PROGRESS REPORT
Covering Period from 15 Sept. 1965
to 15 March 1966

RADIATION DAMAGE TO SEMICONDUCTORS BY HIGH-ENERGY ELECTRON AND PROTON RADIATION

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INTRODUCTION

The results presented in this report were obtained during the six month period 15 September 1965 to 15 March 1966. The following personnel were actively engaged in the research program:

Faculty:

Dr. John C. Corelli (half time)

Adjunct Professor, James W. Corbett*

Graduate Students:

Mr. Li-Jen Cheng (Left January 21, 1966)

Mr. John E. Fischer (Left January 21, 1966)

Mr. Arne H. Kalma (On pre-doctoral NASA Traineeship)

Mr. William Bohlke

Undergraduate Participant:

Mr. Martin Weinhous (Physics Department)

Research Technician:

Mr. James W. Westhead

Both Mr. Fischer and Mr. Cheng finished their Ph.D. programs during the current report period. Mr. Cheng is now in the Metallurgy Division, Chalk River Laboratory, Ontario, and is sponsored by a National Research Council Fellowship. Mr. Fischer is now at École Normale Supérieur, Paris, France where he has an appointment in the Laboratoire de Physique.

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* Served in the research program as a part time consultant, lecturer, etc., and is a full time scientist at the General Electric Research and Development Center, Schenectady, New York.

A brief summary of each phase of the research to be reported here is given below.

1) Infrared spectroscopy was used to identify the 1,8, 3.3 and 3.9 μ defect absorption bands in silicon as being due to the divacancy defect. The silicon samples were oriented and were irradiated either with 45 Mev electrons or fast neutrons ($\gtrsim$ 1 Mev). Stress alignment of the defect in addition to polarized infrared light were used to study the defect symmetry by measuring dichroic ratios and comparing them to what has been learned from spin resonance experiments on electron-irradiated silicon.

2) Radiation damage induced in n-type germanium by 6-88 Mev electrons was studied by means of electrical properties and carrier lifetime measurements. A comparison of arsenic and antimony-doped samples was made to check the effect of the impurity type (and concentration). A correlation of the radiation-induced acceptor defects and radiation-induced traps has been made for n-type germanium.

3) The effect of phosphorus and arsenic concentration on the production and annealing of the divacancy defect - as detected by the 1.8 μ radiation-induced band - was found to be important. Briefly stated we find that the higher the phosphorus or arsenic concentration the greater its effect on the annealing of the divacancy defect.

4) Results on the use of a vacuum infrared monochromator for photoconductivity studies are given for the first time. The high resolution of the newly acquired instrument and the

apparent lack of water vapor or CO_2 background absorption in the photoconductivity spectrum have been demonstrated.

Portions of results obtained in the research program have been given in various presentations and papers during the period 15 September 1965 to 15 March 1966 and are listed below.

1. "Infrared Properties of 40-60 MeV Electron-Irradiated Germanium", J. F. Becker and J. C. Corelli, J. Appl. Phys. 36, 3606 (1965).

2. "Recovery of Electrical Properties in 45 MeV Electron-Irradiated n-Type Silicon from 80 to 350°K", L. J. Cheng and J. C. Corelli, Phys. Rev., 140A, 2130 (1965).

3. "A Study of the 1.8, 3.3 and 3.9 Micron Radiation-Induced Absorption Bands in Silicon", L. J. Cheng and J. C. Corelli, Bull. Am. Phys. Soc., 11, 53 (1966).

4. "Comparison of Radiation-Induced Oxygen-Defect Complexes in Silicon and Germanium", J. C. Corelli, L. J. Cheng, J. F. Becker and M. R. Gaerttner, Bull. Am. Phys. Soc., 11, 53 (1966).

I. "Study of the 1.8, 3.3 and 3.9 μ Radiation Induced Defect Bands in Silicon", Li-Jen Cheng and Arne H. Kalma -

Introduction

In the last report[1] we concluded that the 1.8 μ defect absorption band was due to the divacancy[2] in one of its charge states. We tentatively assigned the 1.8 μ defect absorption band to the neutral charge state of the divacancy defect. During the past six month period we have performed experiments on annealing and stress response of the 3.3 and 3.9 μ bands. The techniques utilized in the stress response experiments involve the use of oriented samples and have been described in detail elsewhere.[1] The radiation-induced defects responsible fo the 1.8, 3.3 and 3.9 μ band were produced either by 45 Mev electrons or fast neutron bombardment ($E \gtrsim 1$ Mev, with total integrated neutron fluxes of $\sim 3 \times 10^{15}$ n/cm^2).

An additional radiation-induced broad absorption band has been found and is located in the wavelength range from the fundamental absorption edge of silicon (≈ 1.2 μ) up to higher wavelengths. The first reported result on this near edge absorption was given by Fan and Ramdas[3]. We find that the intensity of this near band edge absorption is a monotonically decreasing function of wavelength and appears in both n-type and p-type silicon after irradiation.

Experimental Results

In Fig. 1 is shown the dichroic behavior of the 3.3 micron defect absorption band to polarized light after stressing at $\approx 160^{\circ}$C for 15 minutes (stress = 2000 g/cm^2). The results given

in Fig. 1 have been corrected for background absorption. Dichroism exhibited by the 3.9 μ absorption band is shown in Fig. 2, and here again we have corrected for background absorption. The production rate of the 3.3 μ band is lower in floating zone silicon than in pulled silicon which is similar to what was observed for the 1.8 μ band.[1] The precise role played by the oxygen atoms in the defect responsible for the 1.8, 3.3 and 3.9 μ bands is still not understood. The production of the 3.9 μ band depends on the total dose which the sample has received. The absorption band at 3.9 μ (measured at 300°K) increases with dose initially then decreases and finally disappears with additional dose. The reason for the strong dose dependence of the 3.9 μ band is due to the rise of the Fermi level toward the middle of the forbidden gap caused by irradiation. When the Fermi level is above E_V + 0.25 eV the 3.9 μ band is not observed.

The isochronal annealing of the 3.3 μ band is shown in Fig.3 for two 100 ohm-cm pulled silicon crystals and a 1 ohm-cm floating zone (FZ) silicon crystal. The annealing exhibits two stages similar to 1.8 μ band annealing for the floating zone crystal, phosphorus doped, the first stage is located at $\approx$160°C. From radiation damage studies in phosphorus doped (FZ) silicon a defect consisting of a phosphorus-vacancy complex (a radiation-induced defect formed by a vacancy trapped to a phosphorus atom) anneals out around 160°C.[4] Watkins and Corbett[5] have demonstrated that the phosphorus-vacancy complex disappears in silicon by means of a process in which the vacancy escapes from the phosphorus atoms.

The vacancies may then be trapped by the defects causing the 1.8 and the 3.3 μ bands, transforming the defects and thus allowing the defects to lose their properties of infrared absorption.

Let us examine the last stage of annealing in the 250-300°C temperature range. In this temperature range the 1.8 μ and the 3.3 μ bands in any specific sample anneal out at the same temperature. Recently we have found that the 3.9 and 1.8 μ band also anneal out together in a specific sample see Fig. 4, thus strongly suggesting the same defect is responsible for the three defect absorption bands at 1.8 μ, 3.3 μ and 3.9 μ.

