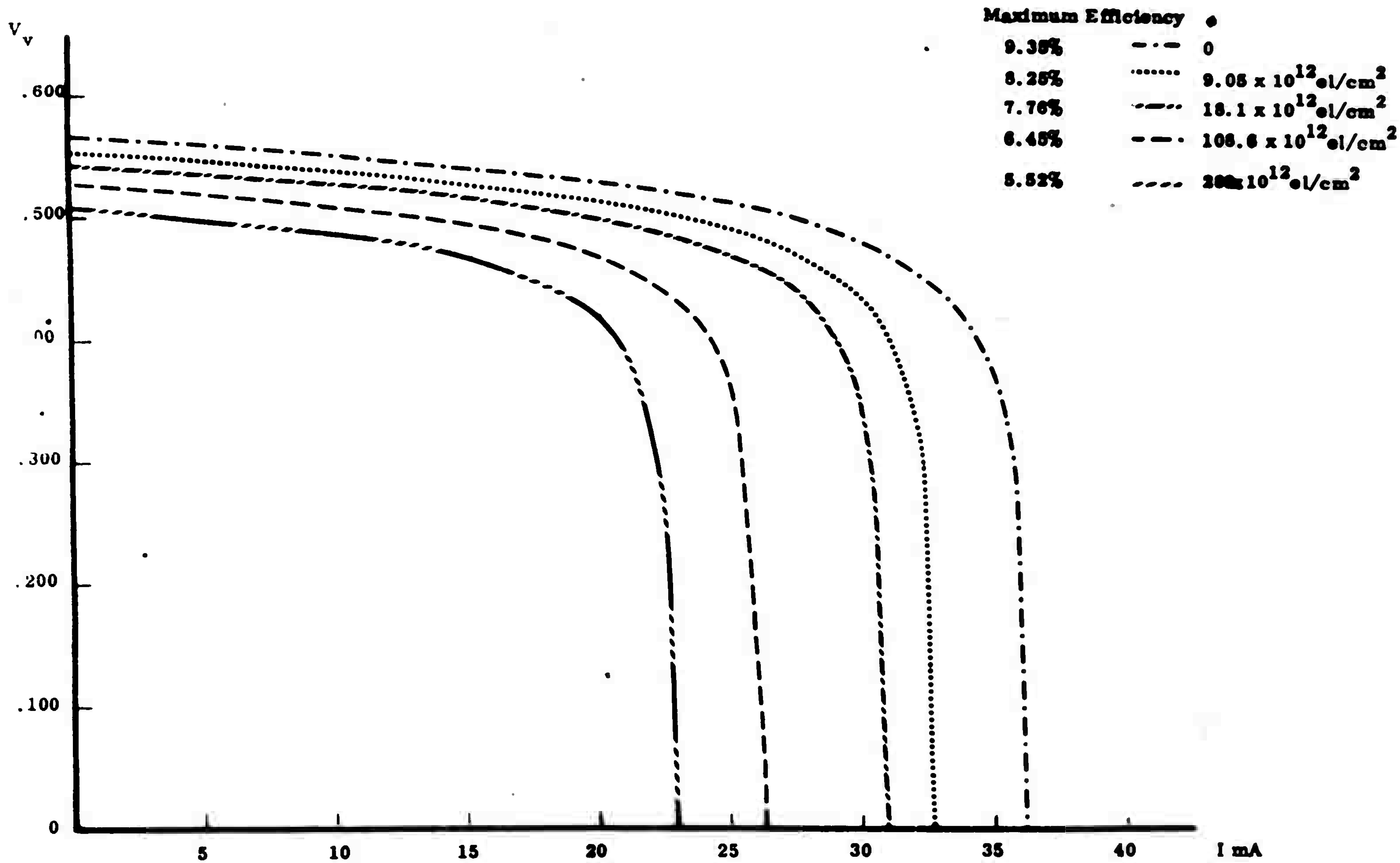
V-I CURVES OF "P ON N" CELL AFTER VARIOUS BOMBARDMENTS BY 3 MEV ELECTRONS

FIGURE 6



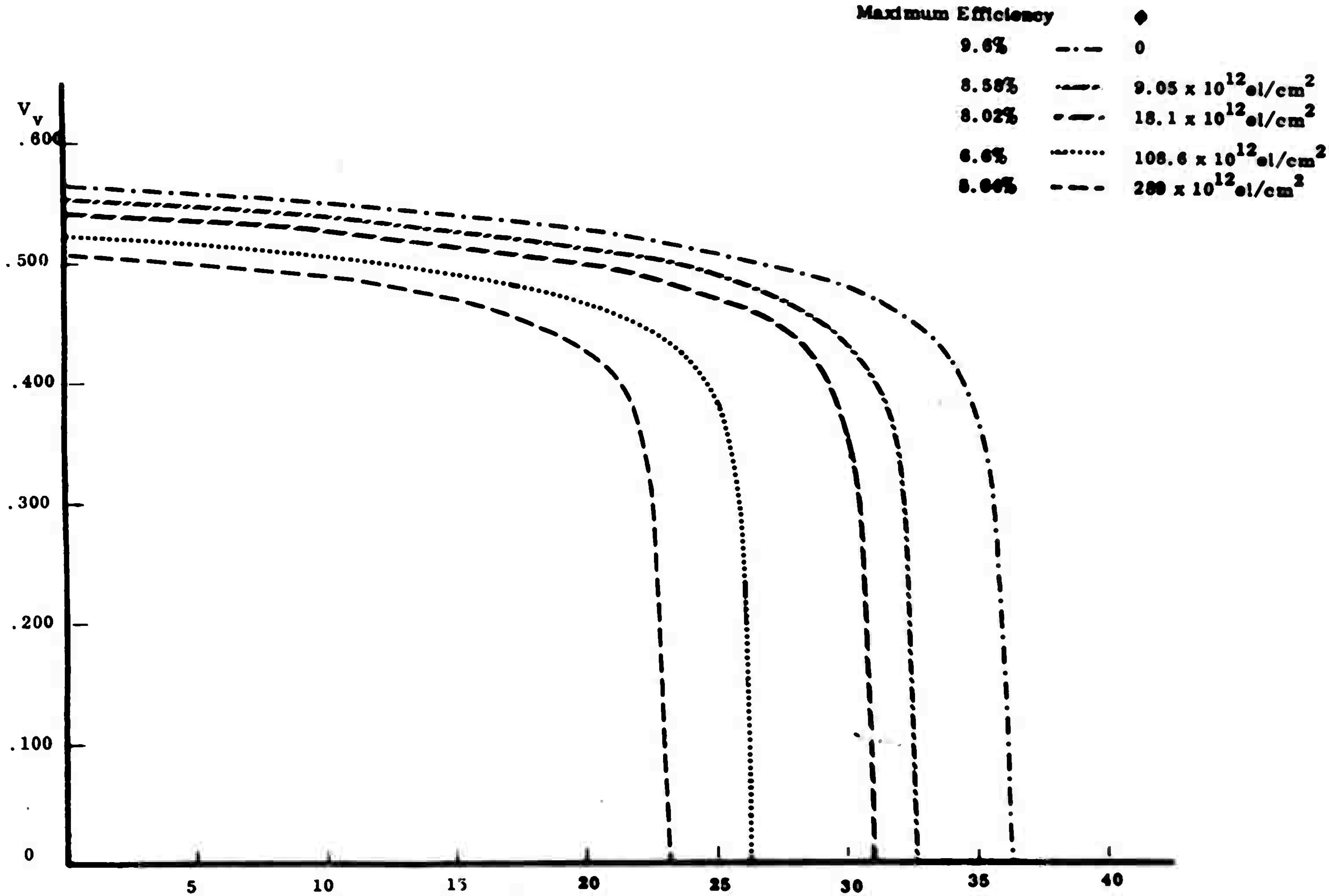
V-I CURVES OF "N ON P" CELL AFTER VARIOUS BOMBARDMENTS BY 2 MEV ELECTRONS

FIGURE 7

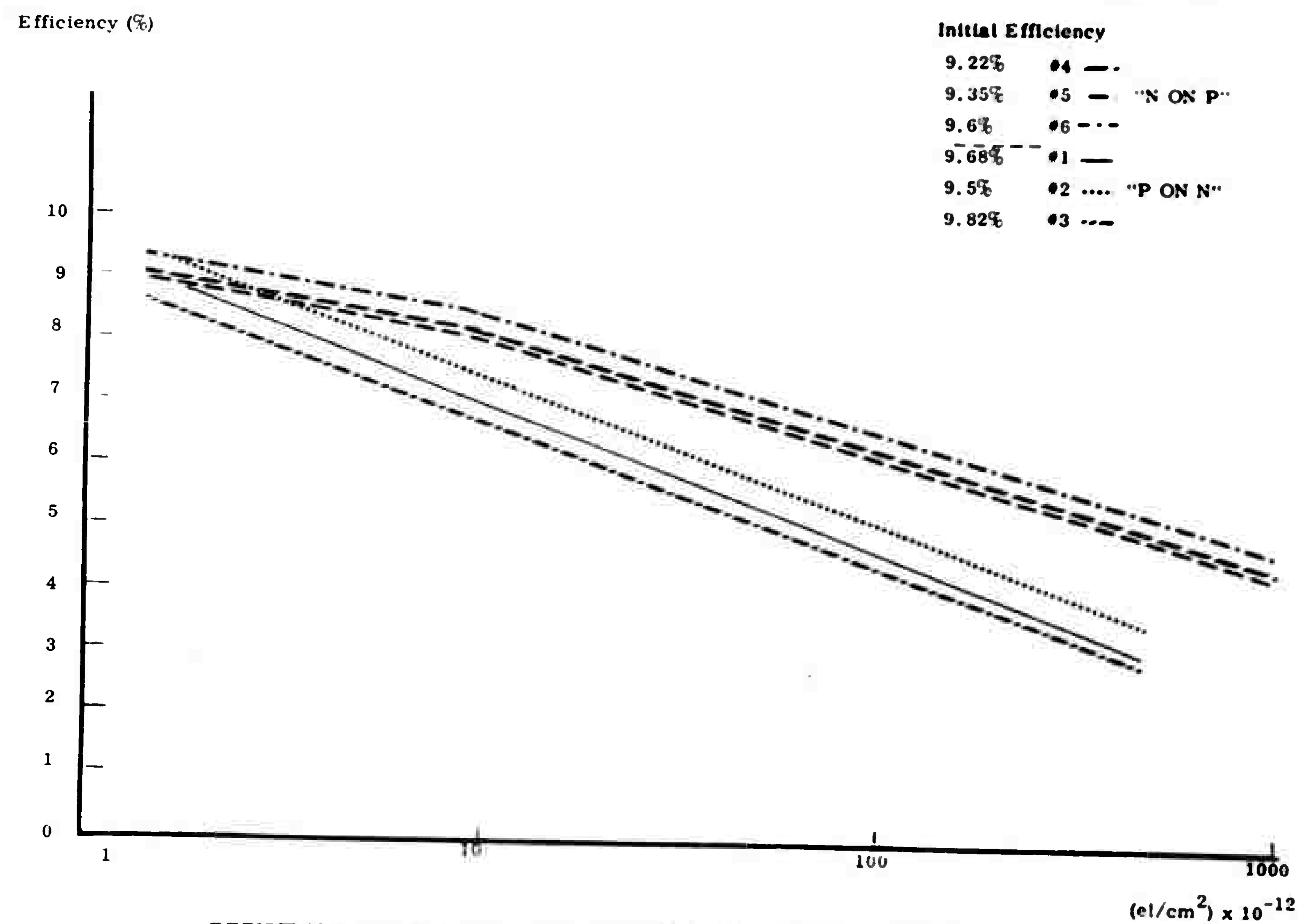


V-I CURVES OF "N ON P" CELL AFTER VARIOUS BOMBARDMENTS BY 2 MEV ELECTRONS

FIGURE 8



V-I CURVES OF "N ON P" CELL AFTER VARIOUS BOMBARDMENTS BY 2 MEV ELECTRONS
FIGURE 9



EFFICIENCY AS A FUNCTION OF ELECTRON BOMBARDMENT INTENSITY FOR VARIOUS SOLAR CELLS USING 2 MEV ELECTRONS

FIGURE 10

"N ON P" SOLAR CELLS

INTRODUCTION

During the early part of 1960, the Solid State Division of USASRDL undertook a study of the properties of "N on P" cells. This program was under the direction