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FIRST PROGRESS REPORT ON

Investigation of the Structure of Radiation Damage in Lithium Diffused Solar Cells

3 February 1969 to 30 June 1969

Contract No. 952456
(Subcontract under NASA Contract
NASA-100 Task Order No. RD-26)

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Introduction

A.) Level of Personnel Effort

In this first report we shall give the results of our research effort during the period 3 February 1969 to 30 June 1969 under the present contract (No. 952456).

The personnel supported by the contract together with their time commitment is given below.

Faculty:

Prof. John C. Corelli (1/4 time)

Graduate Student:

Mr. T. Mortka (1/2 time)

Research Technician:

Mr. J. W. Westhead (3/4 time)

from above we can see that the total effort to be reported or represents approximately 0.6 man years.

B.) General Statement of Work

The primary objective of this program was to begin a study on the experimental investigation of the effects of ~1 to 5 Me V electrons on the optical properties of silicon doped to lithium concentrations in the range $\sim 10^{15}$ Li/cm^3, to $\sim 10^{17}$ Li/cm^3. The probes used to detect the damage consist primarily of 1.) Infrared spectros copy (IR) 1 to 50 Microns and 2.) Photoconductivity 0.5 to 10 microns. The electron irradiations were performed at $\approx$ 300°K. We shall have occasion to repeat in this report some earlier statements given in our quarterly letters 5 May '69 and 16 June '69.

Experimental Methods

In the early portion of the current report period a major effort was spent to set up a complete laboratory for producing samples of lithium - diffused silicon. Our technique* involves a "painting" procedure whereby a "paste" composed of dispersed lithium metal** ($<$15 micron particle size) and 15 micron alumina mixed in mineral oil is applied on the surface of a silicon sample. The sample is given a heat treatment at $\approx$450°C in an environment through which argon or helium gas flows.

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* We thank Mrs. Marla Hoke Moore of NASA Goddard Space Flight Center for teaching us this technique.

** Available from the Lithium Corporation of America, Bessemer City, North Carolina. The sodium impurity content in this lithium metal dispersion is $<$0.01% as specified by the manufacturer.

The diffusion times vary from 10-15 minutes up to several hours depending on the sample thickness and the lithium concentration desired. Standard temperature controllers are used on the diffusion furnaces which maintain constant temperatures to within ± 3°C.

The lithium concentration is monitored by measuring the electrical resistivity at 300°K. The dc voltages are measured using a digital volt meter. Most of the measurements are made using a linear 4-point probe (manufactured by A&M Fell Ltd., Sussex, England) In some cases, we have made contacts using As-doped gold (for n-type S$_i$) to obtain cross checks on the electrical resistivity. These checks show differences of resistivity $< 2\%$ as measured by the contactless 4-point probe and by the applied gold contacts. By careful shielding of the switches, batteries, resistors etc., we can obtain a measure of the resistivity with an accuracy better than 3%. We have routinely produced samples of lithium concentrations of $\sim 10^{15}$ cm^{-3} , $\sim 10^{16}$ cm^{-3}, and 10^{17} cm^{-3} from starting material of 1 and 10 ohm-cm phosphorus doped silicon (both floating-zone and pulled, crucible grown). A total of 115 samples were prepared for our radiation experiments thus far in this contract.

In order to check the homogeneity of the diffused lithium throughout the bulk of the sample we measured the resistivity of a sample initially 1.63 mm thick and then ground the sample down to a thickness of 0.78 mm. The two values of resistivity measured on this sample (before and after grinding) were within 2% of each other. Additionally, we measure resistivity on opposite faces of all samples before irradiation and find values which differ by at most by ± 5% thus, these measurements imply a distribution of lithium throughout the sample having inhomogeneities no larger than ± 5% of the nominal value with the majority of the samples having concentration inhomogeneities less than $\approx$3%.

The electron irradiation experiments* were performed with the sample kept at 300°K. We have made irradiation experiments at 1.5 and 5 MeV. On the basis of results obtained thus far it appears unlikely that irradiations will have to be performed at an intermediate energy of 3MeV electron-irradiated silicon. The results at 1.5 and 5 MeV are reasonably similar and will allow us to make well founded conclusions as regards the radiation damage one would expect to produce at 3 MeV.

