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"Photovoltaic Effect and Utilization of Cells"

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Abstract

The effects of 115 keV electron irradiation (this energy is below the threshold for bulk damage) on the surface recombination velocity s of n- and p-Si of various resistivities is determined from studies of changes in the photovoltaic short circuit current I_{sc} resulting from strongly absorbed light. The cells were special solar cells made on various resistivity base material. Both the "diffused" face and the "base" face were subjected to irradiation. It was found that as a result of irradiation, the value of s for n-Si generally decreases while that of p-Si generally increases. The changes can be as large as factors of 4, but are more commonly of the order of 10 to 20%. The recovery of the pre-irradiation state is also described and discussed. A new apparatus for conducting experiments in an organic vapor free vacuum is also described.

I. Introduction

In earlier reports⁽¹⁾ we discussed the concepts underlying the experimental technique which we adopted for this study of the effects of low energy electron irradiation on the surface properties of germanium and silicon. Briefly, it can be shown that the short circuit current I_{sc} of a photovoltaic cell exposed to strongly absorbed light ($\alpha l \gg 1$ where α is the absorption constant and l is the distance between the surface on which light is incident and the position of the p-n junction) is given by

$$I_{sc} = \frac{2q N_o (1-R)}{\frac{Ls}{D} + 1} \quad (1)$$

where q is the electronic charge; N_o is the number of photons incident on unit area per second, R is the reflection coefficient; L is the diffusion length; and D is the diffusion constant in the region of the semiconductor between the surface and the junction, and s is the surface recombination velocity. This relation predicts that I_{sc}^{-1} should be a linear function of s .

The experimental technique involves measurement of I_{sc} of a photovoltaic cell illuminated by light for which $\alpha l \gg 1$; exposing this surface to electrons whose energy is too low to produce bulk damage and then remeasuring the response to the light. The data are then plotted as I_{sc} vs integrated electron flux.

The photovoltaic cells used in the previous portions of this investigation were alloy junctions in n and p-Ge, and n- and p-Si made in our laboratories. The studies on Ge cells showed that rapid changes in I_{sc} occurred during the first 1500 $\mu\text{coul}/\text{cm}^2$ (about 1×10^{16} electrons/ cm^2), after which saturation appeared to have set in for virtually all the Ge resistivities used in the experiments. The observed changes were often greater than an order of magnitude, indicating that the assumptions underlying the derivation of Eq. (1) were satisfied. Consequently, it was possible to associate the changes in I_{sc}^{-1} to changes in s . However, it was not possible to fit the data to any simple scheme involving the introduction or removal of surface recombination centers by the irradiation.

Experiments on the silicon alloy-type photocells proved to be virtually impossible because the cells did not have enough sensitivity to short wavelength, strongly absorbed light. We, therefore, resorted to another procedure to provide us with silicon surfaces of various resistivities. A number of diffused junction silicon cells made from wafers of both conductivity types and various resistivities were obtained from the Naval Research Laboratory, Washington, D. C.². The solder forming the base contact was removed from these cells and the exposed base surface was subjected to lapping, polishing and etching. Both the newly exposed surface of the base crystal and the surface into which diffusion occurred were irradiated and studied. In what follows we shall refer to the surface prepared by removing

the rear contact as the "Base Face" and the surface into which diffusion had occurred as the "Diffused Face". In this report, we describe the preparation and properties of these Si cells prior to, and after exposure to electrons of energy below the threshold for bulk damage (~ 150 keV). We shall also describe a modification of our experimental apparatus intended to eliminate organic vapor from the environment of a cell during irradiation.

II. Preparation of the "Base Face" of the Si Cells

In our experiments on the silicon alloy junctions, we established that the diffusion length in the finished cells was considerably less than the distance between the surface and the junction and therefore the cells had very little short wavelength response. It was hoped that the diffused junction cells might have a greater response in the short wavelength region.

The cells used in these experiments had the following initial properties. The n/p cells were made by diffusing phosphorus into boron doped p-Si wafers whose initial resistivities were 1, 20 and 50 ohm cm. The p/n cells were made by diffusing boron into phosphorus doped p-Si wafers whose initial resistivities were 1, 20 and 50 ohm cm. These cells were subjected to the following treatment.

The cell was first cleaned by trichloroethylene, acetone and methanol. Then the diffused face of the cell was attached to a glass slide with glycol plthalate. Part of the soldered area on the "base face" was covered by glycol phthalate to preserve an ohmic contact to the base. The uncovered part (which comprised most of the back surface) was lapped on wet, pressure sensitive abrasive papers (Buehler #30-5160; Grid #240, #400 and #600, successively). The samples were then lapped on glass with #1000 and #3200 grit carborundum. Next the sample was polished by hand on a polishing cloth which lay on a smooth glass. Three different alumina particle sizes were used: 5μ , 0.3μ and 0.05μ . Finally, the samples were etched in 30% NaOH at 50°C for 2 min. The final sample thickness was about 0.005" as compared to an initial thickness of about 0.012". The glycol phthalate was removed with boiling acetone. The samples were lapped so thin in order to assure that their thickness would be of the order of a diffusion length.

Prior to irradiation, the diffuse faces of the cells were always cleaned with trichloroethylene, acetone and methanol successively and then etched in 30% HF to remove any silicon monoxide layers.

III. Experimental Procedure

The silicon irradiations were performed in the diffusion pump vacuum of the Van de Graaff machine which served as the electron source. The experimental arrangement is shown schematically in Fig. 1. The samples were irradiated individually at an accelerating voltage of 115 keV. The beam current I_B was identified with the current absorbed by the sample whose thickness was sufficient to stop the beam. No correction was made for

reflection of electrons from the surface. The beam current was fed into an Elcor Current Integrator and the integrated charge received by the sample was determined in this way. The vacuum produced by the oil diffusion pumps and liquid nitrogen traps of the Van de Graaff was always between 10^{-5} and 10^{-6} mmHg as measured by a cold cathode ionization guage attached to the irradiation chamber.

The samples were mounted on metallized Al_2O_3 wafers with silver paste or GE cement acting as binder. The Al_2O_3 wafers were in turn attached to copper holders which finally were in pressure contact with the water cooled copper block. (See Figs. 2 and 3).

The temperature was monitored with the help of a copper-constantan thermocouple attached to the soldered ohmic contact of the cells. The temperature remained around $5^\circ C$ throughout the experiments and it was not allowed to change by more than $0.5^\circ C$ during irradiation.

The light source consisted of a Hg lamp and Kodak 18A (0.365μ) glass filter. The absorption constant of this light in silicon was $\alpha \sim 2 \times 10^5 \text{ cm}^{-1}$, so that the light was absorbed in a thin layer near the surface $\sim 0.05\mu$.

The electron beam was incident normal to the surface, while the light was reflected onto the surface at nearly normal incidence by a first surface mirror.

Only d.c. measurements were made i.e. the light was not modulated. The parameter measured was the voltage across a load resistor connected across the sample. The magnitude of the load resistance was so chosen that the signal was proportional to I_{sc} (it usually had a value between 10Ω and 1000Ω).

The illumination level was kept low enough so that the i-V characteristic remained linear. The voltage across the load resistor was measured by a Hewlett-Packard dc Microvoltmeter whose output as a function of time was displayed by a Moseley x-y plotter.

The output of the cell was a function of time of exposure to the 0.365μ light. After about 40 min. exposure, the response saturated. Irradiation proceeded only after light induced changes had saturated.

IV. Experimental Results

Prior to exposing the samples to electron irradiation, they were allowed to rest in vacuum for several hours in order to allow effects caused by pumping on the surface to saturate. They were also exposed to light long enough for light induced surface changes to saturate. They were then irradiated according to the following scheme. After the samples had been irradiated to a pre-selected flux, the electron beam was interrupted by an electrically operated shutter. The photovoltage was quickly recorded on the x-y plotter

for a few seconds and then irradiation was resumed.

Figures 4 through 14 show the results of irradiations of the "diffused" and "base" faces of the cells used in this study.

Figures 4 to 8 show the changes in I_{SC} caused by the indicated integrated fluxes incident on n-Si "Base Faces" whose resistivities were 1, 20 and 50 ohm cm and on p-Si "Base Faces" whose resistivities were 1 and 20 ohm cm.

Figure 4 shows the results for a 1 Ω -cm n-Si "Base Face" cell. I_{SC} increased rapidly by as much as 40%, saturating only at about 1,000 $\mu\text{coul}/\text{cm}^2$ irradiation (since the irradiated surface of the "Base Face" cell and "Diffused Face" cell is about 0.5 cm^2 , the flux values must be multiplied by 2 to obtain $\mu\text{coul}/\text{cm}^2$). These three curves were measured at a beam current $I_B \sim 8\mu\text{A}/\text{cm}^2$ and pressure $p \sim 1$ to 2×10^{-5} mmHg on the same sample. The sample rested in vacuo for about 24 hours between successive measurements.

Figure 5 shows the results for a 20 Ω -cm n-Si "Base Face" cell. Instead of increasing, I_{SC} decreased rapidly by an order of magnitude after about 4,000 $\mu\text{coul}/\text{cm}^2$ irradiation. There was a rest of 12 hours in vacuo between the measurement of the curve #1 and #2. The annealing time was rather short in this case. Within 10 seconds it reached a value of 35% of the initial value and within 30 minutes it reached a value of 65% of the initial value.

Figure 6 shows the results for 50 Ω -cm n-Si "Base Face" cell. I_{SC} increased by as much as 20% and saturated around 1,000 $\mu\text{coul}/\text{cm}^2$. I_B for curve #1 (1st measurement) was much smaller than for the others (2%), but the change of I_{SC} was larger than for the other two. The sample rested for about 10 hours between successive measurements.

Figure 7 shows the results for a 1 Ω -cm p-Si "Base Face" cell. I_{SC} decreased by about 40% and saturated at about 5,000 $\mu\text{coul}/\text{cm}^2$ irradiation. There was a rest of a half day between these two measurements.

Figure 8 shows the results for a 20 Ω -cm p-Si "Base Face" cell. I_{SC} saturated after about 7,000 $\mu\text{coul}/\text{cm}^2$ irradiation. Curve #2 was measured 10 hours after curve #1 was measured.

