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ANNEALING OF INFRARED DEFECT ABSORPTION BANDS  
IN 40 MEV ELECTRON-IRRADIATED SILICON\*

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## ABSTRACT

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Oxygen containing n-and p-type silicon ( $100\Omega\text{-cm}$ ) and floating-zone n-type silicon ( $0.1\Omega\text{-cm}$ ) were irradiated by 44 Mev electrons at  $40^{\circ}\text{C}$  to total integrated fluxes of  $1\text{-}2 \times 10^{18} \text{ e/cm}^2$ . The floating-zone silicon remained n-type ( $2500\Omega\text{-cm}$ ) after irradiation and exhibited infrared defect absorption bands at  $1.8\mu$  and were cooled to  $85^{\circ}\text{K}$  defect bands at  $3.46$  and  $3.62\mu$  appeared. The oxygen-containing silicon was n-type after irradiation with resistivity of  $3 \times 10^5\Omega\text{-cm}$  and exhibited bands at  $11.6\mu$  and  $12\mu$  in addition to the  $1.8$ ,  $3.46$  and  $3.62\mu$  bands. Isochronal annealing studies indicated that  $1.8$ ,  $3.46$  and  $3.62\mu$  bands anneal out together and are completely removed in all samples by heat treatment to  $300^{\circ}\text{C}$ . The  $11.6$  and  $12\mu$  bands do not begin to anneal out until a temperature of  $300^{\circ}\text{C}$  is reached and are completely gone at  $400^{\circ}\text{C}$ . At temperatures above  $375^{\circ}\text{C}$  a new band at  $11.2\mu$  appears only in oxygen-containing silicon having maximum intensity at  $475^{\circ}\text{C}$  and then disappears at  $575^{\circ}\text{C}$ . A comparison to other experiments on infrared properties of silicon irradiated by other radiations and energies is given.

*Anderson*

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## I INTRODUCTION

It is the purpose of this paper to show that radiation-induced defect infrared absorption bands produced by 40 Mev electron irradiation of silicon are very similar to defect absorption bands produced in silicon by low energy electron ( $E \leq 4.5$  Mev), deuteron (9.6 Mev), and reactor neutron irradiation. The results show clearly that apart from production rates the radiation-induced defect bands are characteristic of the specific defects as one might expect since the maximum recoil energy acquired by a silicon atom struck by a 40 Mev electron lies between that resulting from an electron ( $\leq 4.5$  Mev) and from fast neutrons in a reactor irradiation.

We shall give results on the radiation-induced defect infrared bands in floating-zone ( $10^{15} - 10^{16}$  oxygen atoms/cm<sup>3</sup>) and crucible grown ( $10^{17} - 10^{18}$  oxygen atoms/cm<sup>3</sup>) silicon. The defects were introduced by 40-44 Mev electrons. We also shall present fairly detailed isochronal annealing results on each of the defect bands observed and show the close similarity in the defects responsible for the induced bands by other radiations and energies and our 40 Mev electron results.

Electrical property measurements on 10-60 Mev electron irradiated silicon showed<sup>(1)</sup> a very close similarity to what has been observed with other energies and particles, e.g. Co<sup>60</sup> gamma rays (1.25 Mev), low energy electrons ( $\leq 4.5$  Mev) and reactor neutrons. The similarities were detected specifically

from the production of defect energy levels in the forbidden gap, and annealing characteristics. It became apparent on account of this similarity in the "bulk properties" of the radiation damage that further measurements of a microscopic property such as infrared absorbtivity would yield results that are helpful in an understanding of the defects formed in irradiated silicon. It was found that the infrared results to be given here are indeed quite similar to the results of others<sup>(2-7)</sup> using different radiations and energies thus implying that there exist basic features of the defects common to all types of radiation.

The use of infrared spectroscopy as a microscopic probe for the study of radiation-induced defects in silicon has been shown to be an important probe by many workers<sup>(2-7)</sup> in recent years. In the past, defects introduced in silicon by reactor neutrons, 9.6 Mev deuterons and electrons of energy less than 4.5 Mev were observed to give rise to new infrared absorption bands in silicon in the wavelength region 1.8 to 20.5 microns. The defect bands found can be divided into two groups<sup>(3)</sup> the first group of bands is associated with electronic excitation and is located in the wavelength range 1.8 to about 6.0 microns. The second group of bands 9 to 20.5 microns are vibrational bands. In general the bands between 9 and 12.5 microns arise only from defects associated with atomically dispersed oxygen in silicon. We shall discuss later the important role that oxygen plays in

radiation-induced defects in silicon.

## II EXPERIMENTAL METHODS

Optically polished discs of floating-zone silicon and of oxygen-containing crucible-grown\* silicon 20-26 mm in diameter were irradiated by  $\sim 40$  Mev electrons from the RPI variable-energy electron linac. The sample impurity, resistivity before and after irradiation, incident electron energy, total integrated flux and thickness for each of the four silicon samples studied is given in Table I.