The measurements of the photoconductivity and infrared spectra are made using cryostats and spectrometers which we have described in detail elsewhere.[1,2]

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* The 1.5 MeV electron irradiations were conducted at the General Electric Research and Development Center, Schenectady, N.Y. and the 5 MeV electron irradiations at U.S.Air Force Cambridge Res. Lab. Bedford, Mass. We thank Mr. Clarence Turner of AFCRL for his assistance.

Results and Discussion

We have just begun to obtain out post irradiation results and we can only present here a relatively small fraction of our findings. We anticipate having a much more complete view of our work within the coming weeks which is the time necessary to finish our current analyses of samples.

In our quarterly letters of 5 May 1969 and 16 June 1969, we reported finding a broad infrared absorption band in the wavelength region 1.6 up to 2.6 microns which appeared in all silicon samples. We have found now that the peak is due to an instrumental effect produced by improper filtering of light from the grating and is not caused by imperfections in silicon.

A.) Photoconductivity of Li-doped Silicon

In Fig. 1, we show the photoconductivity spectrum of a sample of Li-doped silicon ($[Li] = 2.4\text{x}10^{15}\text{cm}^{-3}$) after an irradiation to a 5 MeV electron fluence of 10^{15} e/cm^2. The starting material from which the sample was produced was phosphorus doped 10Ω-cm floating-zone material. The spectrum is only shown up to a wavelength of 2.4 microns, however, this particular sample exhibits some photo conductivity out to $\sim$5 microns. The results for the wavelength region 2.4 to 5 microns will not be given at this time since we have not yet measured the source spectrum which is needed for normalization.

We use either PbS or PbSe detectors cooled to 78°K at the exact sample position in the cryostat to measure the source spectrum. The PbSe detector which covers the range 2.4 to 5 microns was not available during the past weeks.

In Fig. 2 the photoconductivity spectrum is shown for a sample doped with Li to a concentration of $2.5\text{x}10^{15}$ cm^{-3} after irradiation with 5 MeV electrons to a fluence of 10^{14} e/cm^2. In this case the starting material was 10 ohm-cm phosphorus doped pulled crucible grown silicon. Finally, we present in Fig. 3 the photoconductivity spectrum of a 5 MeV electron- irradiated sample (Fluence = 10^{15} e/cm^2) doped with lithium to $2.6\text{x}10^{15}$ cm^{-3} from a starting material of 10Ωcm phosphorus-doped pulled silicon.

In all cases (Figs. 1-3) we find no well defined energy levels in the photo conductivity spectrum. We observe a slight indication of an energy level at 1.8 microns as seen in Fig. 3. Since the signal was relatively weak in these samples necessitating wide spectral slit widths ($\approx$1000 microns) our energy resolution (about 0.1 eV) was poor at 1.5 micron and we may have not resolved all levels. At a wavelength of 2.5 microns the energy resolution was about 0.01 eV. We are not now in a position to make further conclusions on the spectra shown in Figs.

1-3. It must be emphasized that in all cases the defect concentration is very low since the post-irradiation resistivity has only increased by a factor of 2. Such low defect concentrations have not been reported on in the open literature wherein infrared photoconductivity was used to probe the defect. We repeat that the extremely low signal results from the relatively low concentration of defect centers producing photoconductivity.

B.) Infrared Spectroscopy (IR) Results in Irradiated Li-Doped Silicon

A careful investigation has been completed on the IR spectra in Li-doped Si from 1 micron to 50 microns. The Li concentrations in the samples varied from 10^{15} cm^{-3} up to 10^{17} cm^{-3}. Electrons of 1.5 and 5 MeV energy with fluences of from 10^{14} e/cm^{2} up to 10^{16} e/cm^{2} were incident on samples prepared from pulled and float zone refined silicon.

A defect absorption band is observed at 9.9 microns both at 300° and at 78°K in pulled silicon (oxygen concentration $\gtrsim 10^{17}$ cm^{-3}) and not in floating zone silicon (oxygen concentration $\lesssim 10^{16}$ cm^{-3}). In order to observe the 9.9μ band the Li concentration must be $\gtrsim 10^{16}$ cm^{-3}. We have found that this 9.9 micron absorption band is not effected by electron irradiations up to a fluence of 10^{16} e/cm^{2} within our $\pm 5\%$ experimental error. The precise location of the band at 300°K is 1006 cm^{-1} (9.99 microns) with a shift to 1014 cm^{-1} (9.9 microns) when the measurement is made on the sample kept at 78°K. We also observe that the band becomes sharper in width as we lower the temperature.