Figures 9-14 show the change of I_{SC} caused by electron irradiation of the diffused faces on p/n and n/p cells of various base resistivities.

Figure 9 shows two curves for the diffused face of an n/p si cell whose base resistivity is 1 Ω -cm. I_{SC} increased by as much as 25% and saturated at about 4,000 $\mu\text{coul}/\text{cm}^2$ irradiation. I_B for curve #2 was larger than that for curve #1 by more than an order of magnitude. Curve #2 was measured 40 hours after curve #1 was measured.

Figure 10 shows the change of I_{SC} for the diffused face of an n/p cell whose base resistivity is 20 Ω -cm. I_{SC} increased by as much as 150% and

saturated at about 6,000 $\mu\text{coul}/\text{cm}^2$ irradiation. Curve #2 was measured 10 hours after curve #1 was measured. I_B for curve #1 was about twice as large for curve #2.

Figure 11 shows one curve for the diffused face of an n/p cell whose base resistivity is 50 Ω -cm. In this case, I_{SC} increased by about 10% and saturated at about 1,000 $\mu\text{coul}/\text{cm}^2$ irradiation.

Figure 12 shows one curve for the diffused face of a p/n cell whose base resistivity is 1 Ω -cm. I_{SC} decreased by about 50%, saturating at about 6,000 $\mu\text{coul}/\text{cm}^2$.

Figure 13 shows the results for the diffused face of a p/n Si cell whose base resistivity is 20 Ω -cm. I_{SC} increased very rapidly, reaching a maximum within about 300 $\mu\text{coul}/\text{cm}^2$ and then decreased and saturated at about 9,000 $\mu\text{coul}/\text{cm}^2$. Curve #2 was measured at 100 KeV with a little smaller beam current 20 hours after curve #1 was measured.

Finally, in the case of the diffused face of a p/n Si cell whose base resistivity is 50 Ω -cm, instead of decreasing, I_{SC} increased by about as much as 15%, saturating at about 100 $\mu\text{coul}/\text{cm}^2$. Curve #2 was measured 8 hours after curve #1 was measured. I_B for curve 2 is only 25% of that of curve 1.

To summarize, in general I_{SC} of the Si samples changes rapidly during the early stages of irradiation and eventually saturates. The shapes of the I_{SC} vs flux curves are reasonably reproducible in successive runs; however, they do not have exactly similar shapes. Except for the 20 ohm cm n-Si cell, all n-type surface, both "diffused face" and "base face" increased with increasing flux. In the case of p-Si, except for the "diffused face" of the cell made on a p-type base of 50 ohm cm resistivity, all the p-type surfaces decreased with increasing flux.

V. Annealing of the Radiation Induced Changes

As in the case of the germanium⁽¹⁾, the value of I_{SC} returned to its pre-irradiation value or to a value close to the pre-irradiation value if the samples were allowed to rest in vacuo after the electron irradiation. Figure 15 shows the recovery of I_{SC} for two n-type surfaces. The value of I_{SC} for the 50 Ω cm n-Si surface returned to its original value within 10 minutes of cessation of irradiation while the diffused face of an n/p cell made on 20 ohm cm p-type material returned to its original value only after resting in vacuo for about 100 minutes.

Figure 16 shows the recovery of I_{SC} for a 20 ohm cm p-type Si surface. In this case I_{SC} recovered to 90% of its pre-irradiation value within the first 15 sec. but then required 30 minutes to regain its original value.

VI. Discussion of the Results

The first firm conclusion we can reach on the basis of the data presented above is that irradiation of the silicon by electrons whose energy is too low to cause bulk damage can lead to changes in the surface recombination velocity s characteristic of that surface. Thus, I_{sc}^{-1} is a linear function of s as predicted by Eq. (1). Such changes in s can in principle result from either of two causes. Irradiation can cause changes in the position of the Fermi level relative to the valence and conduction bands within the space charge layer at the surface. Such changes involve a redistribution of charges between the surface states and the interior of the semiconductor. They do not involve any change in the concentration of recombination centers at the surface. They should be changes which are brought about by relatively low doses of ionizing radiation.

The second possible cause for a change in s is a change in the concentration of recombination centers at the surface. The mechanism one would invoke here is the removal from the surface or deposit onto this surface of atoms and molecules which can serve as recombination centers. One might expect these processes to occur only at higher integrated fluxes. Whereas changes involving charge redistribution ought to be completely reversible, changes caused by removal or deposit of ions on the surface would be at least partially irreversible. However, because the nature of atoms absorbed on the semiconductor surface depends on the atoms and molecules made available to it by the ambient, it is possible that the surface can be returned to a state closely resembling its initial state if the surface is allowed to rest in the ambient.

In general, the observed changes in I_{sc} and, therefore, in s do exhibit two distinct regions; a rapidly changing part during the early stages of irradiation and a slower part which requires larger fluxes to saturate. These two regions are especially obvious in cases where they lead to opposite directions of change of s (see, for example, Fig. 13). They can also be distinguished in the annealing curves, like Fig. 16, where there is an initial rapid recovery followed by a much slower return to pre-irradiation values. It is not possible at this time to attempt a quantitative explanation of the radiation induced changes or of the subsequent annealing. One quantitative remark is, however, appropriate. The changes in I_{sc} saturated at integrated flux values between 3.6×10^{16} and 6×10^{14} electrons/cm². Now the number of recombination centers present on a semiconductor surface is of the order of 10^{12} /cm². In the case of bulk radiation damage, changes in lifetime begin to occur when the number of radiation defects capable of affecting the lifetime becomes an appreciable fraction of the number initially present in the crystal. If we transfer this reasonable concept to the surface, the saturation of surface changes could be interpreted as the attainment of a radiation induced surface defect concentration comparable to that originally present on the surface. Thus, we would conclude that about 10^{16} electrons/cm² produce of the order of 10^{12} defect states/cm², i.e. the probability that an electron incident on the surface will produce a new recombination center is about 10^{-4} .

Next, we turn our attention to the dependence of the observed changes in I_{SC} and therefore in s on conductivity type and resistivity. The results are summarized in Table 1 which shows the ratio of the saturated value of I_{SC} to the initial value along with the flux needed to attain saturation for samples of different resistivities. The first general observation to be made is that with the exception of the 20 ohm cm specimen, all the n-type surfaces showed an increase in I_{SC} and therefore a decrease in s . By contrast, all the surfaces of p-Si with the exception of the diffused face of the p/n junction built on a 50 ohm cm base exhibited decreased values of I_{SC} after prolonged irradiation. More experiments need to be performed involving irradiation effects on surfaces of a larger selection of resistivities and on more specimens of a given resistivity in order to determine whether the two exceptions were spurious.

Another general observation is in order. The integrated flux needed to produce saturation of I_{SC} was smaller for surfaces on n-Si than for surfaces on p-Si. There are exceptions like the diffused face of the p/n cell built on 50 ohm cm material and the diffused face of an n/p cell built on 20 ohm cm material.

On the basis of our data, it is not possible to discern any other simple behavior pattern. For example, neither the relative amount of change in I_{SC} nor the integrated flux required for saturation changes in any systematic way with resistivity of the bulk material.

The same remarks apply to the annealing data. Because all the experiments reported on silicon were performed in a diffusion pump vacuum of about 10^{-5} mmHg, we did not dwell on the annealing of the samples. We intend to defer any comments on this behavior until after experiments are performed in the organic-vapor free environment provided by the Vac Ion Pump.

VII. Future Plans: Description of the New Ion Pumped Irradiation Chamber

We have designed and constructed a new glass system for performing irradiation experiments in the vacuum provided by our 75ℓ/sec Vac Ion pumping station. The new system uses glass to metal seals, copper gaskets and solder joints and avoids any organic gaskets. It permits cooling the sample to liquid nitrogen temperature, i.e. the sample is mounted on the cold finger of a dewar. An extremely thin (0.0001") Ni window will reduce energy loss and scattering of electrons entering the chamber from the Van de Graaff. This should make possible the delivery of larger currents to the sample than had been possible in our previous pumped system.

In this system, we shall study radiation effects on Si surfaces in order to establish whether the behavior of the surface in organic-vapor free vacua is different. We shall also undertake experiments aimed at direct measurement of surface recombination velocity via measurements of effective minority carrier lifetime.

Table 1. Summary of Changes in I_{sc} Caused by Electron Irradiation of Si Surfaces.

Conductivity Type	Resistivity (ohm-cm)	Flux at Which I_{sc} Saturated ($e\ell/cm^2$)	Ratio of Final to Initial Values of I_{sc}	Comments
n-type	1	2×10^{15}	1.3	Base Face
" "	20	1.5×10^{16}	0.3	Base Face
" "	50	3.6×10^{15}	1.15	Base Face
" "	$10^{-2}?$	6×10^{15}	1.15	Diffused Face; Base $\rho = 1$ ohm cm
" "	$10^{-2}?$	1.8×10^{16}	2.2	Diffused Face; Base $\rho = 20$ ohm cm
" "	$10^{-2}?$	2×10^{15}	1.15	Diffused Face; Base $\rho = 50$ ohm cm
p-type	20	1.8×10^{16}	0.25	Base Face
" "	1	1.2×10^{16}	0.60	Base Face
" "	$10^{-2}?$	1.8×10^{16}	0.50	Diffused Face; Base $\rho = 1$ ohm cm
" "	$10^{-2}?$	2×10^{16}	0.6	Diffused Face; Base $\rho = 20$ ohm cm
" "	$10^{-2}?$	6×10^{14}	1.1	Diffused Face Base $\rho = 50$ ohm cm

In these experiments, we shall inject carriers into the specimen by pulsing the electron beam and observe the decay of the "photoconductivity" pulse. If the specimens are thin enough, then the measured lifetime is surface dominated and it is possible to deduce the absolute value of τ_s . These experiments can be used to calibrate the photovoltaic experiments.

References

1. J. J. Loferski, W. Giriat and I. Kasai, First Semiannual Report NASA Grant NGR-40-002-026, October, 1965; Second Semiannual Report NASA Grant NGR-40-002-026, June, 1966.
2. We wish to thank Dr. Bruce Faraday and Mrs. Regina Tauke for making the cells available to us.