We shall demonstrate that the 1.8, 3.3 and 3.9 μ bands are associated with the divacancy defect in silicon. Watkins and Corbett[2,6] identified two electron paramagnetic resonance spectra (Si-G6) and Si-G7) as arising from two different charge states of the divacancy, and they[6] presented a model of the microscopic configuration of the defect and the electronic structure in each charge state. Under uniaxial stressing a localized electronic configuration can occur, as was observed by Watkins and Corbett. The distribution of paramagnetic electrons from spin resonance measurements had a preferential orientation close to the $\langle 110 \rangle$ direction. If we use the model of the divacancy to interpret our infrared data we find that the directions of the electric dipole transition moments of the 1.8, 3.3 and 3.9 μ bands are close to the $\langle 110 \rangle$ direction.

Using the divacancy model one can estimate the expected dichroism for [100] stressing from the following

$$\text{DICHROISM} = \frac{\alpha_{E_\perp}}{\alpha_{E_\parallel}} = \frac{1 + e^{-\frac{\Gamma S}{kT}}}{2} \qquad \ldots\ldots\ldots\ldots (1)$$

where S is magnitude of stress, and Γ is defined in such a way that ΓS is equal to the energy difference between two non-equivalent states of the electronic distribution under the stress, k and T are the Boltzmann constant and absolute temperature respectively. The absorption curves of the 3.9 μ band measured with light of different polarization for various magnitudes of the stress along [100] at room temperature are plotted in Fig.5. From these data and equation (1) we can estimate the value of $e^{-\frac{\Gamma S}{kT}}$ for the 1.8[1] and3.9 μ bands for various magnitudes of the stress. The result is plotted in Fig. 6. We have analyzed our data in a fashion similar to that used by Watkins and Corbett.[2,7] They assumed that the change in energy of the electronic distribution was determined primarily by the change in the distance between two atoms forming the covalent bond in the strained lattice. The change in energy per unit strain along a covalent bond direction is defined as

$$M = \left(\frac{dE}{d\varepsilon}\right)_{Si-Si} \qquad (2)$$

From the slopes of the lines in Fig. 6 we obtain

M =+26 eV/unit strain for the 3.9 μ band

M =+18 eV/unit strain for the 1.8 μ band

The values given by Watkins and Corbett[2] from their EPR work on the divacancy are +24 and +32 eV/unit strain for the single positive and single negative charged states respectively. In what follows we give arguments in support of the fact that the 3.9 μ band may be associated with the single positive charge

state of the divacancy. The charged state of the defect causing the 1.8 μ band is still unknown, although our results suggest it may be the neutral state. Our values for the energy per unit strain for the divacancy are reasonable, being similar to values of Watkins and Corbett[2] for the divacancy defect.

Upon close examination of the model of the divacancy one can observe that there is an additional "degree of freedom" amenable to study which is the reorientation of the vacancy-vacancy axis, among the four different orientations in the crystal. This reorientation can be made to occur by stress alignment at elevated temperature ($\sim$150-170°C), as was reported by Watkins and Corbett.[2] We have observed that the defects causing the 1.8, 3.3 and 3.9 μ bands can be redistributed among the crystallographically allowable orientations under a uniaxial stress at 160°C. The stress is kept on the sample until it cools down to room temperature. Significant dichroisms were observed in the 1.8, 3.3 and 3.9 μ bands in the samples after the high temperature stressings along $[110]$, and for all three bands the observed dichroisms are larger than unity. Detailed results on the 1.8 μ band have been given previously.[1] Our experimental data from high temperature stressing along various crystalline orientations are given in Fig. 1 (3.3 μ band) and Fig. 2 (3.9 μ band). No significant dichroism is observed for the 1.8, 3.3 and 3.9 μ bands after stressing along the $[100]$ direction at a temperature of $\approx$160°C for 15 minutes, thus demonstrating that the defects causing the three bands have an atomic symmetry axis along a $\langle 111 \rangle$ direction, since any cube axis makes equal angles with all four cube

diagonals. This result fits the divacancy model well since the vacancy-vacancy axis of the divacancy is in a $\langle 111 \rangle$ direction. The detailed tabulation of all our measured dichroisms are found in the Ph.D. Thesis of Li-Jen Cheng and will be published in a separate paper later.

Isochronal annealing experiments were carried out on the recovery of the stress-induced dichroisms of the 1.8, 3.3 and 3.9 μ bands. The results are shown in Fig. 7 and also shown for comparison are the EPR annealing data on the divacancy given by Watkins and Corbett.[2] It can be seen that the dichroisms of the three bands anneal out in the same manner as the annealing of the dichroism of the divacancy reported by Watkins and Corbett.[2] (Note: the EPR polarization data converted to dichroism by use of divacancy model.)

Discussion of Results and Conclusions

The large body of evidence given above and in the previous report[1] leads us to conclude that the 1.8, 3.3, and 3.9 μ bands arise from the same defect. The important experimental evidence supporting this conclusion is (1) all bands have same annealing temperatures, (2) all bands exhibit same effect of uniaxial stressing on the electronic distributions (3) all bands exhibit same effect of uniaxial stressing on atomic reorientation of the defect, and (4) high temperature stress-induced dichroisms in the three bands anneal out at the same temperature. In addition to the conclusion that the same defect gives rise to all three bands we have no experimental evidence which goes contrary to the conclusion that defect in question is the DIVACANCY. Both the divacancy and the defect causing the 1.8, 3.3, and 3.9 μ bands have an atomic symmetry axis along $\langle 111 \rangle$. The response of the

electronic distribution of the defect to the uniaxial stress fits the divacancy model well and agrees with results of Watkins and Corbett[2] on the divacancy defect. The recovery of the stress-induced alignments of the defect is exactly the same as for the divacancy.[2]

Two minor experimental facts relating to the above conclusion still remain and require further study for their explanation, they are 1) production rate of divacancy in pulled crystals is higher than in floating zone samples indicating the role played by oxygen atoms is important, 2) no anisotropic production of the defect was observed in our experiments. We can explain the lack anisotropic production in our work as being due to its relatively small magnitude $\approx$15% which is just on the margin of our experimental capability. Only a qualitative and speculative explanation of the role oxygen atoms play in the divacancy production process has been given and will be included in the final report of this work.

II. Studies of Defects Induced in 6-88 MeV Electron-Irradiated N-Type Germanium by Carrier Concentration, Conductivity and Carrier Lifetime Measurements, John E. Fischer

This work has been completed and formed the basis of the Ph.D. thesis of J. E. Fischer. A paper* was written and submitted for publication in the Journal of Applied Physics, March 1966, and for the purposes of this progress report we have only included the abstract of the paper.

Production and Annealing of Defects in
6-88 MeV Electron-Irradiated N-Type Germanium

J. E. Fischer and J. C. Corelli

ABSTRACT

Two classes of defect acceptor levels, three classes of minority hole traps, and recombination centers are introduced by 48 MeV electron bombardment of As- and Sb-doped (n-type) germanium at 85°K. The recovery of traps and acceptors occurs together in five stages, suggesting that the traps and acceptors are due to the same defects. The stages are centered at 150°K, 200°K, 360°K, 460°K and about 540°K. The dominant acceptor energy levels are at or below the middle of the forbidden gap, and the dominant trapping energy levels are within 0.16 eV of the valence band. Less than 15% of the removed electrons are trapped by a level 0.20 eV below the conduction band. The recombination centers recover completely below 200°K. After 300°K irradiation with 6, 47 and 88 MeV electrons, only one trapping level located at 0.10 ± 0.01 eV above the valence band

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* Pre-prints were transmitted to NASA February 8, 1966. The preprint is considered an integral part of this progress report for the period 15 September 1965 - 15 March 1966.

in all samples (As- or Sb-doped), is observed. The introduction rate and recovery behavior of this trapping level is independent of As and Sb concentration up to 2×10^{15} donors/cm^3. The decay of excess carriers is analyzed in terms of the large-injection model due to Baicker.[8] The applicability of this model is criticized in light of the present results. The effect of arsenic and antimony on the nature and recovery of the various defects is investigated. The results are compared with those obtained in low energy electron ($\gtrsim$1 MeV) and Co-60 gamma irradiation.