In previous IR spectroscopy studies Chrenko, McDonald and Pell[3] found that the absorption band at 9.9 microns was due to the vibrational modes resulting from the interaction of Li ions with isolated interstitial oxygen atoms to form a positively charged complex (OLi+). The activation energy of the (OLi+) complex was observed to be 0.42(3) eV and represents the energy for dissociation of a Li^{+} and an oxygen atom. The annealing behavior of the 9.9 micron band is different markedly from what we observed in our previous work(1) in which we irradiated pulled Li-containing silicon samples with 50 MeV electrons to a fluence of $\sim 10^{18}$ e/cm^{2}. The 50 MeV electron bombardment results were that the 9.9 micron band annealed out completely after 15 minutes at 100°C with concomitant production of several other defect absorption bands at longer wavelength. In the present work using lower energy electrons at lower fluence we have observed that the 9.9 micron band is stable even after annealing up to temperatures of 400°C.

We have not detected A-centers (oxygen plus vacancy complex) as determined by the 12 micron (834 cm^{-1} infrared absorption band in any of our irradiated pulled silicon samples. We argue that there are several plausible reasons to explain the lack of A-centers, 1.) competition from the reaction forming LiO^+ 2.) deactivation of A centers by Li to form a neutral complex (LiO^+ plus Vacancy) 3.) the trapping of primary rediation-induced defects by lithium thus tying up such defects as single vacancies and 4.) low electron fluence did not cause sufficient number of defects for us to observe A-centers using infrared spectroscopy.

We conclude that no infrared active defect absorption bands are formed in Li-doped silicon samples irradiated to fluences of $\sim 10^{16}$ e/cm^2 and that higher fluences $\gtrsim 10^{17}$ e/cm^2 will be required for us to make further infrared spectroscopy studies.

Plans on Research to be conducted in the next Four Months

Since we now have a much clearer overview after 5 months of work on the problem involved in studying the Li-defect complexes in irradiated silicon we can use this knowledge to guide us in our future work. The following items must be covered in our work:

1.) Make additional photoconductivity studies on 1.5 and 5 MeV electron-irradiated Li-doped silicon in pulled and float zone refined samples irradiated up to 10^{16} e/cm^2. In particular , we shall emphasize study of the wavelength region 1 to 6 microns with subsequent annealing studies at several temperatures in the range 150-450°C.

2.) Continue our study on the effects of radiation on the 9.9 micron defect absorption band in Li-doped pulled silicon. This band is only observed in silicon containing $\gtrsim 10^{16}$ Li/cm^3 and $\gtrsim 10^{17}$ O/cm^3 as impurities.

3.) We now find that electron fluences of about 5×10^{17} e/cm^2 may be needed to observe infrared active absorption bands, and for this reason we plan on one long irradiation run, during the next 3 months.

4.) To complete the study of the contract we will run two more electron irradiations one at 1.5 MeV and another at 5 MeV. These experiments will require producing additional Li-doped samples.

In a longer range program we must include Hall effect studies to compare electrically active defect energy levels with those found in photoconductivity studies.

Figure Captions

Fig. 1) Photoconductivity of Li-doped Si, ([Li] = 2.4x10^{15}cm^{-3}) after a 5 MeV electron irradiation to a fluence of 10^{15} e/cm^2. Before lithium diffusion the sample was 10 Ω-cm phosphorus doped floating zone material. Wavelength range 1 to 2.6 microns.

Fig. 2) Photoconductivity of Li-doped Si, [Li] = 2.5x10^{15}cm^{-3} after a 5 MeV electron irradiation to a fluence of 10^{14} e/cm^2. Before lithium diffusion the sample was 10Ω-cm phosphorus-doped pulled crucible grown material. Wavelength range 1 to 2.4 microns.