The samples were mounted in a metal box through which water flowed so that the sample temperature never exceeded  $40^{\circ}\text{C}$  during irradiation. The electron beam was incident on all samples in the  $\langle 111 \rangle$  direction.

The infrared spectra from 2 to  $40\mu$  were measured using a Perkin-Elmer model 421 grating spectrometer with a CsBr interchange. A second spectrometer, Perkin-Elmer Model 21 was used to measure the infrared spectra from 0.9 to  $2.5\mu$ . The measurements were made at both  $295^{\circ}\text{K}$  and  $85^{\circ}\text{K}$ . The low temperature measurements were made using an evacuated cell\*\* with NaCl or CsBr windows. The sample was cooled by mounting it to copper

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\* The crucible-grown samples were kindly supplied to us by the Instrument Research Division of the NASA Langley Research Center, Hampton, Va.

\*\* We thank Dr. H. Richtol of the RPI Chemistry Department for the use of his cell.

rings in contact with liquid nitrogen.

The annealing experiments were performed using a temperature-controlled furnace. The samples were immersed in an oil bath for temperatures in the range 175°C to 275°C and from 300°C to 600°C air served as the heat transfer medium. The temperature was controlled to  $\pm 1^\circ\text{C}$  in the range 175 - 275°C and to  $\pm 3^\circ\text{C}$  in the range 300 - 600°C. The samples were annealed at each temperature for 20 minutes.

### III EXPERIMENTAL RESULTS

Except where stated explicitly the infrared spectra were measured with the sample at 85°K for all defect absorption bands except the 1.8  $\mu$  band.

Figure 1 shows the infrared spectra measured at 85°K and 295°K in the range 1-3 microns for oxygen containing (crucible grown) and floating zone n-type silicon samples after 36 and 40 Mev electron irradiations respectively. The radiation-induced defect absorption band at 1.8 microns is sharpened and shifts to shorter wavelength when the sample is cooled to 85°K. The fundamental absorption edge can be seen to shift slightly to longer wavelengths. We have observed exactly the same results for the 1.8  $\mu$  band shown in Figure 1 in p-type silicon (boron-doped) which converted to n-type after irradiation by 44 Mev electrons to integrated fluxes of  $2 \times 10^{18} \text{ e/cm}^2$ .

Proceeding on to the longer wavelength region the next radiation-induced defect absorption bands observed were in the  $3\text{-}4\mu$  range. Figure 2 shows infrared spectra of the pulled p-type (now n-type after irradiation) and floating zone n-type silicon samples measured at  $295^{\circ}\text{K}$  and  $85^{\circ}\text{K}$  in the range  $3\text{-}4\mu$ . The results in Figure 2 for the pulled p-type sample are similar to what we observe in the pulled n-type silicon sample. In all cases sharp bands appear at  $3.46$  and  $3.62\mu$  when the sample is cooled to  $85^{\circ}\text{K}$  with the effect appearing more pronounced in the thicker floating-zone sample. From Figure 2 it can be seen that the thicker floating-zone sample exhibits broad absorption at  $295^{\circ}\text{K}$  and this is not the case for the pulled crystal.

The longest wave-length defect absorption bands which we observed were in the 10-12 micron region. These very sharp bands at 11.6 and 12.0 microns were observed only in the oxygen-containing samples. It has been shown by Watkins and Corbett<sup>(8)</sup> and Corbett, Watkins, Chrenko and McDonald<sup>(4)</sup> using both spin resonance and infrared absorbtivity measurements that the defect configuration which is responsible for the  $12\mu$  band is an oxygen vibrational band composed of a substitutional oxygen atom coupled to a vacancy. The defect was called the Si-A center<sup>(8)</sup>. These workers used 1.4 Mev electrons to introduce the defects. The temperature dependence of the  $12\mu$  band which we observe is the same as found by what Corbett et.al.<sup>(4)</sup> in that the absorption peak shifts to shorter wavelength as the temperature

is decreased from room temperature down to 85°K.

The isochronal annealing results on the 1.8, 3.46 and 3.62  $\mu$  bands are given in Figure 3 where we plot fraction remaining vs. annealing temperature. The determination of the fraction remaining (i.e. fraction of defect band remaining) was made directly by measuring the area under the absorption peak. When this procedure was not feasible the height of the band relative to one point in the spectrum was used as a measure of the defect concentration. The data were normalized at 175°C. The annealing peak exhibited by sample 4 at 225°C (see Figure 3) is apparently real since a close inspection has shown that the peak is not due to experimental systematics.