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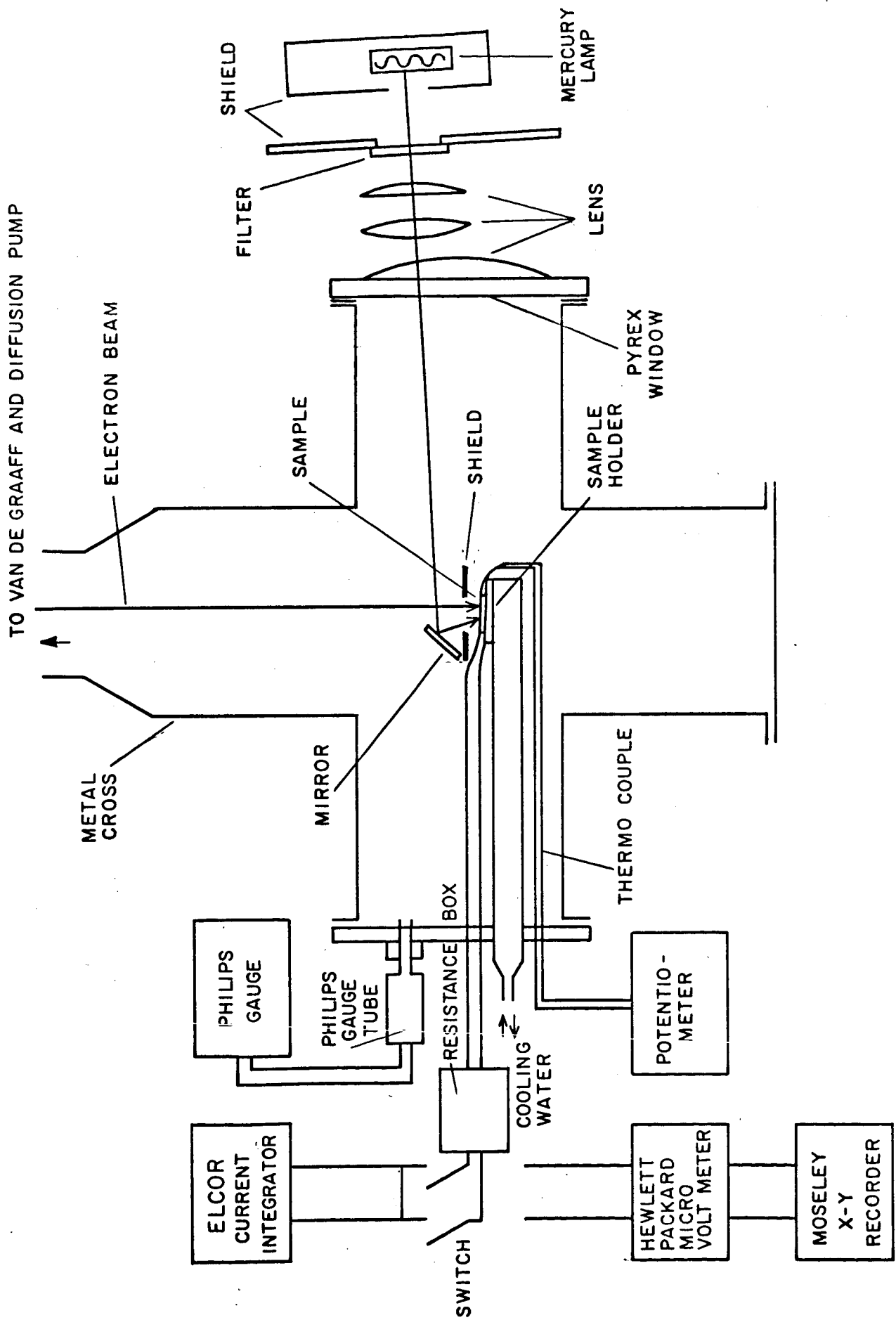