III. Study of the Effect of Phosphorus Concentration on the Radiation-Induced 1.8 μ band in Silicon, A. H. Kalma and W. Bohlke

Previous studies of the 1.8 μ absorption band in $\approx$45 MeV electron-irradiated n-type silicon doped with phosphorus have shown that the isochronal annealing of the band occurs in two stages in floating zone material but only one stage in pulled crystals. Some of the differences in the production and annealing of the 1.8 μ band in the two types of materials has been found to be due to the difference in oxygen content, but an explanation of the lower temperature annealing stage in floating zone material has not been given. We have begun some further studies to determine the nature of this stage. Figure 8 shows the isochronal annealing of the 1.8 μ band for several n-type silicon samples. It can be seen that lower temperature stage accounts for a larger percentage of the annealing in lower resistivity, floating zone material than it does in the higher resistivity, floating zone material. The temperature of this lower stage ($\approx 170^{\circ}$C) is about the same temperature at which the silicon E center (phosphorus plus vacancy complex) has been observed to anneal.[4] Since E centers are a dominant radiation-induced defect in floating zone crystals but not in pulled crystals, this suggests that the annealing of the E center has an effect on the 1.8 μ band. The higher the E-center concentration as results from irradiation of the lower resistivity material (1 ohm-cm, see Fig. 8) the larger the effect on the annealing of the 1.8 μ band (divacancy). Not enough work

has been done yet to pinpoint the nature of this effect. Two possible explanations are given here; either the mobile entity from the annealing E center becomes trapped at the divacancy (which causes the 1.8 μ band) changing it to a new type of center or, since the 1.8 μ band is Fermi level dependent, the annealing of the E center changes the Fermi level in such a way as to decrease the absorption in the 1.8 μ band. Further study will be carried out in the future on this effect.

IV. Photoconductivity Studies in ≈45 MeV Electron Irradiated Silicon, A. H. Kalma and W. Bohlke

In order to perform photoconductivity experiments on silicon and germanium without having absorption of the infrared beam by water and CO_2 in the air interfer with the results, we have obtained an evacuable grating monochromator from Spex Industries, Metuchen, N. J. The light sources we are using are a Sylvania Sun Gun up to $\approx 2.5\ \mu$ and a globar above $\approx 2.5\ \mu$. We presently have gratings blazed at $2\ \mu$ and $6\ \mu$ and plan to purchase one blazed at about $3.5\ \mu$. With this equipment and a system of filters, we will be capable of performing experiments in the wavelength region from 1-10 μ. At present, we are set up to do only DC measurements. We are currently getting instrumentation set up to use chopped light (13 cps) and a lock-in amplifier to greatly improve our sensitivity. Figure 9 shows a DC photoconductivity spectrum of an As doped 100 ohm-cm silicon sample irradiated with neutrons. The points on the figure were taken at a spacing that is at least 50 times greater than the wavelength resolution available on the instrument. Thus, the wavelength resolution of the monochromator is much higher than needed for the present application. The results in Fig. 9 are presented as an example of what we can do and will not be analyzed except to say that two energy levels at 0.8 eV and 0.63 eV are apparent.

We hope to be able to uniaxially stress the samples and then examine the photoconductivity with polarized light to determine the orientation properties of the defects in much the same way as we have done previously with infrared absorption. In this

way, we will be able to identify energy levels with various defects. Eventually, we hope to have the capabilities for irradiation and measurement at liquid helium temperature and thus be able to look at the vacancy.

REFERENCES

1. Progress Report covering period from 15 March 1965 to 15 September 1965, Rensselaer Polytechnic Institute.

2. G. D. Watkins and J. W. Corbett, Phys. Rev., 138A, 543 (1965).

3. H. Y. Fan and A. K. Ramdas, J. Appl. Phys. 30, 1127 (1959).

4. Orrin H. Merrill, Masters Thesis, Rensselaer Polytechnic Inst., June 1965, (unpublished). See also H. Saito, M. Hirata, and T. Horiuchi, Proc. Intl. Conf. Latt. Def. J. Phys. Soc. Japan 18, Suppl. III, 246 (1963).

5. G. D. Watkins and J. W. Corbett, Phys. Rev., 134A, 1359 (1964).

6. J. W. Corbett and G. D. Watkins, Phys. Rev., Letters, 7, 314 (1961).

7. G. D. Watkins and J. W. Corbett, Phys. Rev., 121, 1001 (1961).

8. J. A. Baicker, Phys. Rev., 129, 1174 (1963).

FIGURE CAPTIONS

Fig. 1 Dichroism exhibited by the 3.3 μ absorption band in silicon at 80°K resulting from 15 minute stress at $\approx$160°C.

Fig. 2 Dichroism exhibited by the 3.9 μ absorption band in silicon at room temperature resulting from 15 minute stress at $\approx$ 160°C.

Fig. 3 Isochronal annealing (20 minutes at each temperature), of the 3.3 μ absorption band in pulled and in floating-zone silicon irradiated by 45 MeV electrons at $\lesssim$40°C.

Fig. 4 Isochronal annealing (20 minutes at each temperature) of the 1.8 μ and 3.9 μ absorption band in the sample of Si-P-1-B (FZ).

Fig. 5 Dichroism of the 3.9 μ absorption band in silicon due to room temperature stressing in the 100 direction.

Fig. 6 Experimental value of $e^{-\frac{\Gamma S}{kT}}$ plotted as a function of stress.

Fig. 7 Comparison of the recovery of stress-induced dichroisms of the 1.8, 3.3, and 3.9 μ bands with the EPR annealing results[2] on the divacancy.

Fig. 8 Isochronal annealing of the 1.8 μ defect absorption band for two floating zone silicon samples (1 and 100 ohm-cm before irradiation) and one pulled silicon sample (100 ohm-cm before irradiation). The samples were irradiated with 45 MeV electrons at 300°K, the spectra shown in the figure were measured at 300°K.

Fig. 9 Photoconductivity spectrum of a 100 ohm-cm floating zone n-type silicon sample measured at $\approx$80°K after irradiation with $\approx$45 MeV electrons at $\approx$300°K.