Figure 4 shows the infrared spectra (810 - 930  $\text{cm}^{-1}$ ) of a typical oxygen-containing sample measured at 85°K after various stages of heat treatment (20 minutes at each temperature). It can be seen that as the Si-A center (at 834  $\text{cm}^{-1}$ ) and the band at 865  $\text{cm}^{-1}$  anneal out a band at 894  $\text{cm}^{-1}$  begins to appear and is present in maximum intensity after the Si-A center disappears. The 894  $\text{cm}^{-1}$  band was first reported by Watkins, Corbett and McDonald in 1.5 Mev electron-irradiated pulled silicon. Finally after 20 minutes at 600°C no defect bands are detectable. In Figure 5 is shown the isochronal annealing of the 834 and 865  $\text{cm}^{-1}$  bands together with the growth and decay of the 894  $\text{cm}^{-1}$  band for both oxygen-containing silicon samples studied.



## IV DISCUSSION OF RESULTS AND CONCLUSIONS

Fan and Ramdas<sup>(2)</sup> have found that the bands at  $1.8\mu$  and  $3.46$  and  $3.62\mu$  are associated with a defect energy level lying  $0.21$  ev below the bottom of the conduction band. They suggest that these bands may be associated with the same defect centers. The annealing results shown in Figure 3 lend some support to this conclusion insofar as the defect responsible for the  $1.8$ ,  $3.46$  and  $3.62\mu$  bands has completely annealed by heat treatment to  $300^{\circ}\text{C}$ . Fan and Ramdas<sup>(2)</sup> also state that the bands at  $3.46$  and  $3.62\mu$  appear to be excited states of the defect giving rise to the absorption. The similar annealing behavior of the  $3.46$  and  $3.62\mu$  bands (Figure 3) strongly suggests that the possibility proposed by Fan and Ramdas<sup>(2)</sup> is correct.

The results given in Figure 1 on the temperature dependence of the  $1.8\mu$  band is the same as has been observed by Fan and Ramdas<sup>(2)</sup> for n- and p-type silicon irradiated to high resistivities by: a) reactor neutrons, b)  $9.6$  Mev deuterons and c) electrons of energy less than  $4.5$  Mev. An exception was found by Fan and Ramdas<sup>(3)</sup> in that they do not observe the  $1.8$  micron band in floating-zone silicon irradiated by  $4.5$  Mev electrons. A conclusion regarding the  $1.8\mu$  band can be drawn from the results of Figure 1. Taking into account the different sample thicknesses (see Table I) we conclude that the  $1.8\mu$  band is produced about four times more efficiently in oxygen-containing

silicon than in floating-zone. This effect has also been observed by recent experiments in 60 Mev electron irradiated silicon and we always find a larger band at  $1.8\ \mu$  in silicon containing oxygen. Fan and Ramdas<sup>(3)</sup> also observe this effect in 9.6 Mev deuteron irradiated silicon and suggest that although the oxygen is not a part of the defect it assists in its formation. The precise role of oxygen in this defect is not known now and can perhaps be ascertained by spin resonance measurements.

We can compare our annealing results on the  $1.8\ \mu$  bands to those of Fan and Ramdas<sup>(2)</sup> who performed a series of isothermal anneals at 140, 170 and 200°C and conclude that the annealing process appears to be first order and governed by an activation energy of 0.8 ev. In three of the four samples annealed (Figure 3) the results suggest two distinct stages of annealing centered at 215°C and 285°C respectively. Using a 0.8 eV activation energy and first order annealing kinetics we have transformed Fan and Ramdas<sup>(2)</sup> isothermal annealing data to an isochronal. The comparison is shown in Figure 1. It appears that the simple conclusion of Fan and Ramdas<sup>(2)</sup> is not justified in view of the poor fit with the results shown in Figure 1. We conclude that the annealing process is more complex than what has been proposed by Fan and Ramdas<sup>(2)</sup>. The annealing behavior of the Si-A center at  $834\ \text{cm}^{-1}$  is very similar to what has been observed in oxygen-containing silicon by Corbett et.al.<sup>(4)</sup> who used 1.4 Mev electrons in their irradiation. Corbett et.al.<sup>(4)</sup> do not

report evidence for the band at  $865\text{ cm}^{-1}$ , however Ramdas and Fan<sup>(5)</sup> observed the  $865\text{ cm}^{-1}$  band in neutron-irradiated oxygen-containing silicon. It is possible that formation of the  $865\text{ cm}^{-1}$  band requires more energetic recoils than can be produced by 1.5 Mev electrons.

The growth of the  $894\text{ cm}^{-1}$  band as the Si-A center ( $834\text{ cm}^{-1}$ ) anneals out (see Figure 4) is exactly the same effect found by Corbett et.al.<sup>(10)</sup> in 1.5 Mev electron irradiated oxygen-containing silicon. However, in addition to the  $894\text{ cm}^{-1}$  band Corbett et.al.<sup>(10)</sup> find three other new bands appearing after the A-center anneals. The appearance of satellite and growth bands between 10.2 and 12.5 microns has also been observed by Ramdas and Fan<sup>(5)</sup> in reactor neutron irradiated silicon containing dispersed oxygen. However, Ramdas and Fan (5) do not report any detailed annealing studies of the growth and satellite bands.