FIG. 1 SCHEMATIC DIAGRAM OF DIFFUSION PUMP SYSTEM

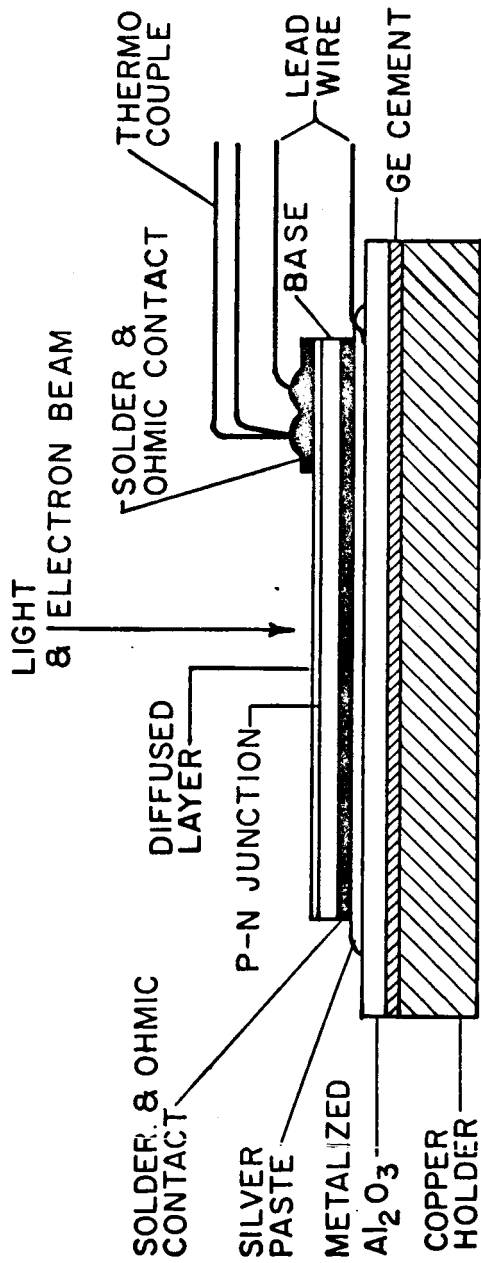


FIG. 2 MOUNTING FOR Si DIFFUSED FACE CELL

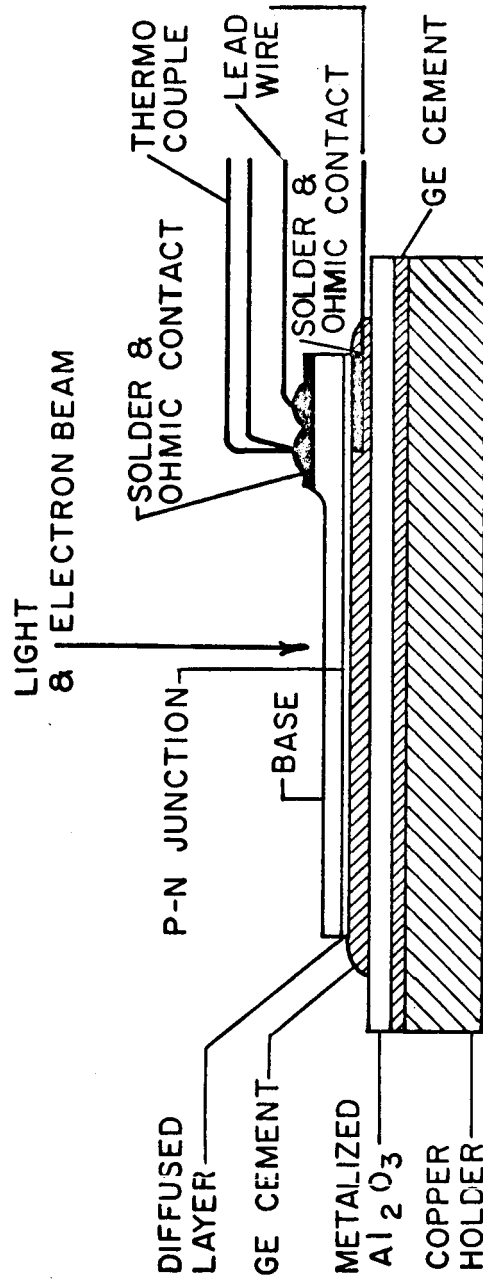


FIG. 3 MOUNTING FOR Si BASE FACE CELL

n-TYPE Si; $\rho = 1\Omega - \text{cm}$

115 KeV; ① $I_B = 8\mu\text{A}/\text{cm}^2$, $P = 1 \sim 2.5 \times 10^{-5} \text{ mmHg}$

② $I_B = 8\mu\text{A}/\text{cm}^2$, $P = 1 \sim 2 \times 10^{-5} \text{ mmHg}$

③ $I_B = 8\mu\text{A}/\text{cm}^2$, $P = 1 \sim 2 \times 10^{-5} \text{ mmHg}$

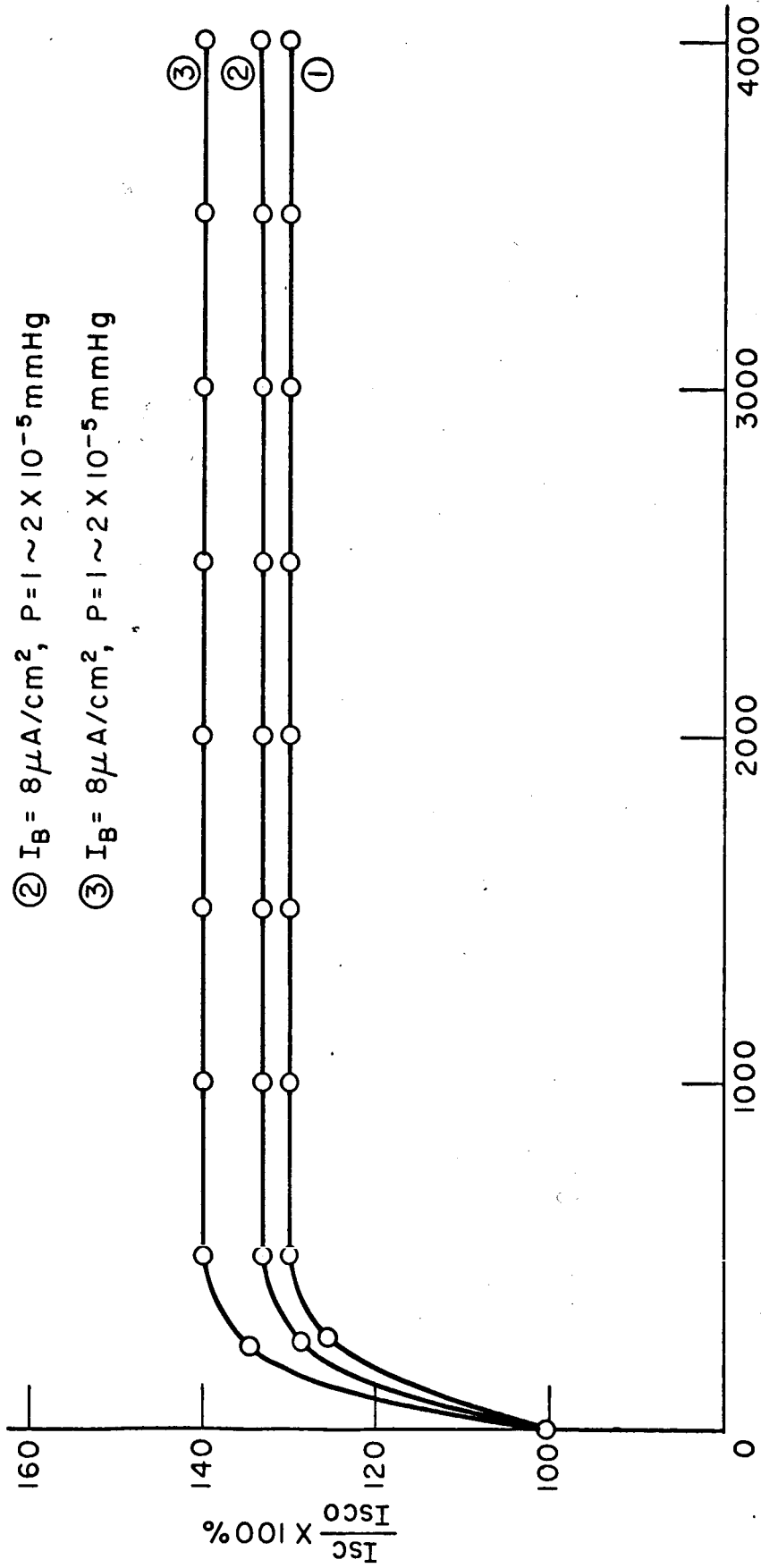


FIG. 4

n-TYPE Si; $\rho = 20\Omega\text{-cm}$

115 KeV; ① $I_B = 4\mu\text{A}/\text{cm}^2$, $P = 1.5 \sim 2.6 \times 10^{-5}\text{ mm Hg}$

② $I_B = 3.4\mu\text{A}/\text{cm}^2$, $P = 1.3 \sim 1.5 \times 10^{-5}\text{ mm Hg}$

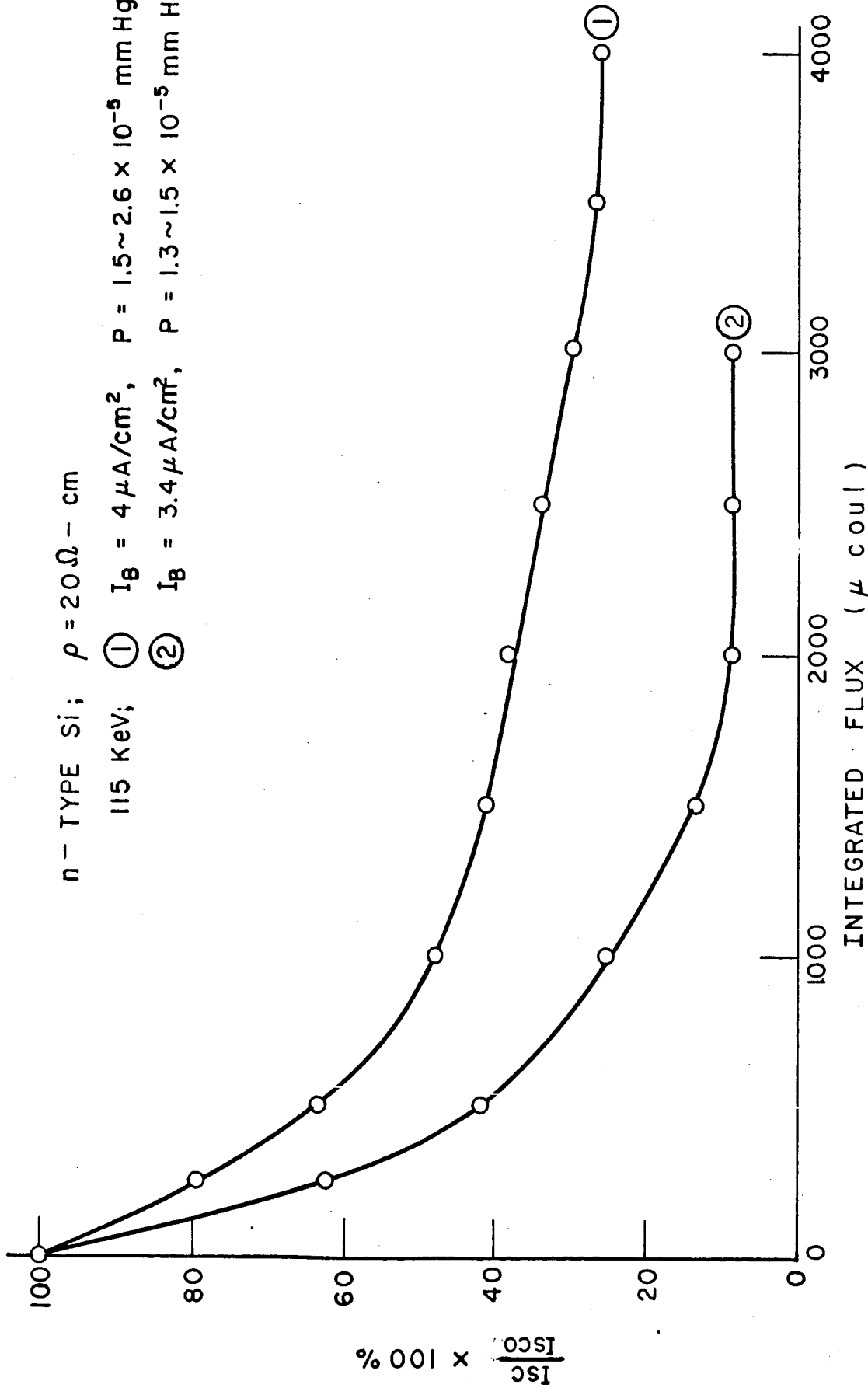


FIG. 5

n-TYPE Si; $\rho = 50 \Omega\text{-cm}$

- 115 keV; ① $I_B = 0.12 \mu\text{A}/\text{cm}^2$, $P = 1.6 \times 10^{-5} \text{mmHg}$
② $I_B = 6 \mu\text{A}/\text{cm}^2$, $P = 1.2 \sim 2.5 \times 10^{-3} \text{mmHg}$
③ $I_B = 6 \mu\text{A}/\text{cm}^2$, $P = 1.3 \sim 2.5 \times 10^{-5} \text{mmHg}$

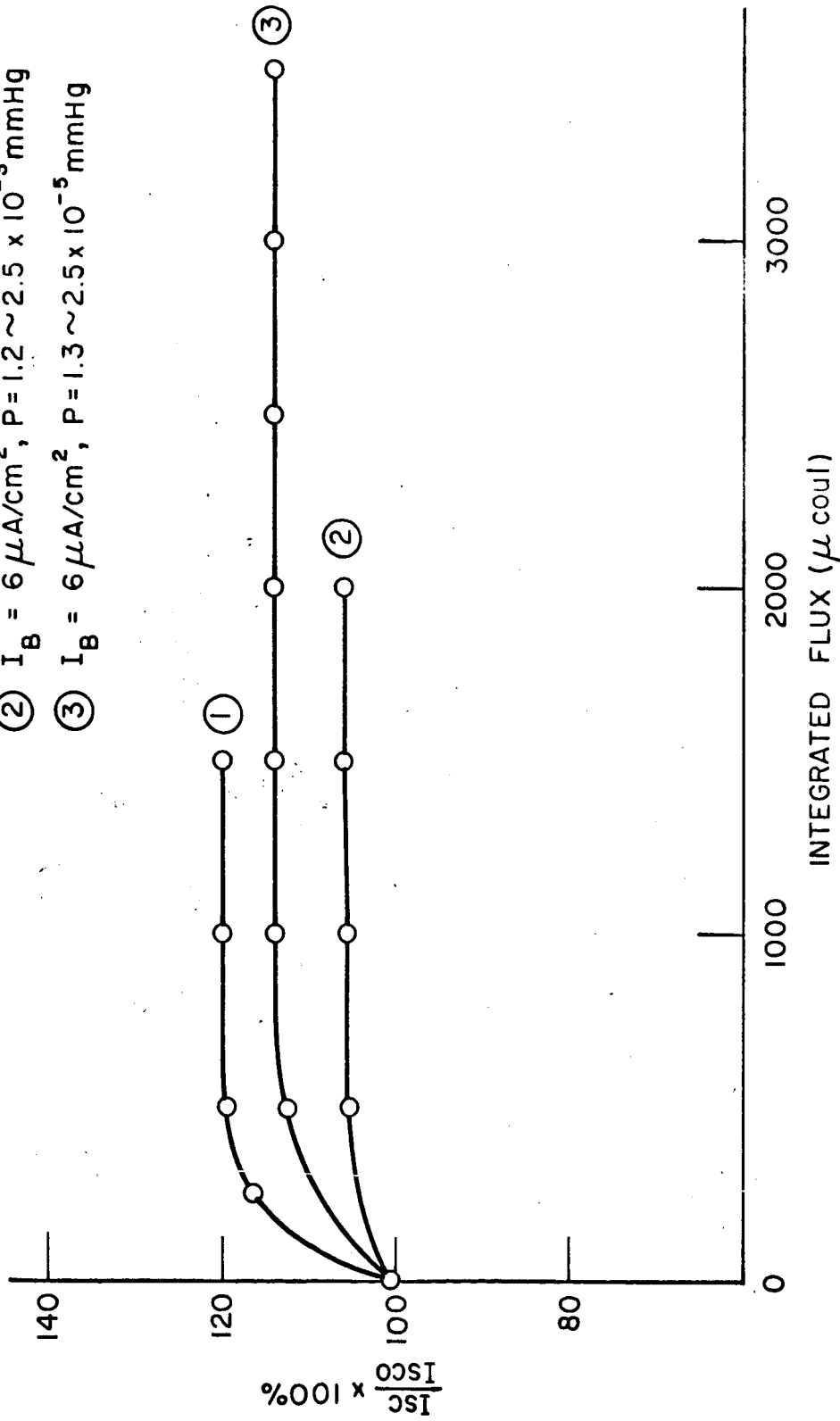


FIG. 6

P-TYPE Si; $\rho = 1\Omega\text{-cm}$

115 keV; ① $I_B = 8\mu\text{A}/\text{cm}^2$; $P = 1 \sim 2.5 \times 10^{-5}\text{mmHg}$