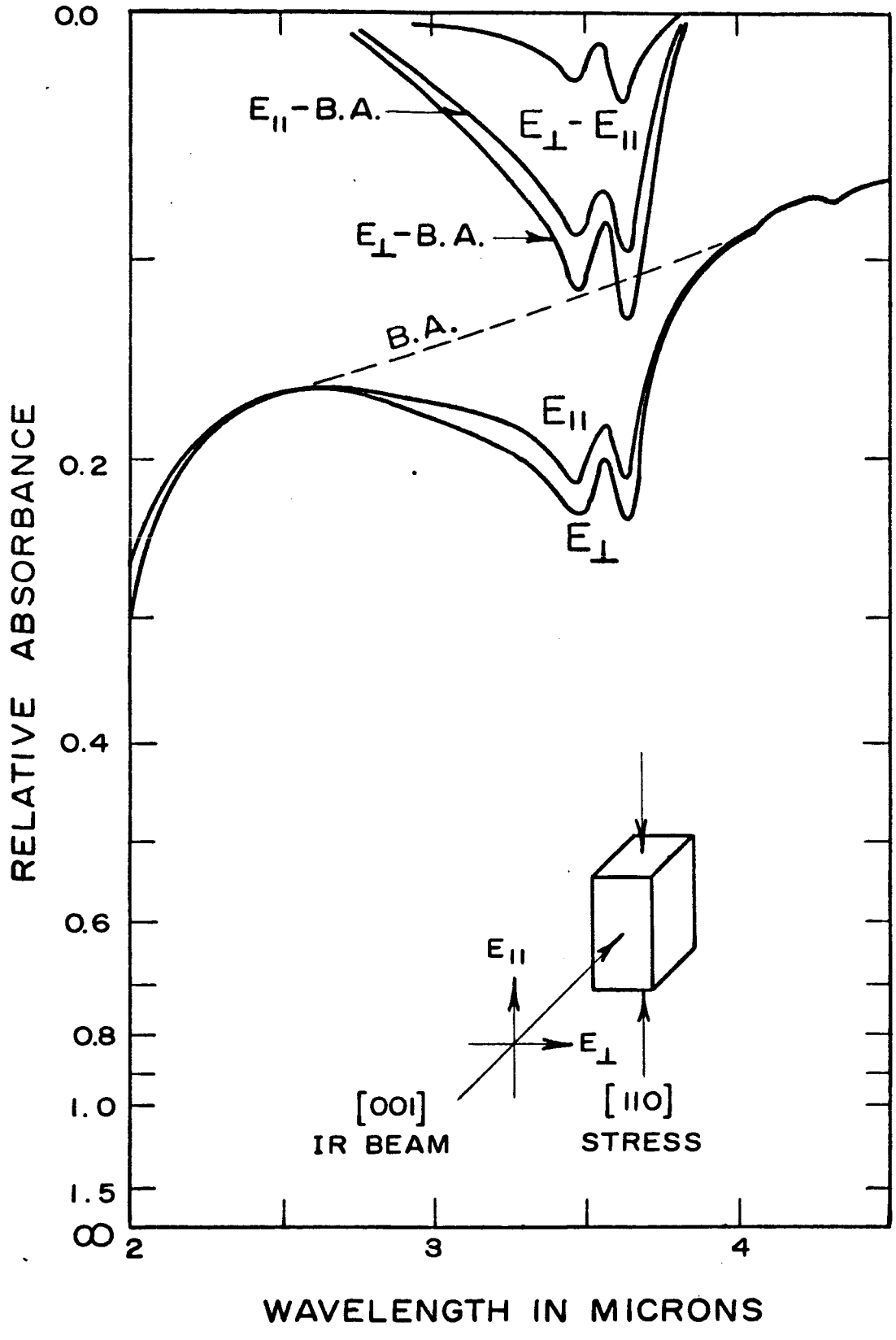
0.0
0.2
0.4
0.6
0.8
1.0
1.5
∞
RELATIVE ABSORBANCE
E_{11}-B.A.
$E_\perp - E_{11}$
$E_\perp$-B.A.
B.A.
E_{11}
$E_\perp$
E_{11}
$E_\perp$
[001]
IR BEAM
[110]
STRESS
2
3
4
WAVELENGTH IN MICRONS

Figure 1

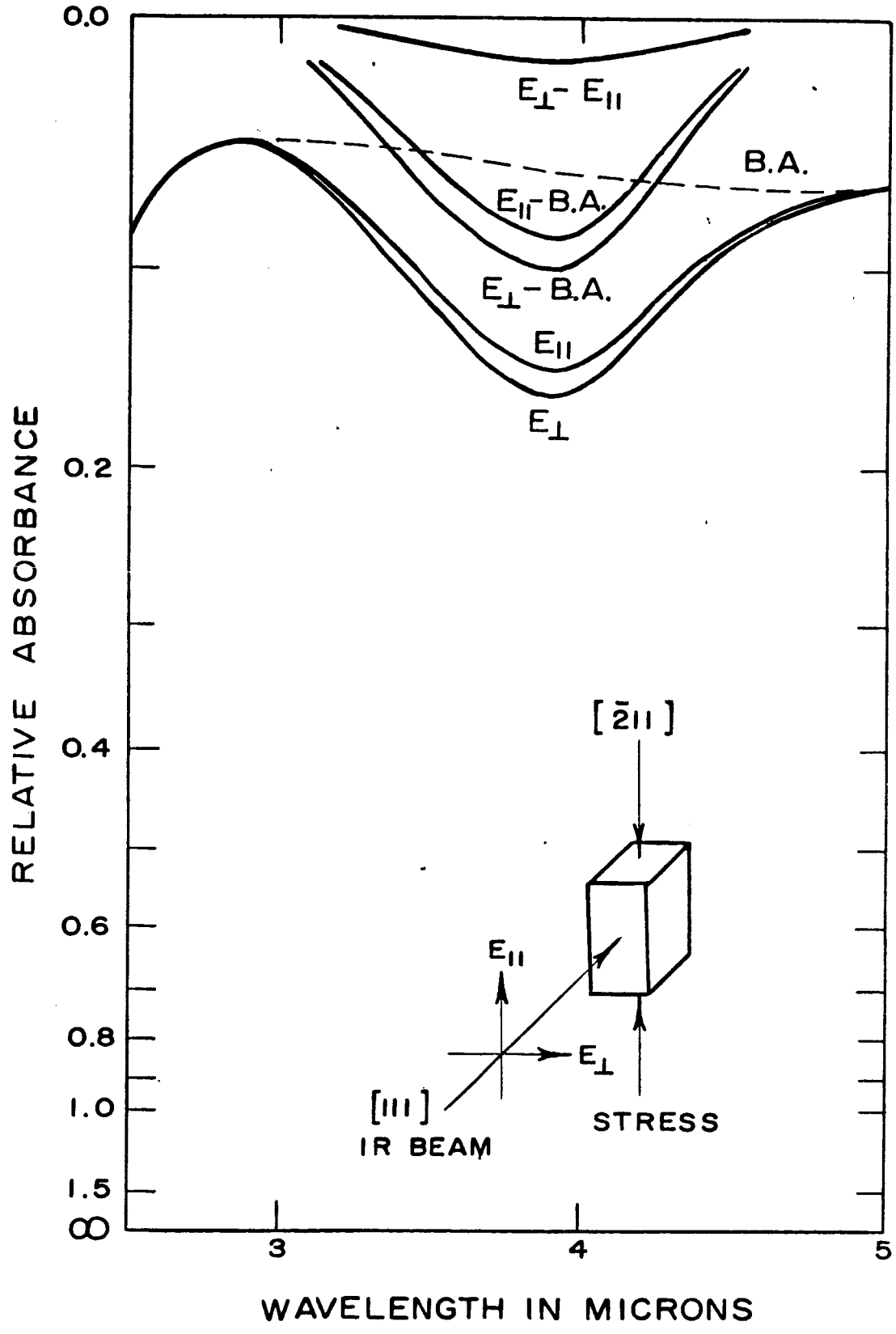
0.0
0.2
0.4
0.6
0.8
1.0
1.5
∞
RELATIVE ABSORBANCE
E⊥ - E||
B.A.
E|| - B.A.
E⊥ - B.A.
E||
E⊥
[2̄11]
E||
E⊥
[111]
IR BEAM
STRESS
3
4
5
WAVELENGTH IN MICRONS