Corbett et.al.<sup>(10)</sup> have suggested a tentative model for the annealing of the Si-A center and the growth bands. They suggest that the oxygen-vacancy complex (comprising the Si-A center) "diffuse" together until another isolated interstitial oxygen atom is attached to the complex. Then the new defect involves the association of two oxygen atoms and one vacancy and would give rise to one vibrational band. Subsequent heat treatment can then cause an additional oxygen to be united to the  $\text{O}_2$  - vacancy pair and cause the emergence of other "growth bands".

This model although speculative appears to describe qualitatively the complex atom movements that are occurring during annealing. It is clear that a combination of electrical, optical, and spin resonance properties performed on the same irradiated material during annealing are necessary to get further insight into what is going on during annealing.

Finally we wish to discuss the isochronal annealing results in Figure 5 on the 834 and 865  $\text{cm}^{-1}$  band. The isochronal annealing data of Corbett et.al.<sup>(4)</sup> on the 834  $\text{cm}^{-1}$  band (1.5 Mev electrons) is in very good agreement with our results. From these results we can conclude that the stable defect configuration giving rise to the Si-A center is independent of electron energy over the range 1.5 to 40 Mev. On a microscopic scale these annealing results (Figure 5) show definite proof that the breakup and atom movements of the defect complex during annealing is independent of the incident bombarding energy although many other defects are formed at the higher energy. This last conclusion can be further substantiated by results from recent experiments using 60 Mev incident electrons. We found the same defect infrared absorption bands in 60 Mev electron-irradiated silicon as those described in this paper on 40 Mev electron-irradiated silicon.

We are presently studying the annealing of the electrical properties conductivity and carrier concentration in electron-irradiated silicon in an attempt to correlate wherever possible

the defect absorption bands to localized energy levels in the forbidden gap. There is not yet sufficient data of this kind available to conclude precisely which electrical level is responsible for the various defect infrared absorption bands.

#### ACKNOWLEDGEMENTS

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T A B L E I

Sample No.	Type and Impurity	Initial* Resistivity	Crystal Growing Method	Incident Energy	Total Integrated Flux	Resistivity After Irradiation	Thickness mm
1	n-Type Phosphorus	0.09 $\Omega$ -cm	Floating Zone	40 Mev	$1.5 \times 10^{18} \text{ e/cm}^2$	2500 $\Omega$ -cm	7.37
2	n-Type Phosphorus	0.1 $\Omega$ -cm	Floating Zone	44 Mev	$1.7 \times 10^{18} \text{ e/cm}^2$	2400 $\Omega$ -cm	9.00
3	p-Type Boron	200 $\Omega$ -cm	Pulled from Crucible	44 Mev	$1.7 \times 10^{18} \text{ e/cm}^2$	$3 \times 10^5 \Omega$ -cm	2.45
4	n-Type Phosphorus	80 $\Omega$ -cm	Pulled from Crucible	36 Mev	$2.2 \times 10^{18} \text{ e/cm}^2$	$3.10^5 \Omega$ -cm	2.41

\* Resistivity values at 300°K.

All samples n-type after irradiation.

## LIST OF FIGURES

- FIGURE 1 Infrared spectra of  $\approx 40$  Mev electron-irradiated n-type silicon (floating zone, and pulled crystal) showing the temperature dependence of the  $1.8\mu$  defect absorption band. The dotted curve is the infrared spectrum measured after annealing for each sample.
- FIGURE 2 Infrared spectra of  $\approx 40$  Mev electron-irradiated n-type silicon (floating zone) and p-type silicon (pulled crystal) showing the  $3.46$  and  $3.62\mu$  defect absorption bands at  $85^\circ\text{K}$  and their absence from the spectra at  $295^\circ\text{K}$ .
- FIGURE 3 Isochronal annealing (20 minutes at each temperature) of the  $1.8$ ,  $3.46$ , and  $3.62\mu$  defect absorption bands in silicon samples 1, 2, 3, and 4 (see Table I for details on each sample). Data of Fan and Ramdas<sup>(2)</sup> on the  $1.8\mu$  band is shown for comparison (see text).
- FIGURE 4 Infrared absorption spectra of oxygen-containing sample 4 in the region  $810$  to  $950\text{ cm}^{-1}$  measured at  $85^\circ\text{K}$  after various anneals at the temperatures shown.
- FIGURE 5 Isochronal annealing (20 minutes at each temperature) of the defect absorption band at  $834\text{ cm}^{-1}$  (Si-A center) and at  $865\text{ cm}^{-1}$  for oxygen-containing silicon samples 3 and 4. Also shown is the growth band at  $894\text{ cm}^{-1}$  for samples 3 and 4. Measurements made at  $85^\circ\text{K}$  after each anneal.