② $I_B = 7\mu\text{A}/\text{cm}^2$; $P = 1.5 \sim 2.5 \times 10^{-5}\text{mmHg}$

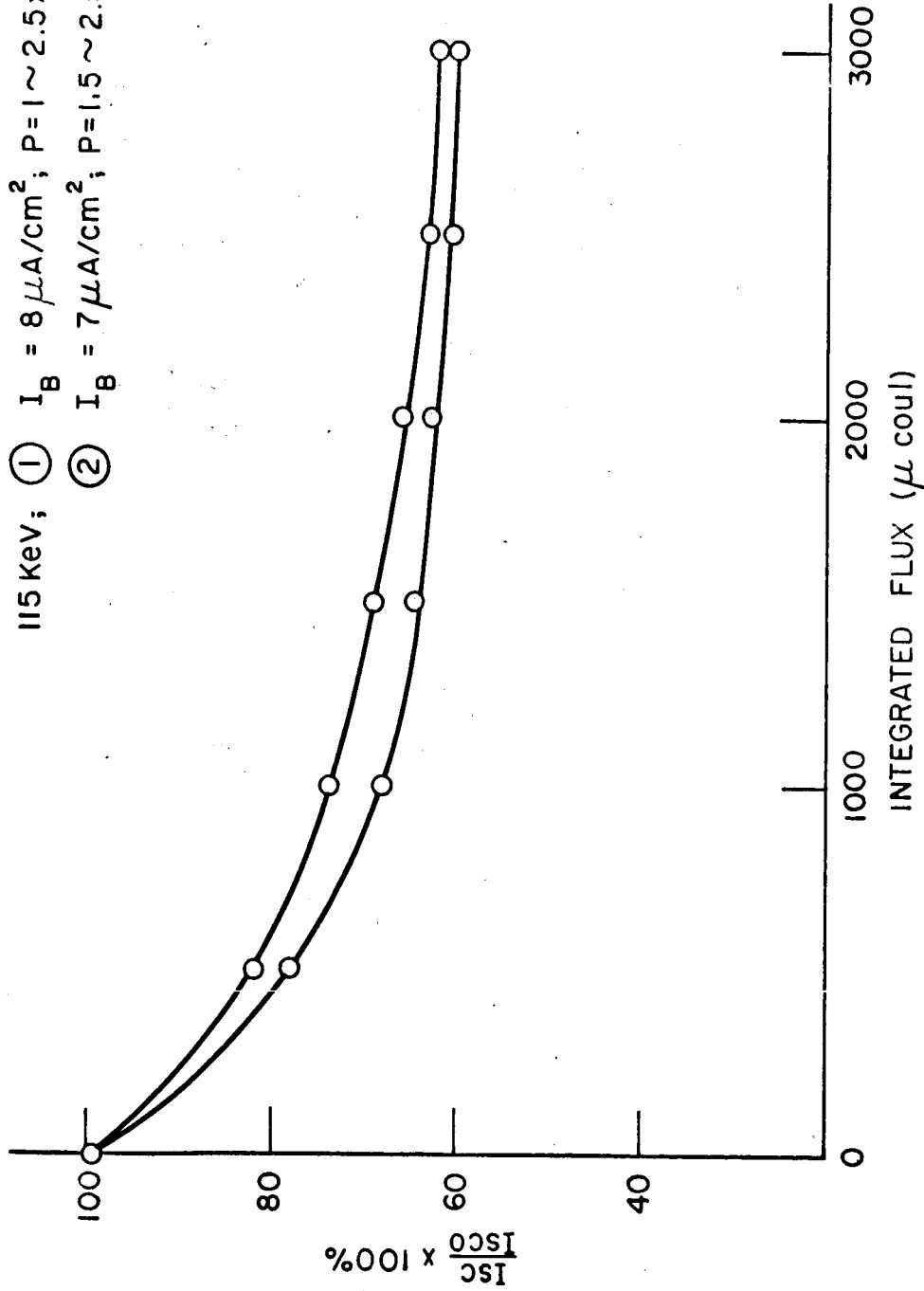


FIG. 7

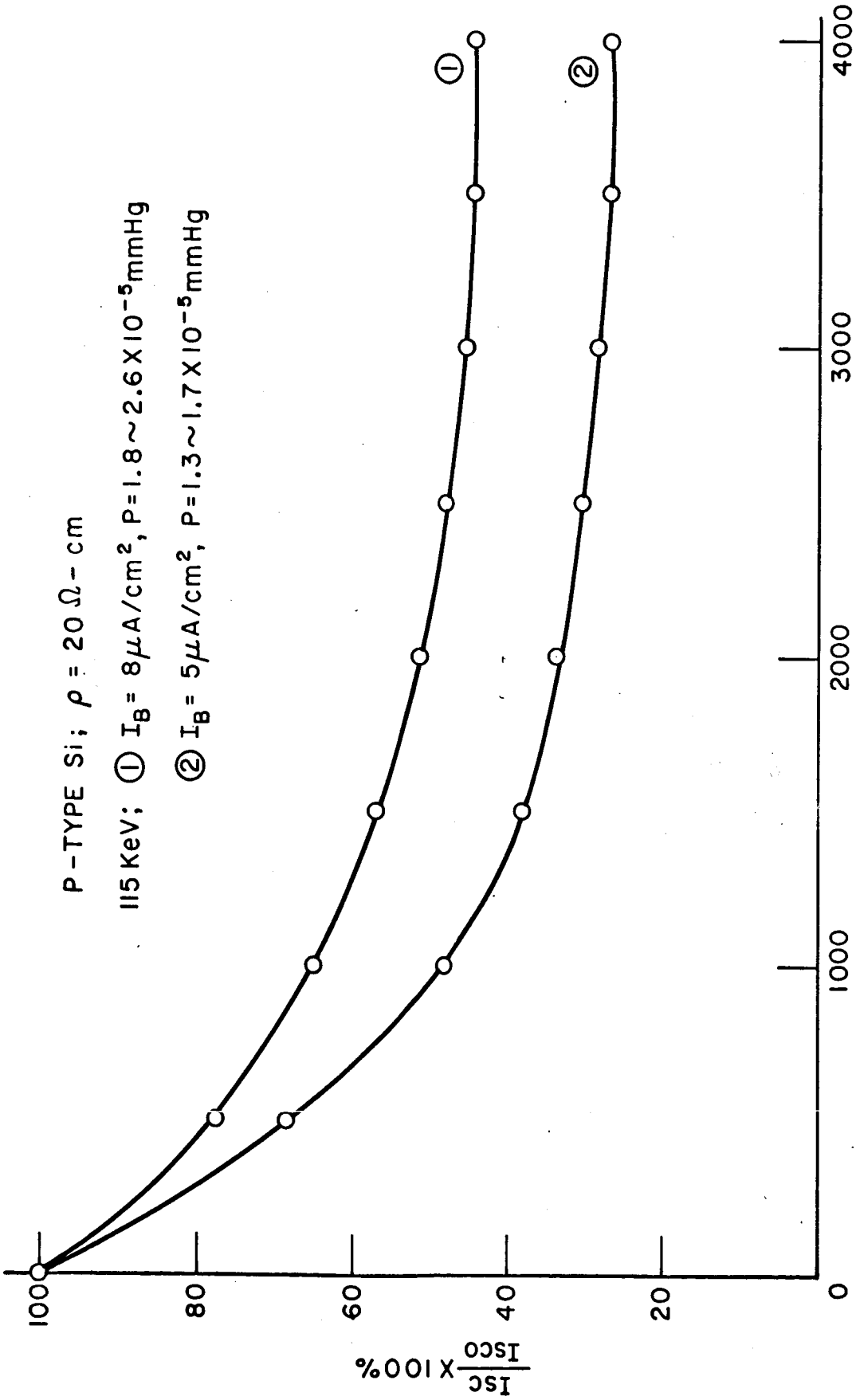


FIG. 8

n/p Si CELL, DIFFUSED FACE (BASE: $\rho = 1\Omega\text{-cm}$)

115 KeV; ① $I_B = 0.6\mu\text{A}/\text{cm}^2$, $P = 1.5 \sim 2.3 \times 10^{-5}$ mm Hg
② $I_B = 8\mu\text{A}/\text{cm}^2$, $P = 1.0 \sim 2.5 \times 10^{-5}$ mm Hg