Figure 2

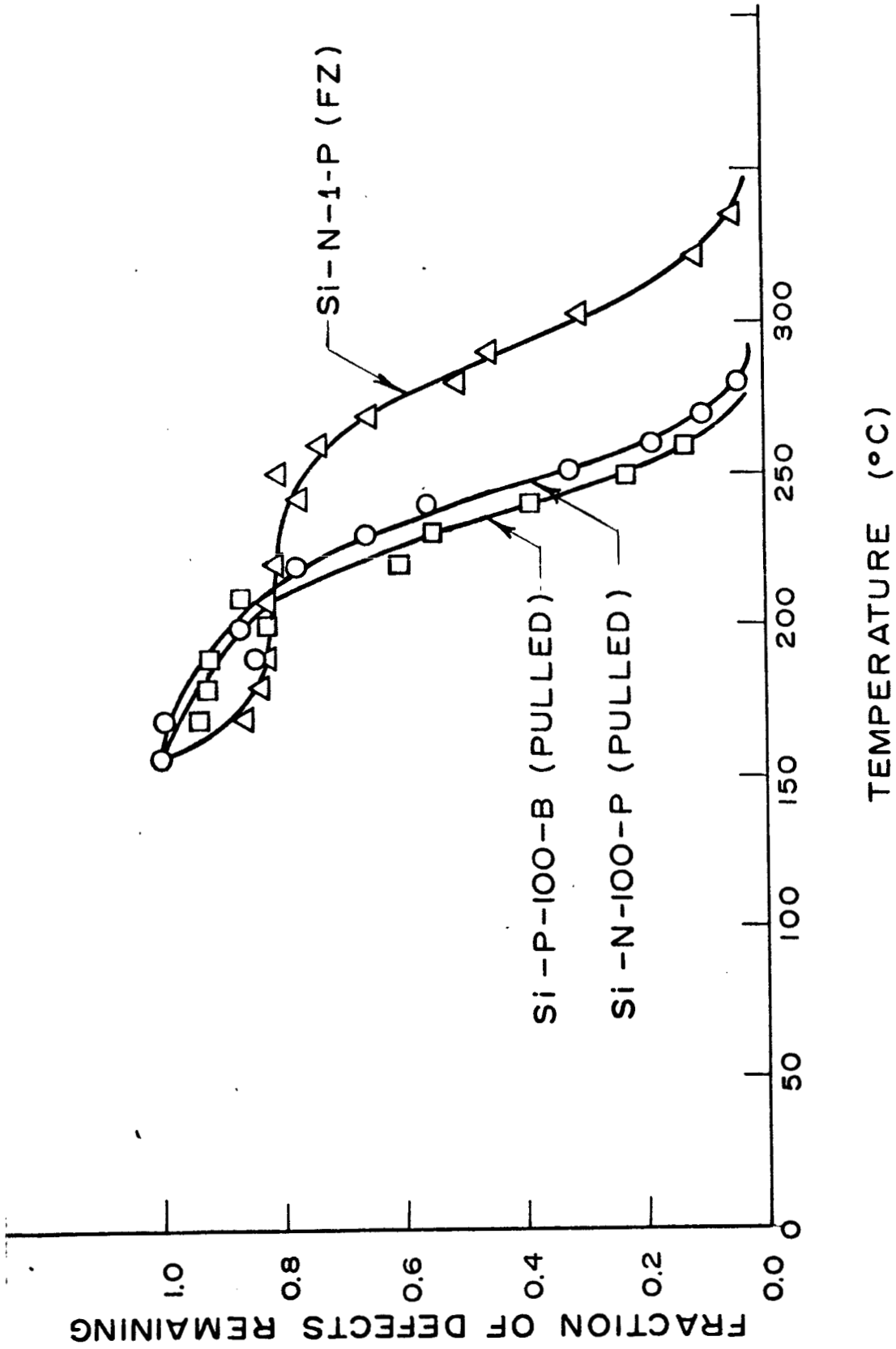
FRACTION OF DEFECTS REMAINING
1.0
0.8
0.6
0.4
0.2
0.0
0
50
100
150
200
250
300
TEMPERATURE (°C)
Si-N-1-P (FZ)
Si-P-100-B (PULLED)
Si-N-100-P (PULLED)

Figure 3

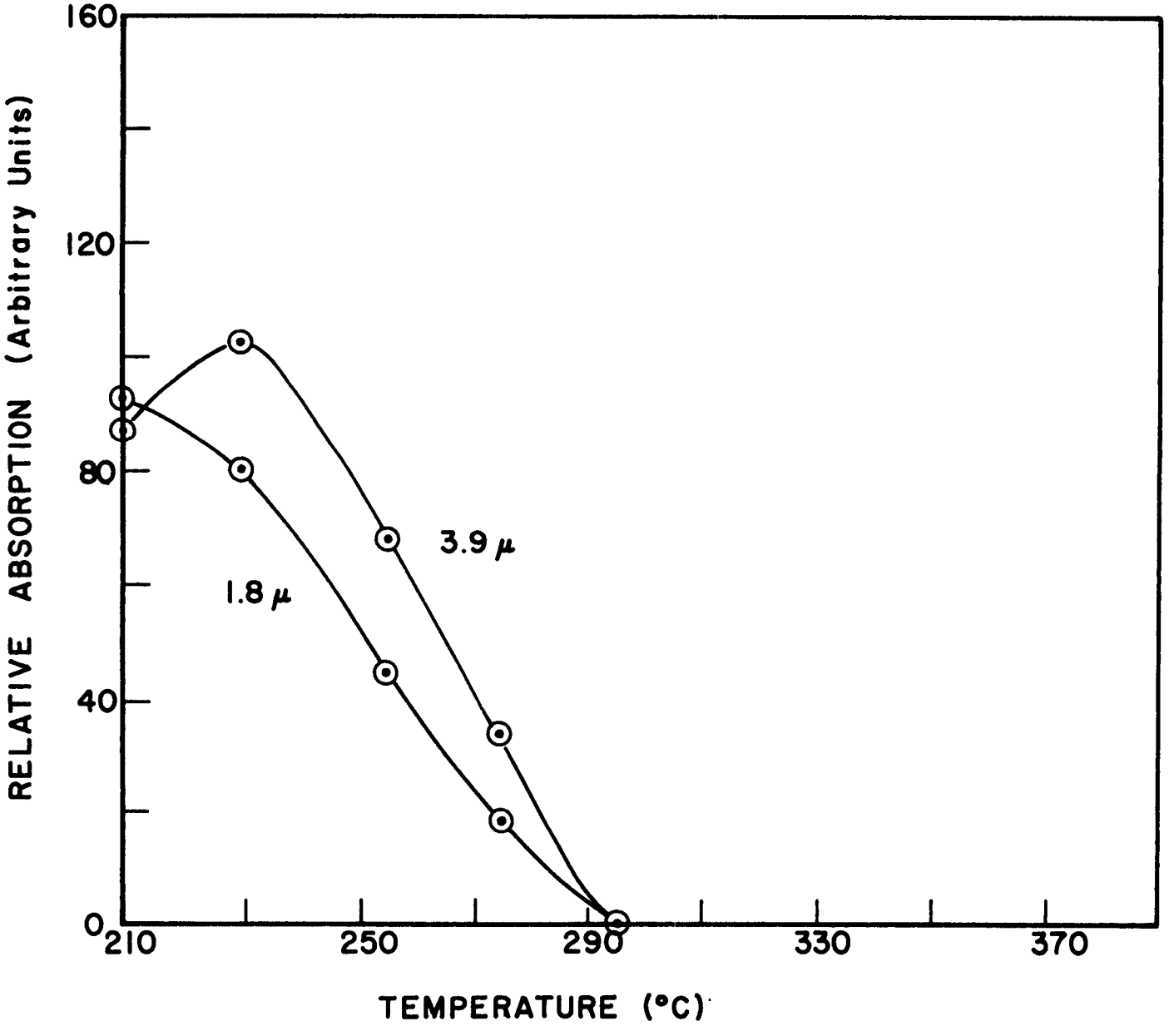
160
120
80
40
0
RELATIVE ABSORPTION (Arbitrary Units)
3.9 μ
1.8 μ
210
250
290
330
370
TEMPERATURE (°C)