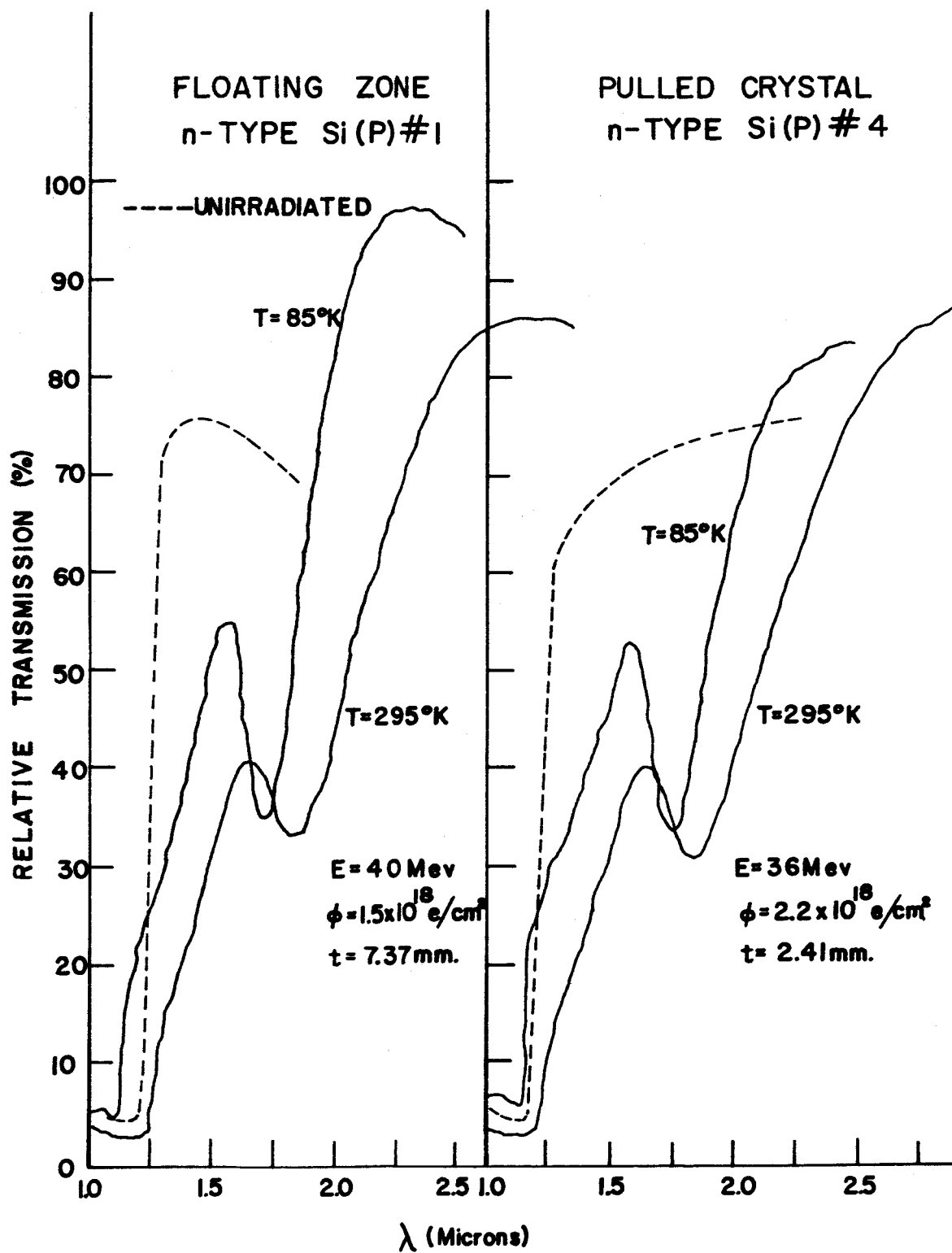


FIGURE 1