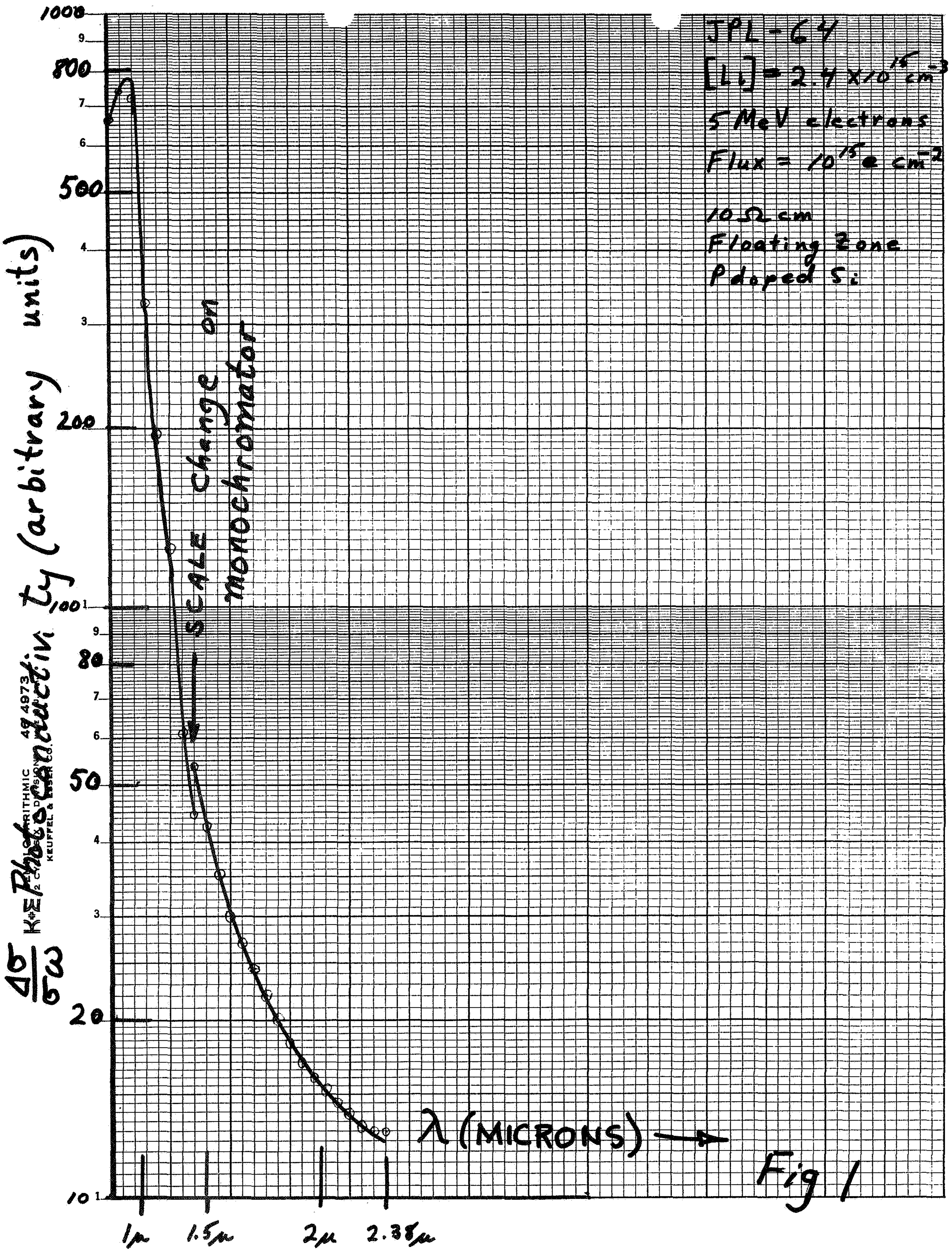
Fig. 3) Photoconductivity of Li-doped Si, [Li] = 2.6x10^{15}cm^{-3} after a 5 MeV electron irradiation to a fluence of 10^{15} e/cm^2. Before lithium diffusion the sample was 10Ω-cm phosphorus-doped pulled crucible grown material. Wavelength range 1 to 2.5 microns.

References

(1) R.C. Young, J.W. Westhead and J.C. Corelli J Appl. Phys. 40, 271 (1969).

(2) A.H. Kalma and J.C. Corelli Phys. Rev 173, 734 (1968).

(3) R.M. Chrenko, R.S. McDonald and E.M. Pell, Phys. Rev 138, A 1775 (1965).