Figure 4

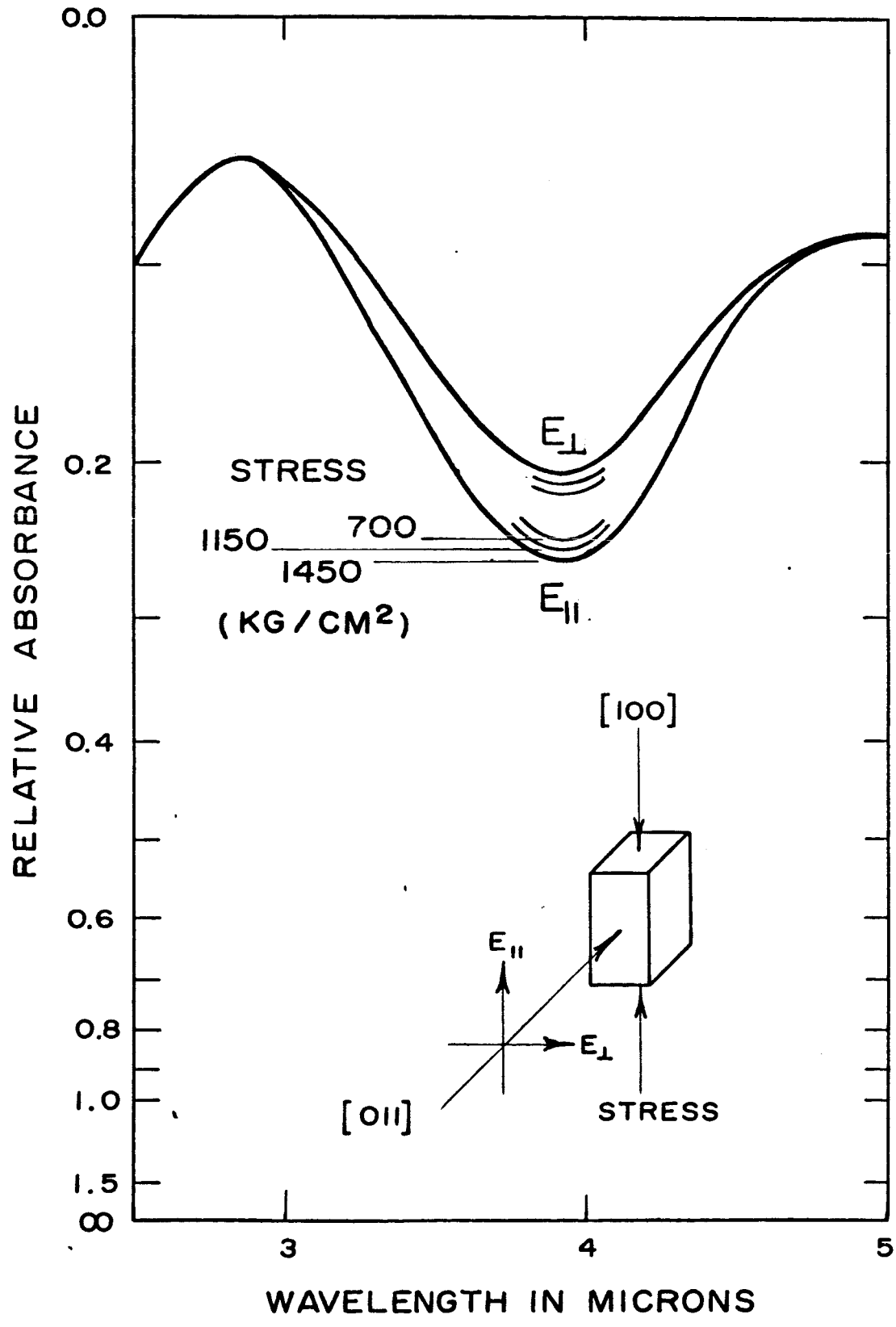
0.0
0.2
0.4
0.6
0.8
1.0
1.5
∞
RELATIVE ABSORBANCE
STRESS
1150
700
1450
(KG/CM²)
E⊥
E11
[100]
E11
E⊥
[011]
STRESS
3
4
5
WAVELENGTH IN MICRONS