of Mr. W. Cherry and J. Mendelkorn. It was found by Transitron and by others that "N on P" cells had a greater radiation resistance to high energy electron bombardment than "P on N" cells. The threshold for radiation damage was also higher.

These results which had been obtained in "N on P" cells given to us by the USASRDL were confirmed some time later when Transitron, in agreement with the Signal Corps decided to produce "N on P" cells under the present contract.

FABRICATION PROCESS

The process that we use to manufacture "N on P" cells is very similar to the one disclosed to us by J. Mendelkorn. However, some simplifications have been introduced to facilitate production of more cells and also to allow the deposition of a grid contact on the N layer.

The "N on P" cells are fabricated using single crystal P type silicon of about 1 ohm-cm resistivity. The crystals are first cut into slabs 1 cm x 2 cm and then sliced into slices 0.5 mm thick. The surface is prepared by lapping and etching preferentially as we want to have a smooth, shiny surface except under the contacts where some roughness helps to obtain a good mechanical contact with the nickel plating which is used subsequently.

A two zone furnace is used for the diffusion of phosphorous into the P wafers: the temperature and time are set to give a junction depth of about 1 micron. The diffusion takes place in a pure dry nitrogen (dew point - 70^{0}C) atmosphere and the silicon wafers are cooled at a slow rate (2^{0} C/minute) to preserve lifetime as much as possible.