JPL-64

$[Li] = 2.4 \times 10^{15}\ cm^{-3}$

5 MeV electrons

$Flux = 10^{15}\ e\ cm^{-2}$

10 Ω cm

Floating Zone

P doped Si

Fig 1

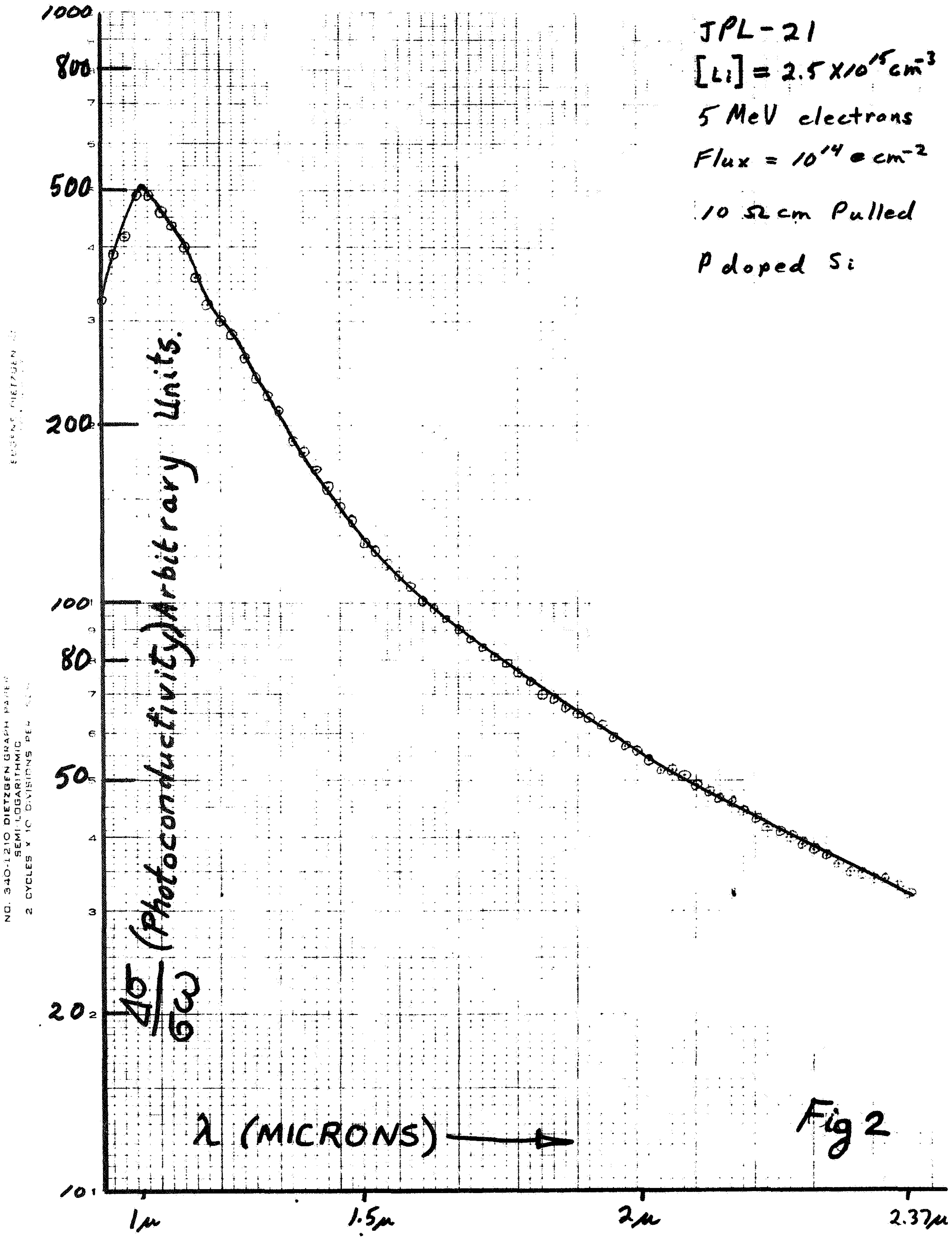

JPL-21
[Li] = 2.5 × 10^15 cm^-3
5 MeV electrons
Flux = 10^14 e cm^-2
10 Ω cm Pulled
P doped Si
Δσ/σω (Photoconductivity) Arbitrary Units.
λ (MICRONS) →
1000
800
500
200
100
80
50
20
10
1μ
1.5μ
2μ
2.37μ
NO. 340-1210 DIETZGEN GRAPH PAPER
SEMI-LOGARITHMIC
2 CYCLES X 10 DIVISIONS PER