Figure 5

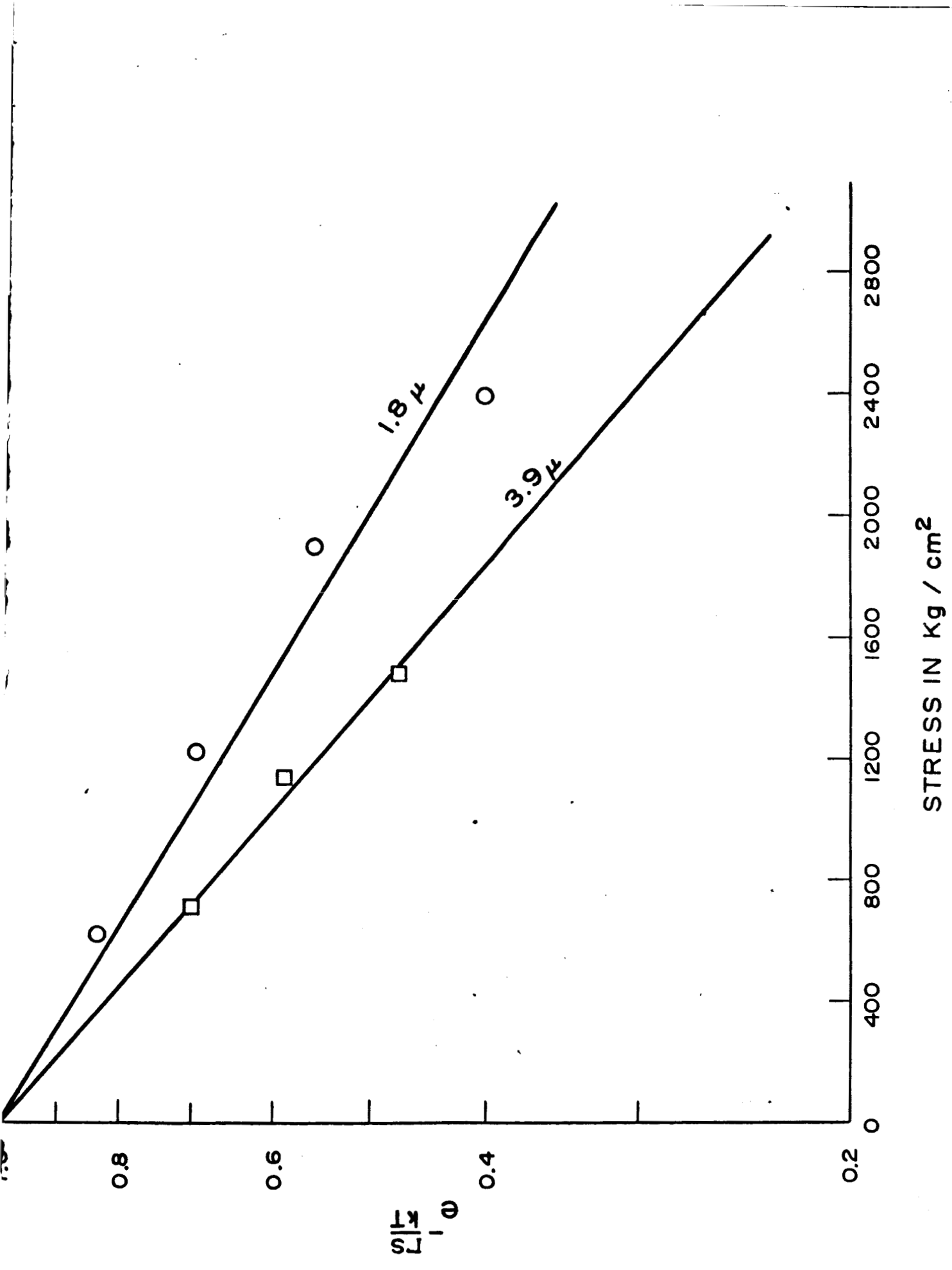
1.8 μ
3.9 μ
STRESS IN Kg / cm²
0
400
800
1200
1600
2000
2400
2800
0.2
0.4
0.6
0.8
e^(-ΓS/kT)

Figure 6

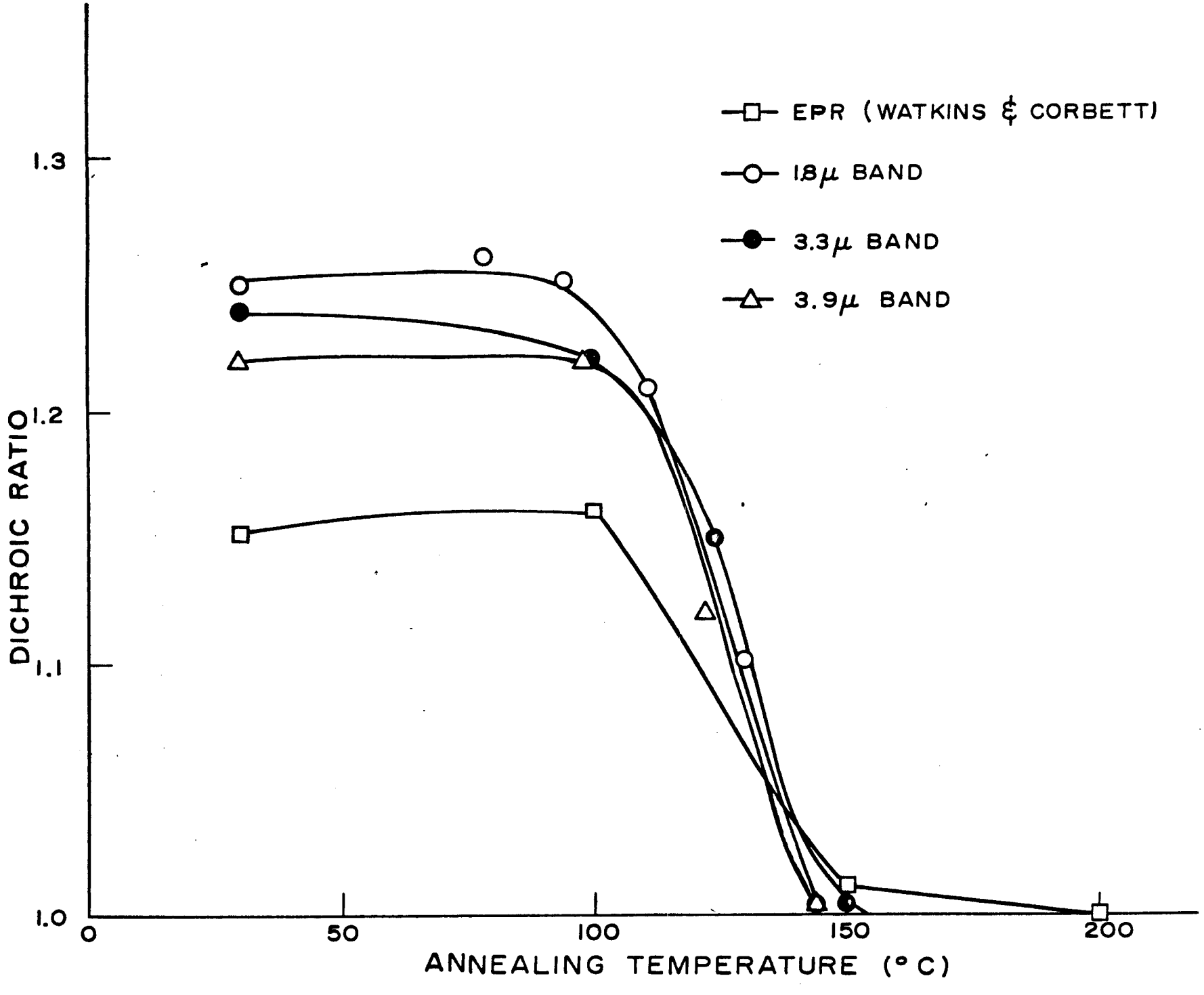
EPR (WATKINS & CORBETT)
1.8μ BAND
3.3μ BAND
3.9μ BAND
DICHROIC RATIO
1.3
1.2
1.1
1.0
0
50
100
150
200
ANNEALING TEMPERATURE (°C)