After diffusion the wafers are lapped on one side, cleaned, and etched in HF to dissolve the oxide layer formed during the diffusion.

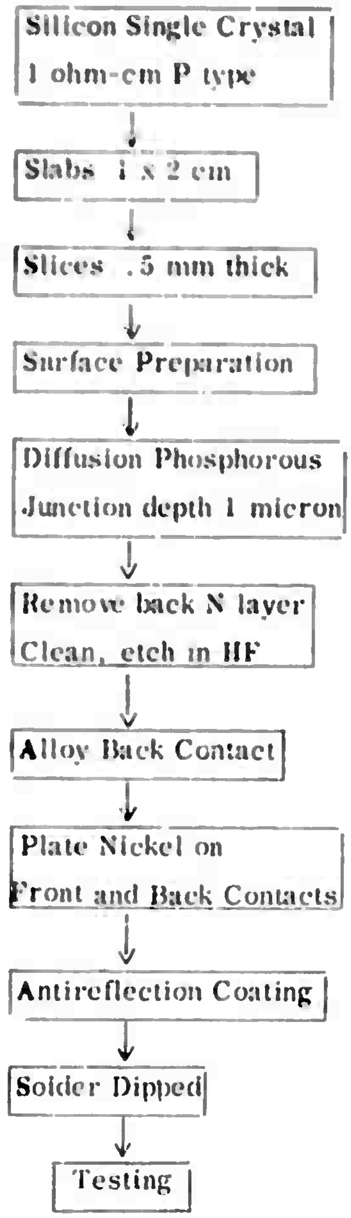
The contact on the P type bulk is made by alloying aluminum to it: this operation is followed by nickel plating both on the aluminum and on the top surface which has been previously masked to obtain a grid structure.

After an antireflection coating is evaporated onto the wafers they are solder dipped. The edges are ground to remove any excess solder. The cells are now ready for testing. The process is summarized in Table III.

PRESENT STATUS

The maximum efficiency attained at this date for "N on P" solar cells, 1 x 2 cm, is 11.5%. However, no "N on P" solar cells have as yet been measured under natural sunlight, so that the efficiency is measured under tungsten light using a "P on N" standard cell of the same junction depths as the "N on P" cells. This is not completely satisfactory because the spectral response of these two types of cell are different, especially for short wavelengths, even if they have the same junction depths and equal bulk lifepaths.

TABLE IV



"N ON P" PROCESS OUTLINE

PLANS FOR THE NEXT PERIOD

Further work will be done on the fabrication process of the radiation resistant "N on P" cells to optimize the efficiency and radiation resistance of the cells. This will include investigations into the mechanisms responsible for the increased radiation resistance of the "N on P" cell structure.

The results of proton bombardment of the "N on P" cells will be evaluated, and additional electron bombardment experiments will be performed.

The use of photoresist methods in the depostion of the grid configuration and in the selective etching process will be evaluated.

CONFERENCES

On July 21, 1960, Mr. Pierre Lamond of Transitron Electronic Corporation attended a conference at the Signal Corps Research and Development Laboratories. At the time, calibration of standard solar cells was also discussed.

On December 8, 1960, Mr. Pierre Lamond attended a conference held at the Evans Signal Corps Laboratories where radiation-resistant, high-efficiency solar cells were discussed.

PAPERS PRESENTED

On October 20, 1960, Mr. Paul Berman of Transitron Electronic Corporation presented a paper entitled "Radiation Damage in Silicon Solar Cells Using 750 Kev and 2 Mev Electrons", at a meeting on "Radiation Damage to Semiconductors by High Energy Protons", held in Washington, D. C., and sponsored by the National Aeronautics and Space Administration.

KEY TECHNICAL PERSONNEL

Berman, P.	Navon, D.
Chopra, A.	Shaw, B.
Dale, B.	Smith, F. P.
Lamond, P.	Rudenberg, H. G.
Mayer, S.	Warren., W.

Mr. Paul Berman has been added to our staff since the publication of the Second Semiannual Report:

Paul Berman	1958	BA Physics, Brandeis Univ.
	1960	MS Physics, Tufts Univ. Thesis Subject: "The Exciton" Laboratory Instructor, Research Assistant.
	1960	TRANSITRON
Recent Work:		High Efficiency Solar Cells, Radiation Damage, Radiation Damage in Solar Cells, Radiation Resistant Solar Cells.
Recent Papers:		"Radiation Damage in Silicon Solar Cells Using 750 Kev and 2 Mev Electrons" (Meeting on "Radiation Damage to Semiconductors by High Energy Protons" - Sponsored by NASA; October 1960).

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