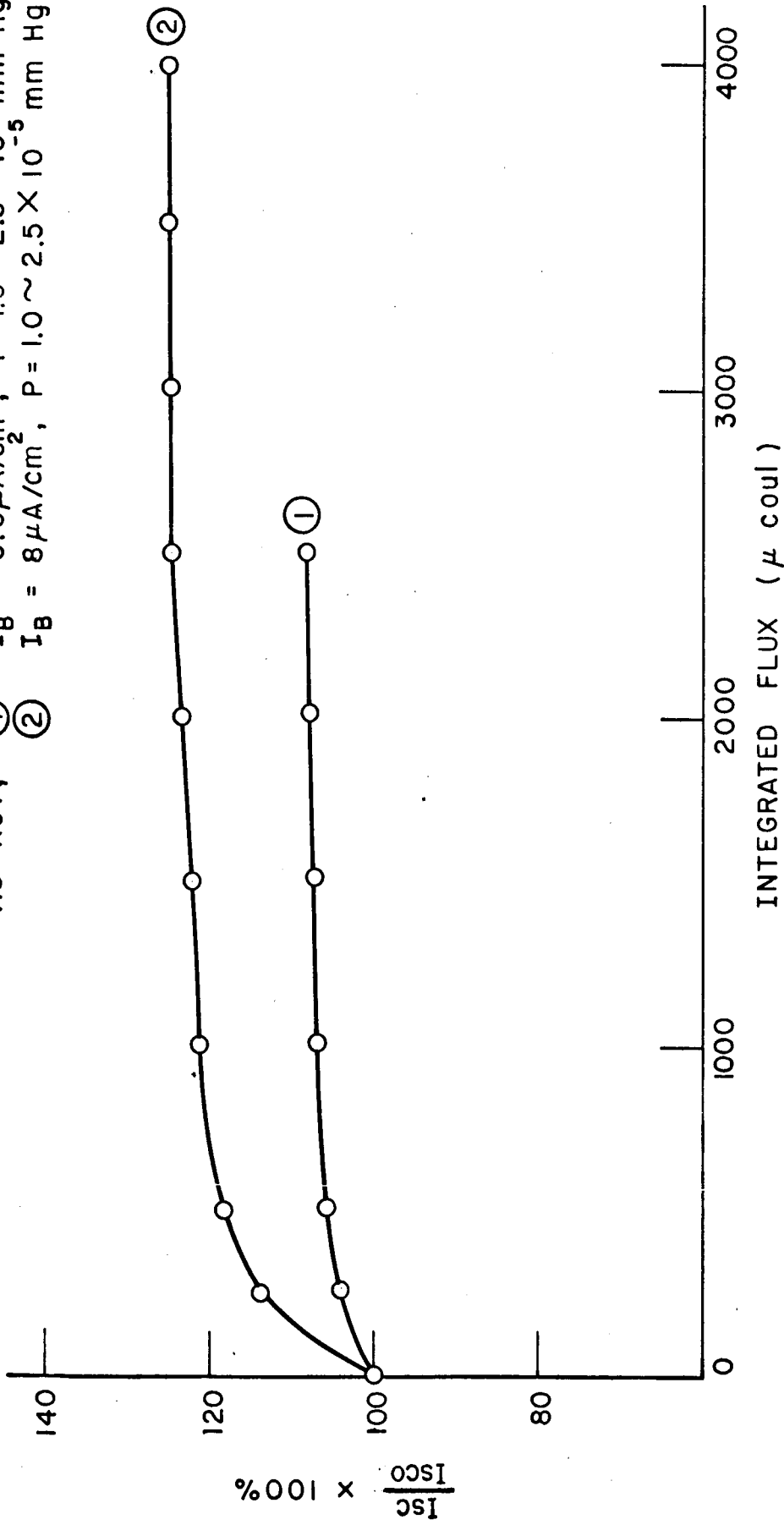
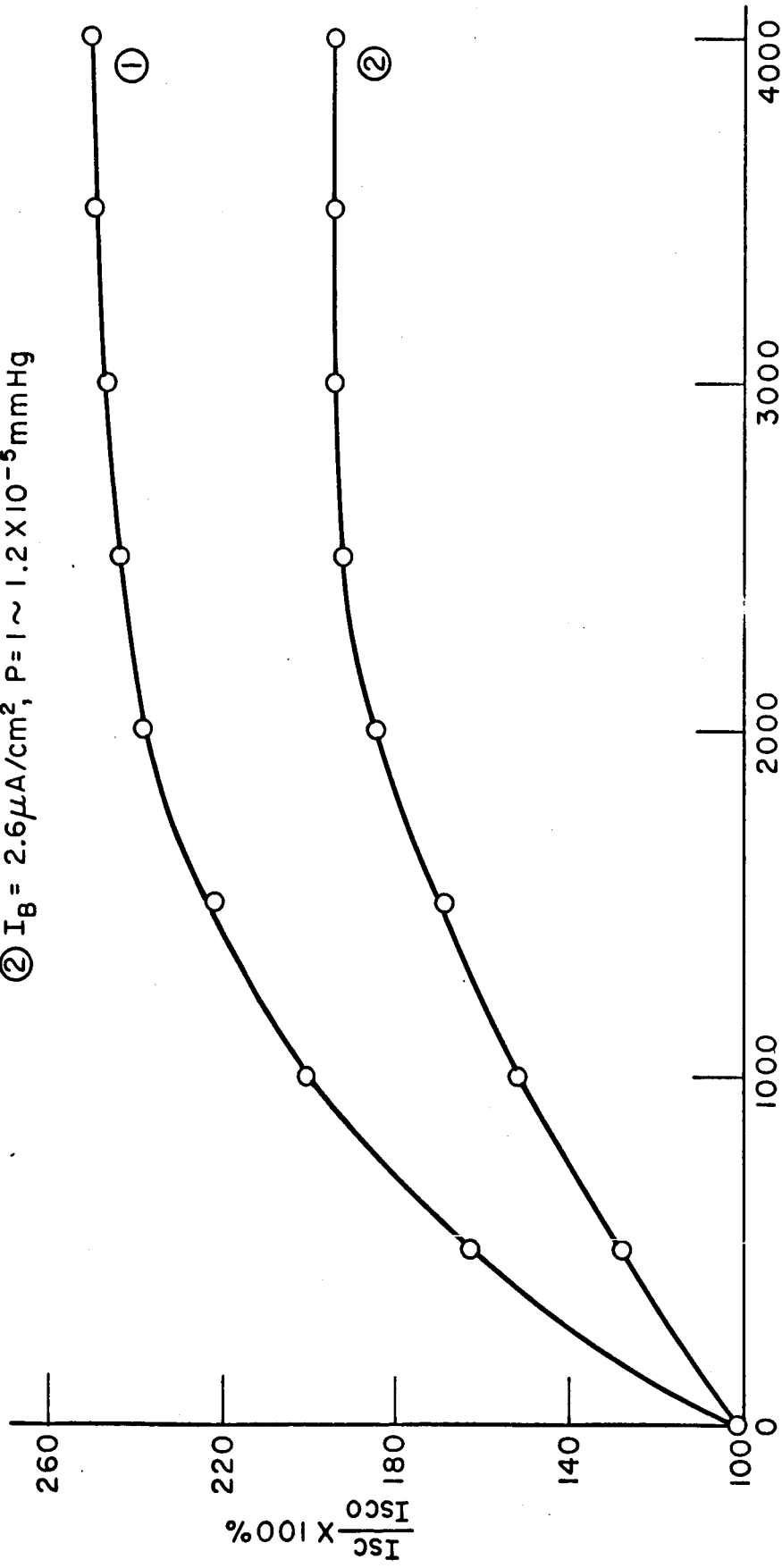


FIG. 9

n/P Si CELL, DIFFUSED FACE (BASE: $\rho = 20 \Omega\text{-cm}$)

115 keV; ① $I_B = 4.6 \mu\text{A}/\text{cm}^2$, $P = 1.8 \sim 2.2 \times 10^{-5} \text{mmHg}$

② $I_B = 2.6 \mu\text{A}/\text{cm}^2$, $P = 1 \sim 1.2 \times 10^{-5} \text{mmHg}$



INTEGRATED FLUX (μ coul)

FIG. 10

n/p si CELL, DIFFUSED FACE (BASE: $\rho = 50\Omega\text{-cm}$)
115 KeV; $I_B = 2\mu\text{A}/\text{cm}^2$; $P = 8.5 \times 10^{-6} \sim 1.5 \times 10^{-5} \text{mmHg}$