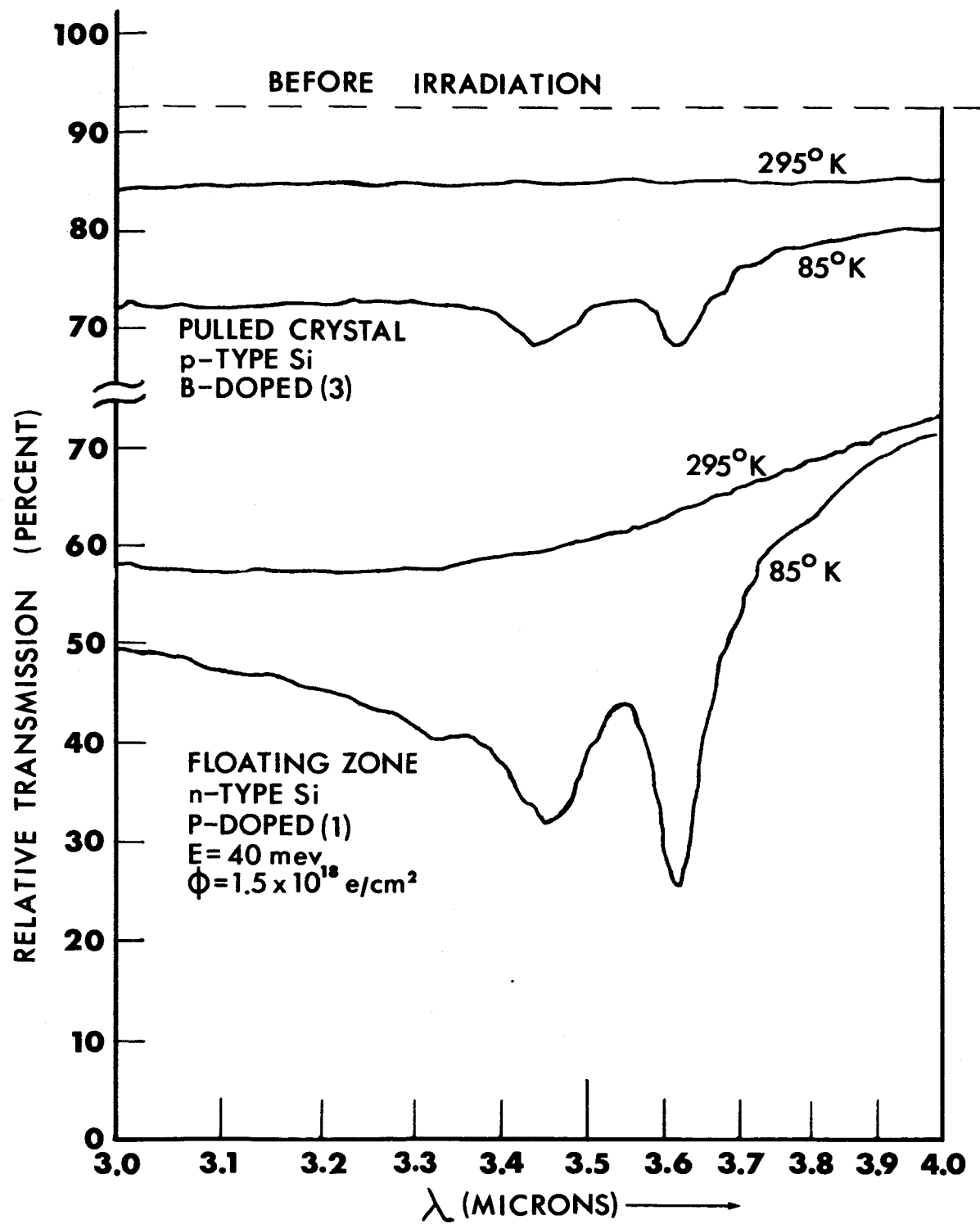


FIGURE 2

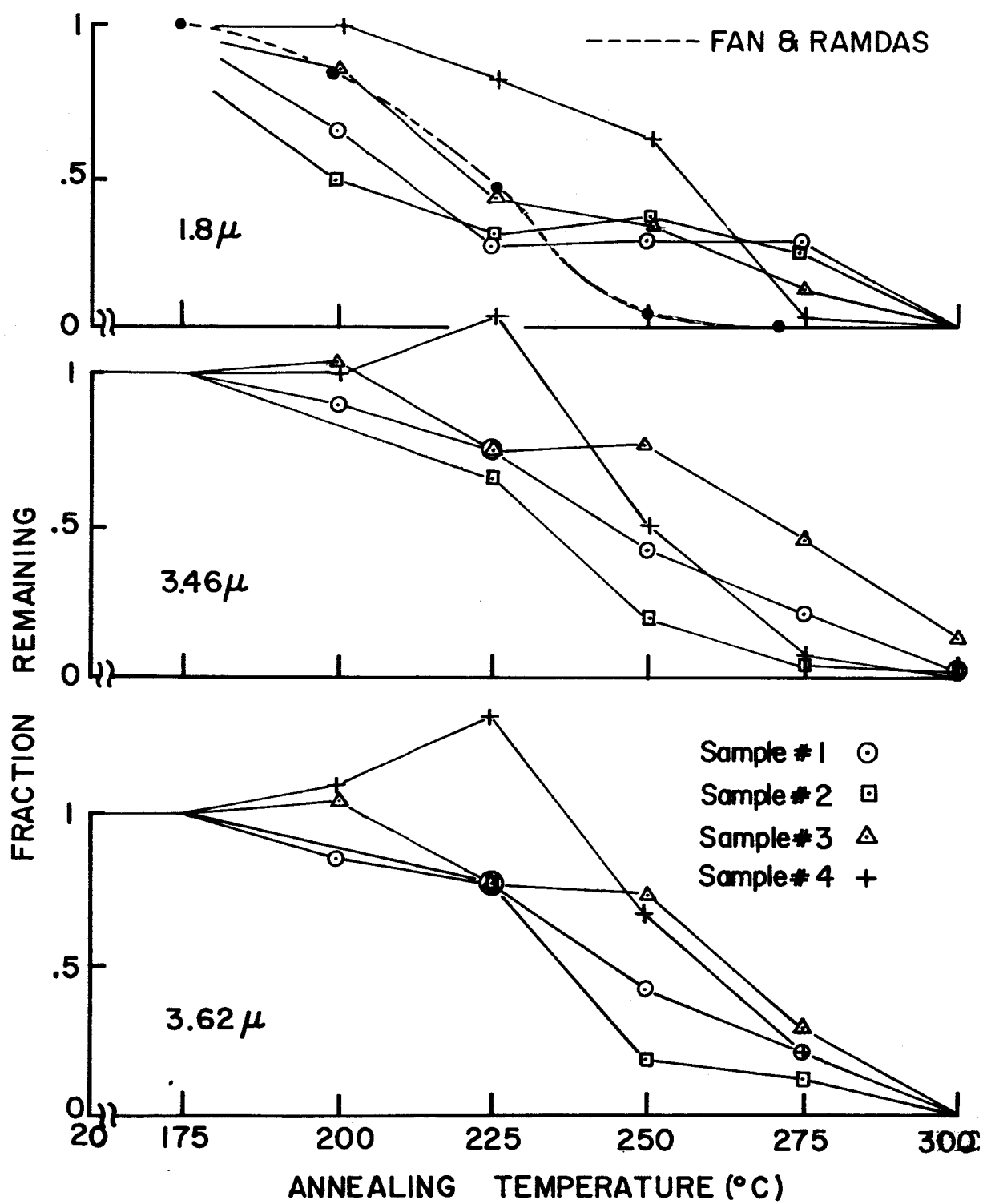