Figure 7

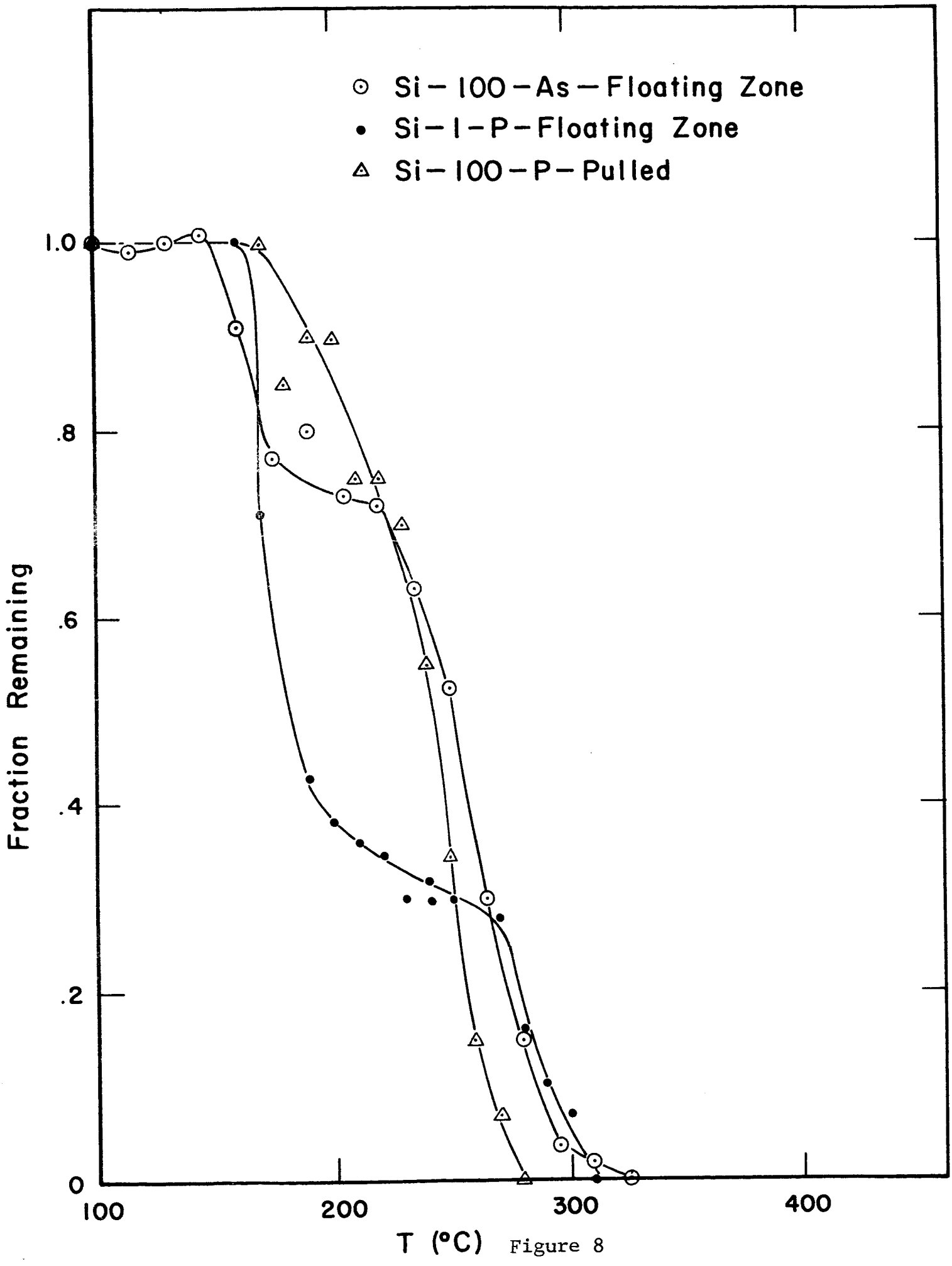
⊙ Si – 100 – As – Floating Zone
• Si – 1 – P – Floating Zone
△ Si – 100 – P – Pulled
Fraction Remaining
1.0
.8
.6
.4
.2
0
100
200
300
400
T (°C)

Figure 8

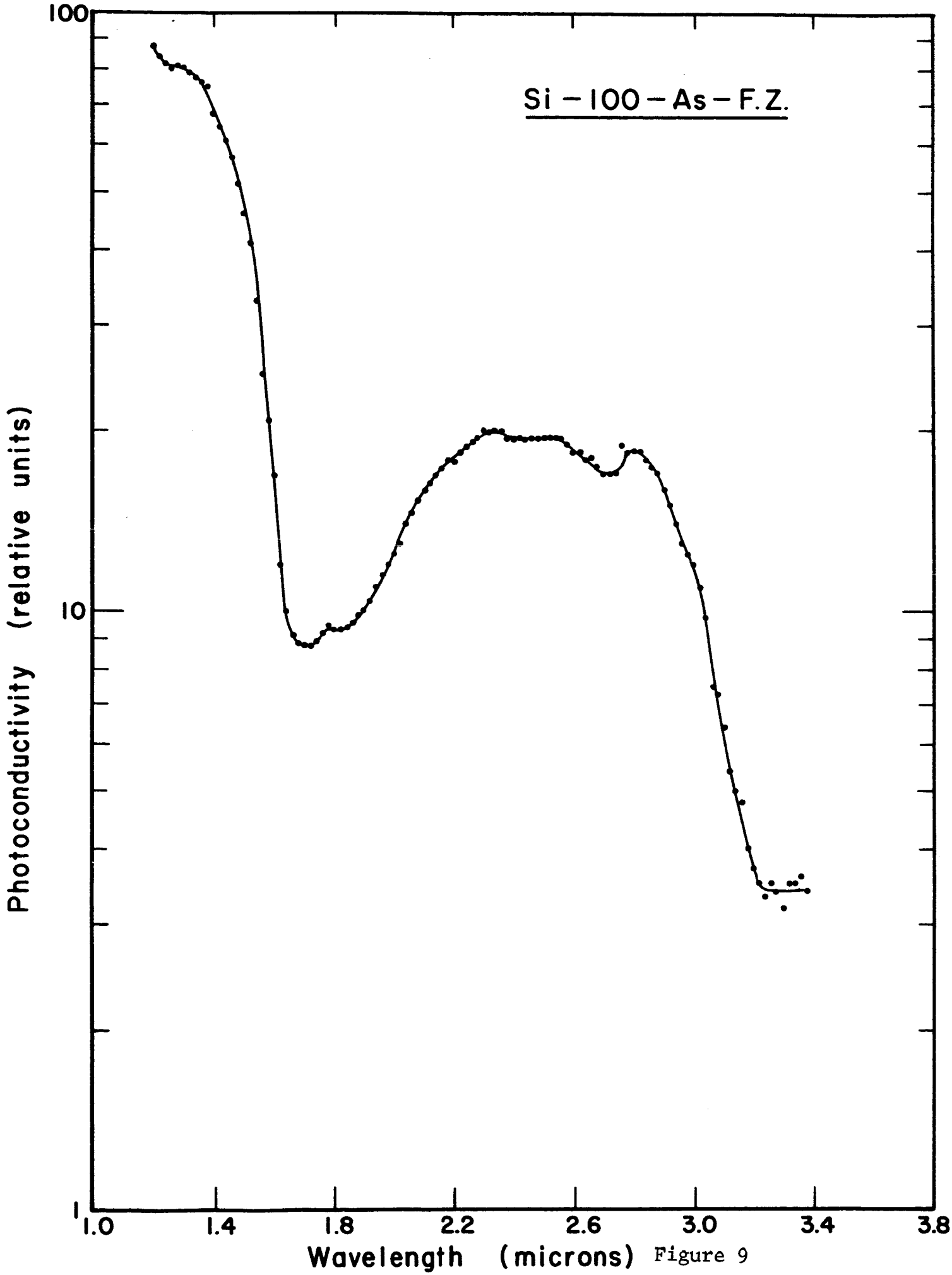
Si – 100 – As – F.Z.
100
10
1
Photoconductivity (relative units)
1.0
1.4
1.8
2.2
2.6
3.0
3.4
3.8
Wavelength (microns)

Figure 9