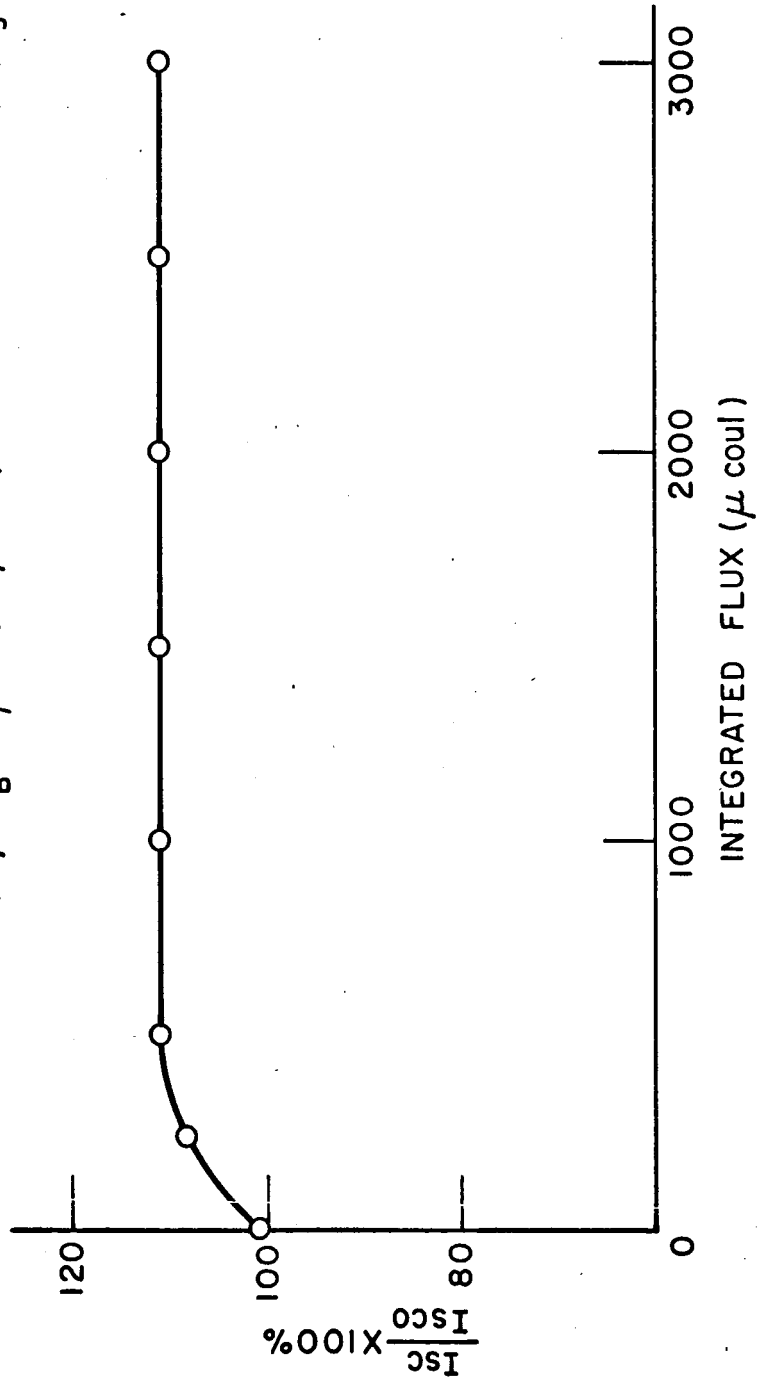


FIG. 11

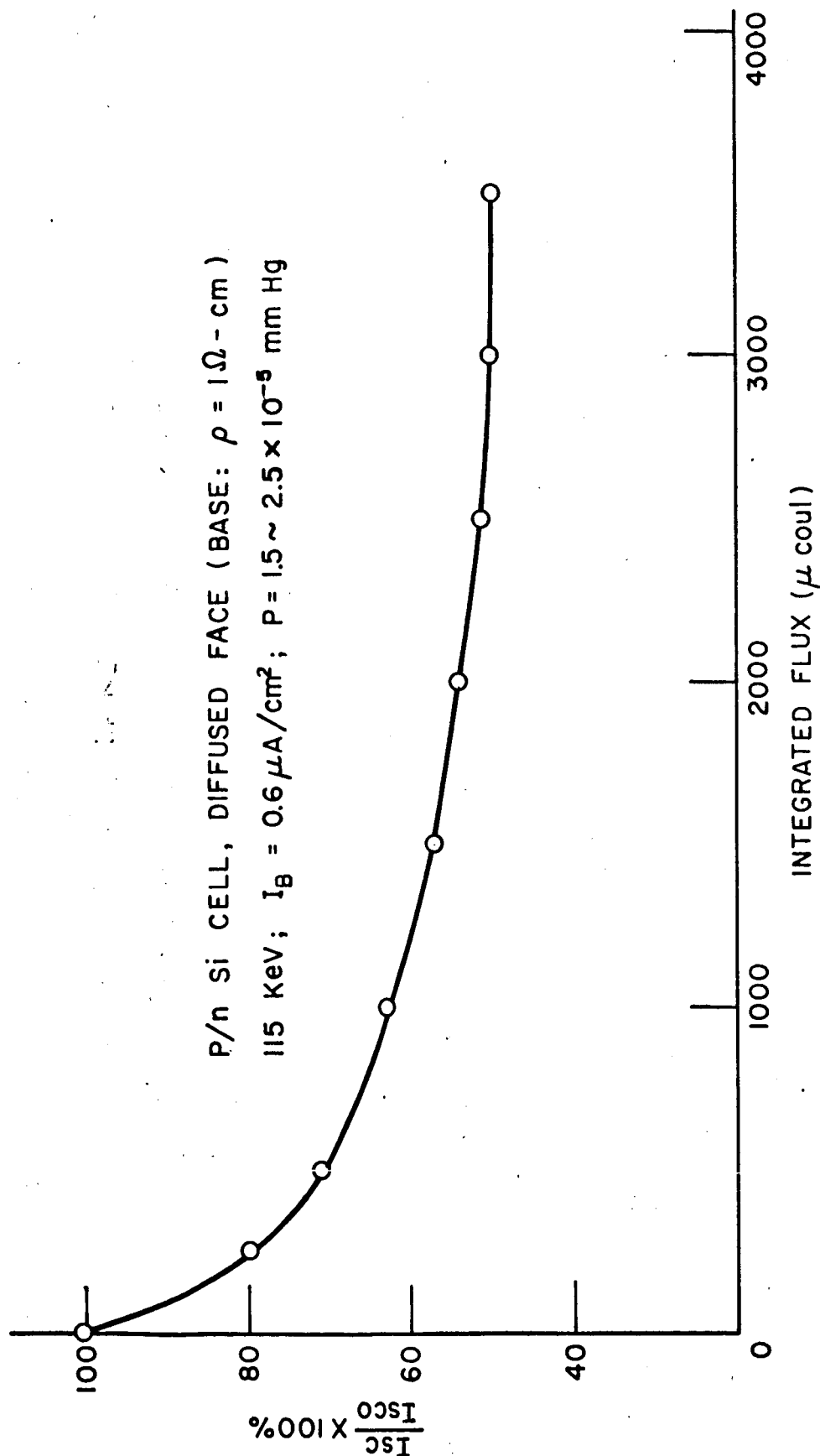


FIG. 12

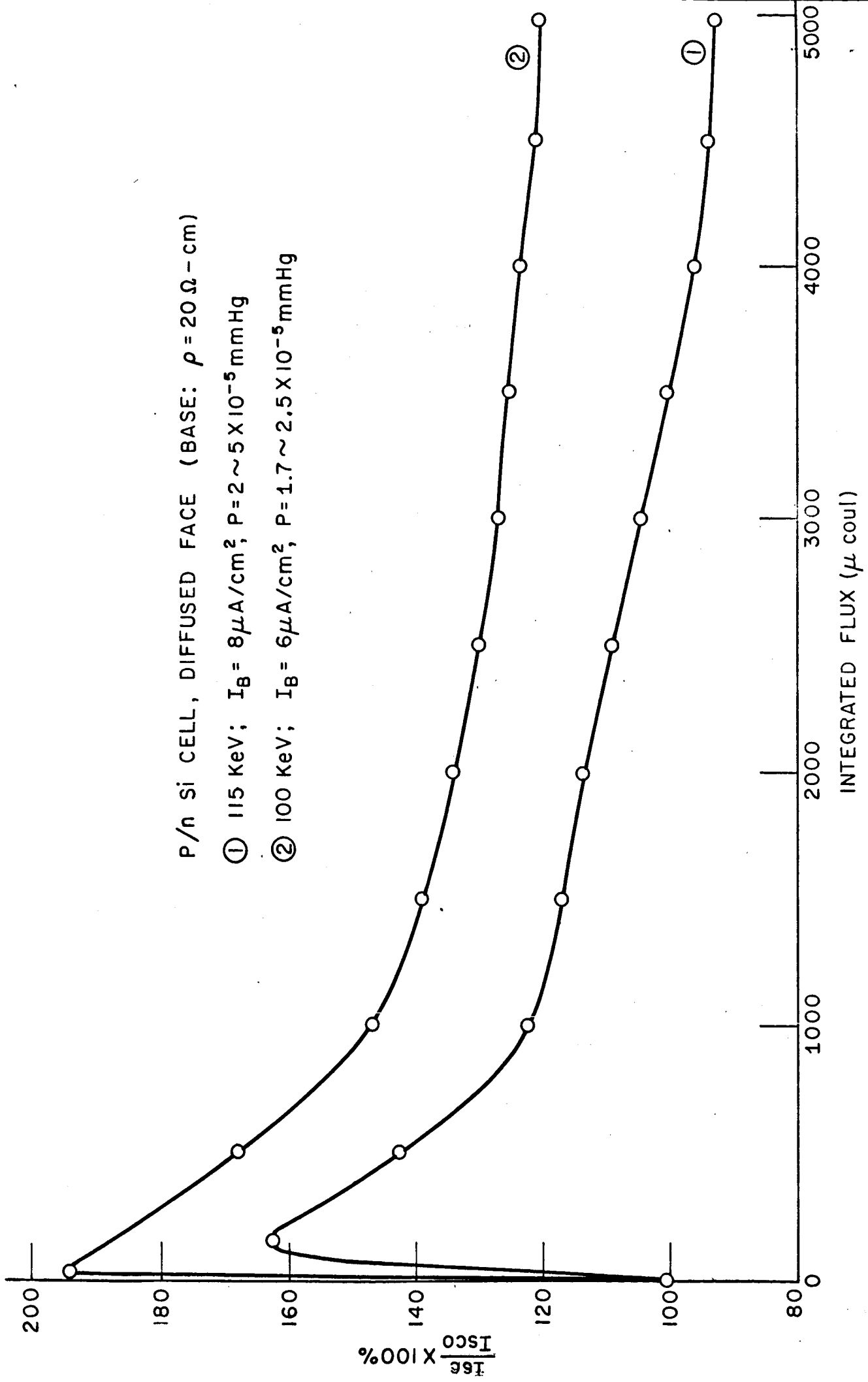


FIG. 13

P/n si CELL, DIFFUSED FACE (BASE: $\rho = 50 \Omega\text{-cm}$)

115 keV; ① $I_B = 6 \mu\text{A}/\text{cm}^2$, $P = 1.5 \sim 2.5 \times 10^{-5} \text{mmHg}$