FIGURE 3

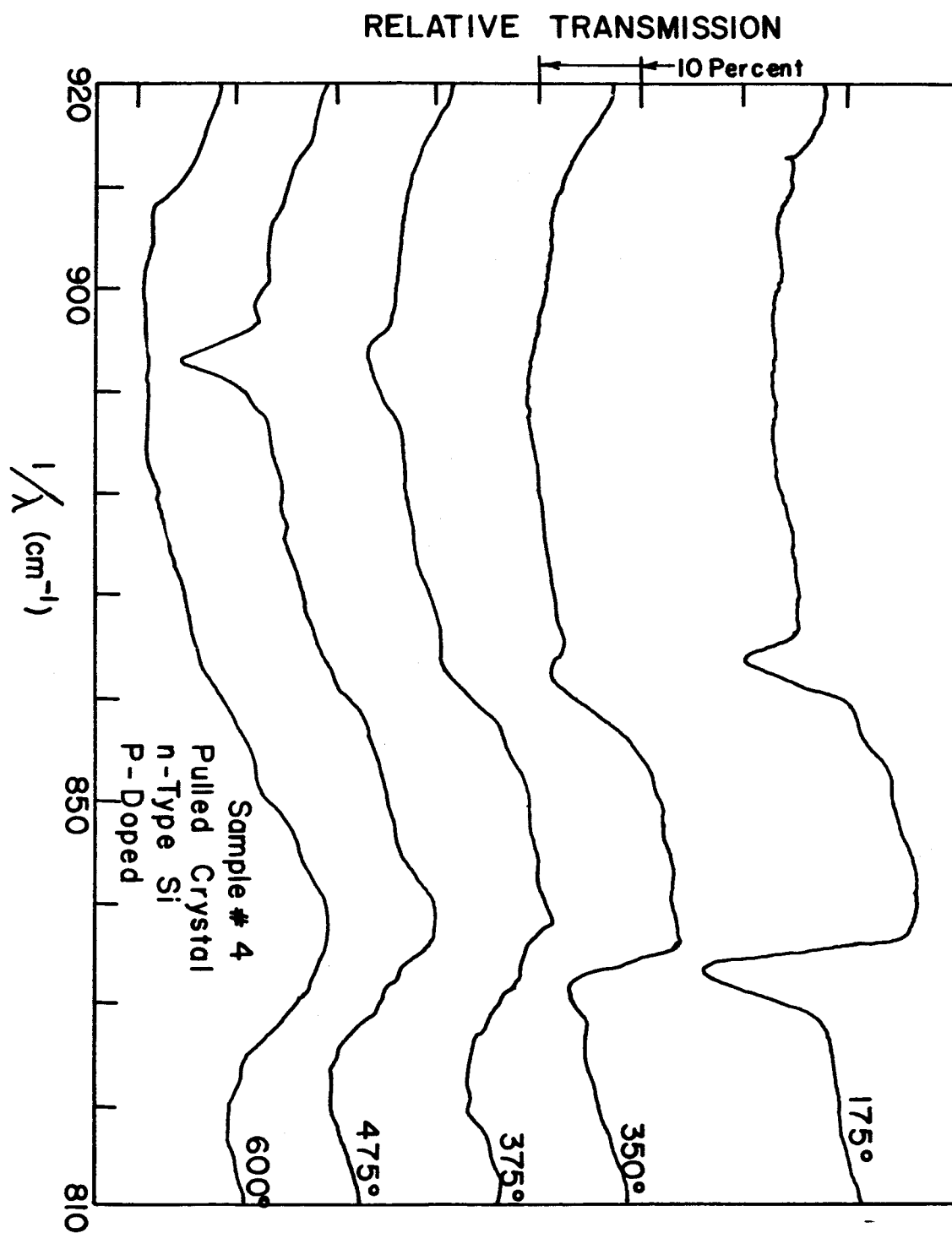