Fig 2

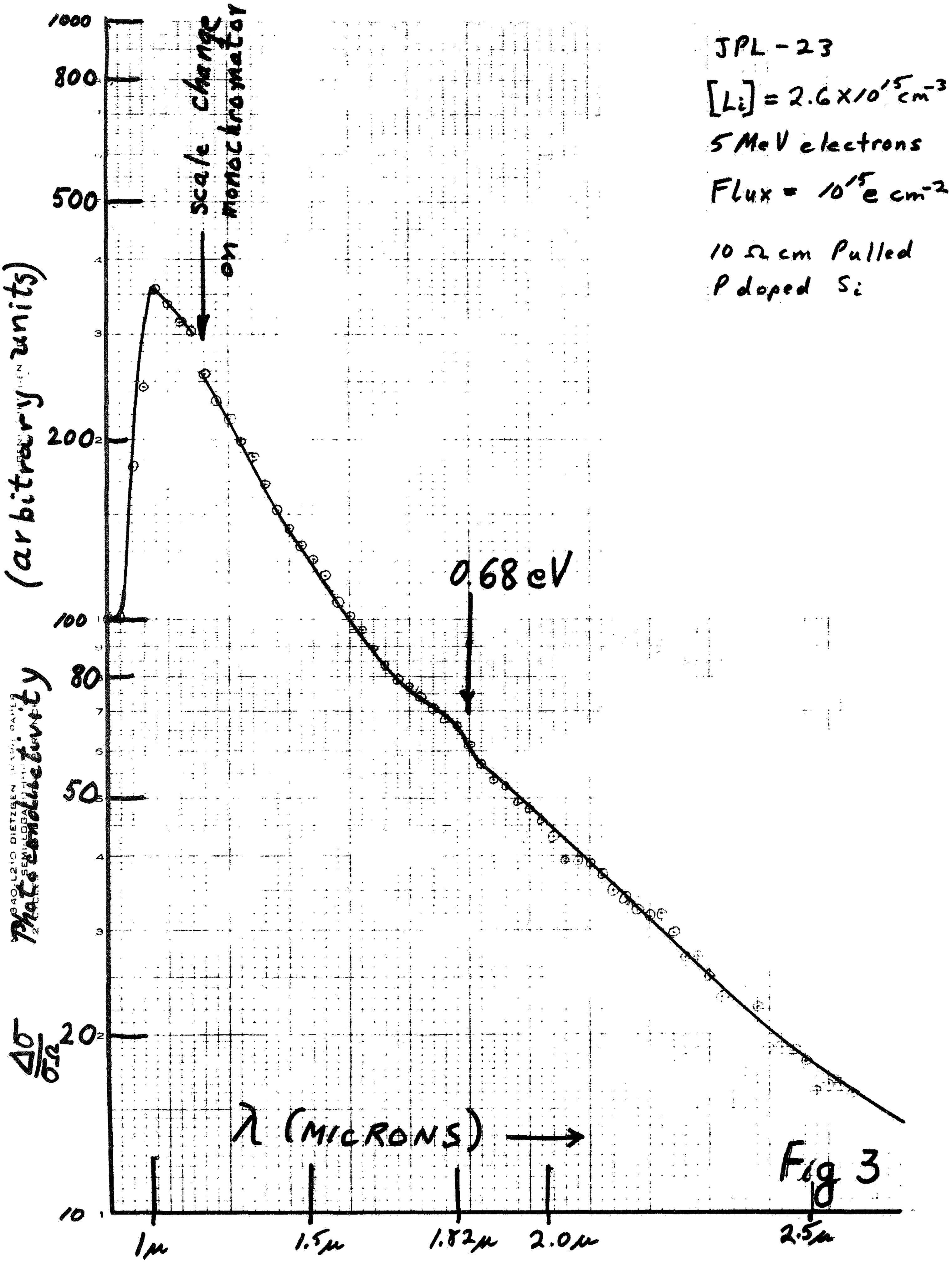

JPL-23
[Li] = 2.6×10^15 cm^-3
5 MeV electrons
Flux = 10^15 e cm^-2
10 Ω cm Pulled
P doped Si
Scale change on monochromator
0.68 eV
Photoconductivity (arbitrary units)
Δσ/σ₀
1000
800
500
200
100
80
50
20
10
λ (MICRONS) →
1μ
1.5μ
1.82μ
2.0μ
2.5μ

Fig 3