② $I_B = 0.14 \mu\text{A}/\text{cm}^2$, $P = 1.2 \times 10^{-5} \text{mmHg}$

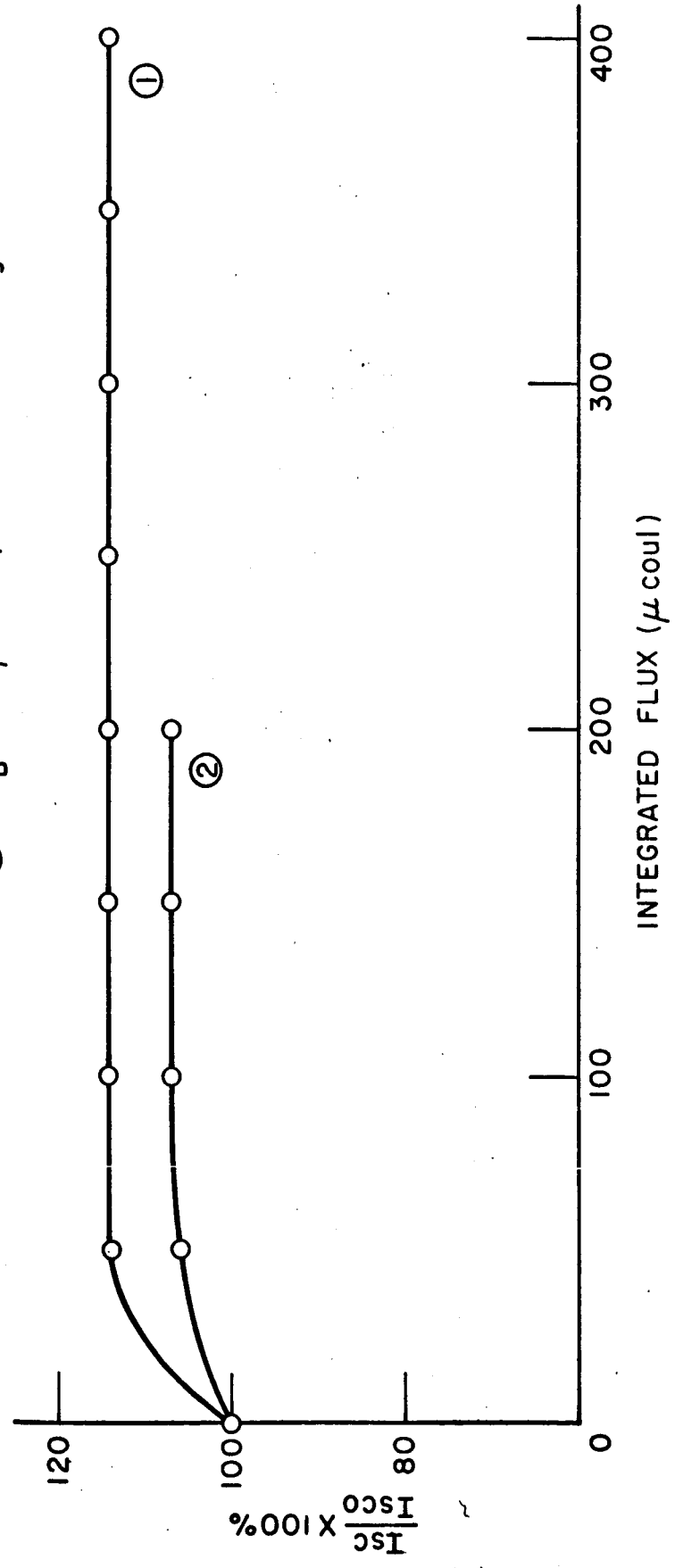


FIG. 14

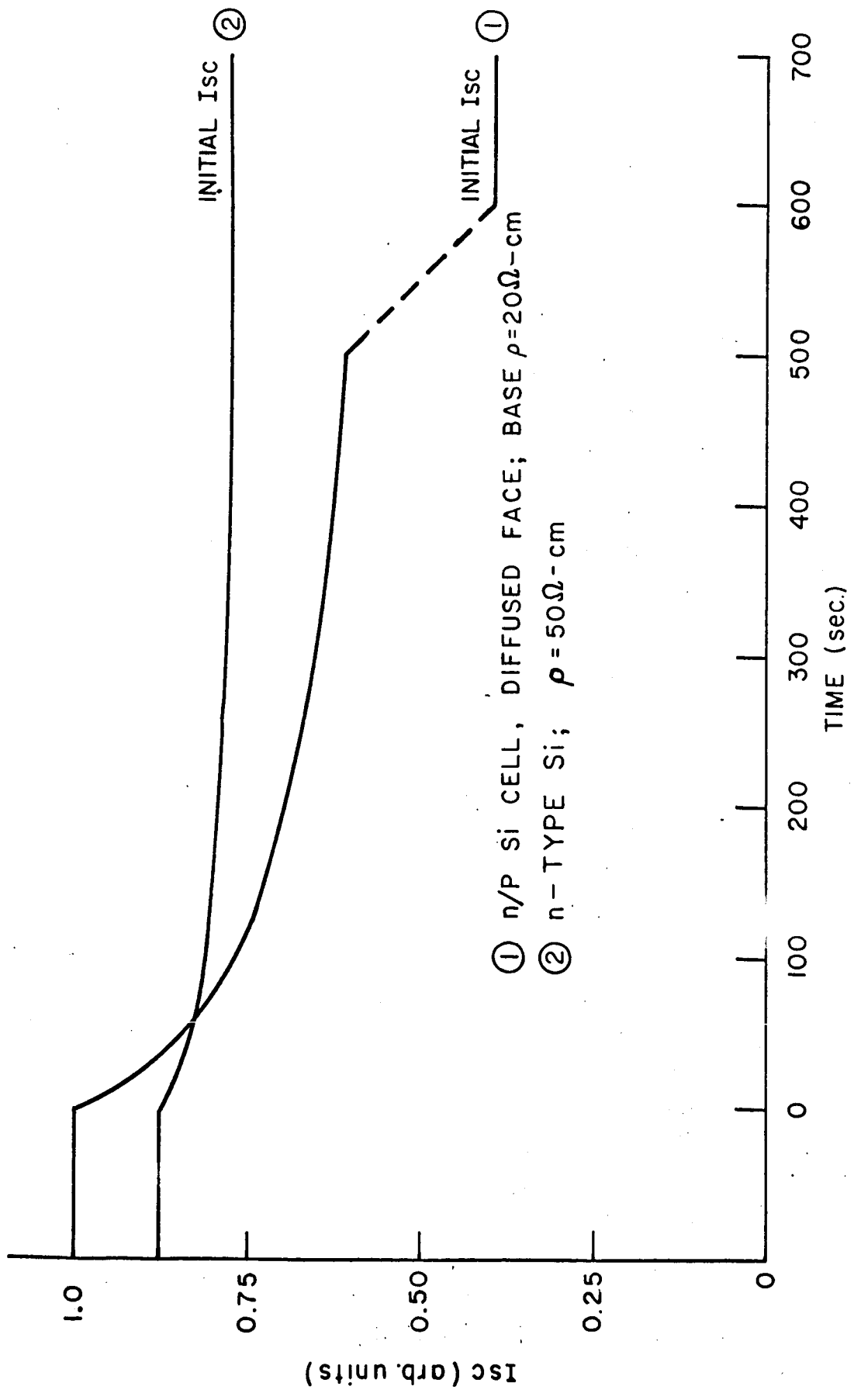


FIG. 15 ANNEALING PROCESS

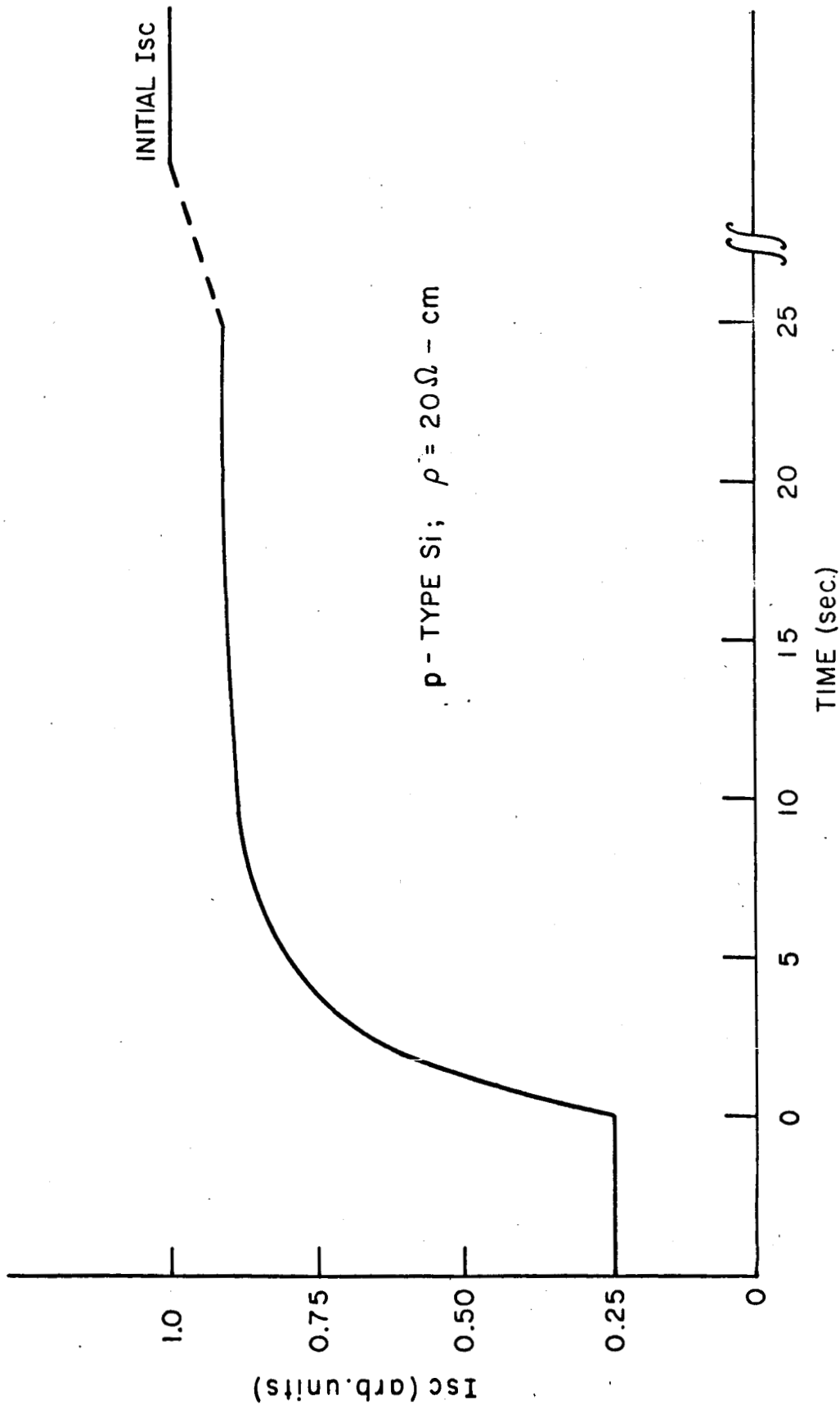


FIG. 16 ANNEALING PROCESS