FIGURE 4

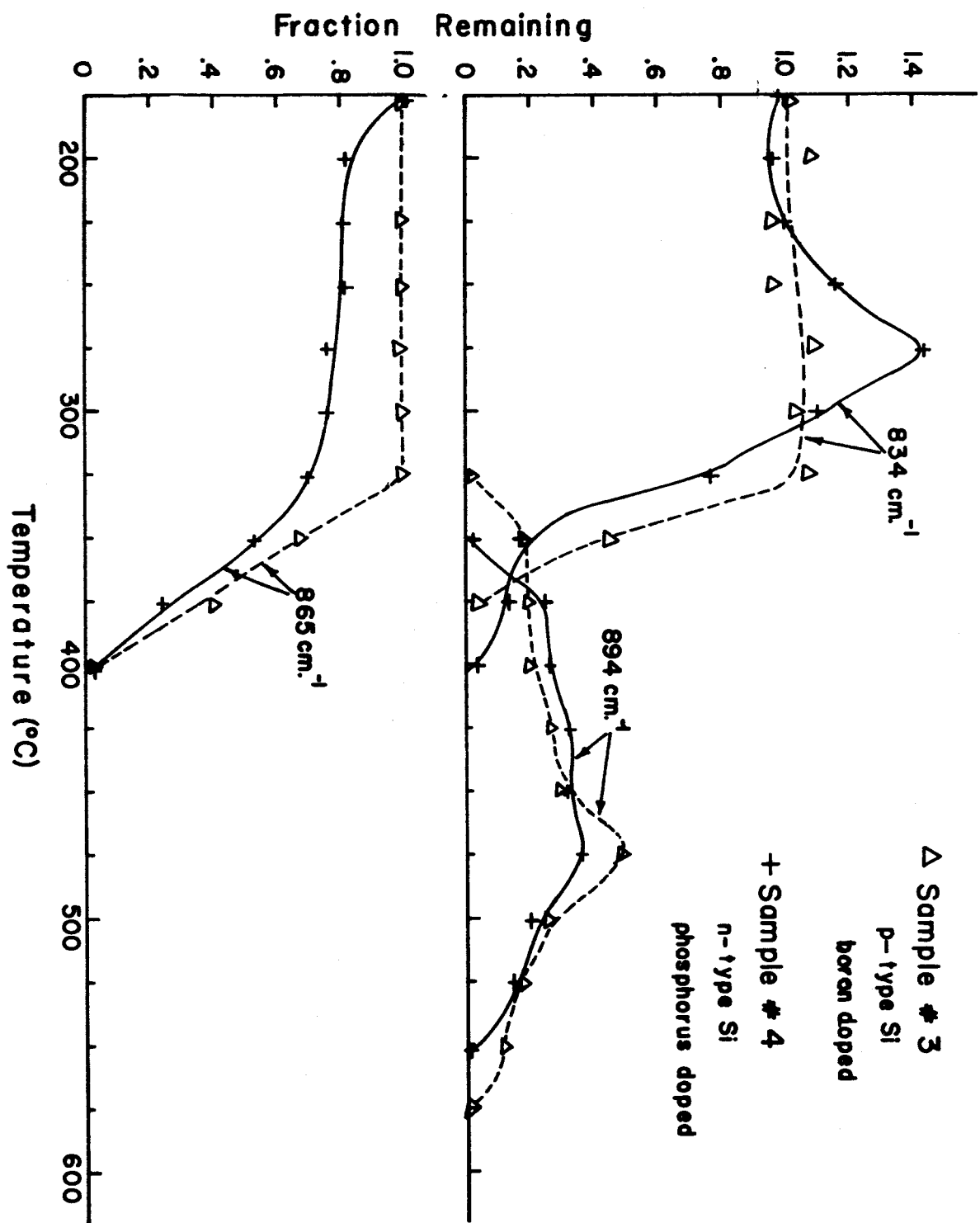


FIGURE 5