ABSORPTION OF ELECTROMAGNETIC RADIATION IN THE FAR INFRARED BY DOPED SILICON

by

RON FU CHU, B.S.

A THESIS

IN

PHYSICS

Submitted to the Graduate Faculty
of Texas Tech University in
Partial Fulfillment of
the Requirements for
the Degree of

MASTER OF SCIENCE

Approved

December, 1979

ACKNOWLEDGEMENTS

I am very grateful to Dr. H. C. Thomas for his guidance in this research, and to the Los Alamos Scientific Laboratory for irradiating samples.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Figure

CHAPTER I

INTRODUCTION

The purest silicon available today contains residual boron, a shallow acceptor, in concentration of the order of 10^{12} B/cm^3. These boron impurities cause some problems in the operation of certain silicon devices. These problems can be eliminated if nearly exact compensation of the boron acceptors is accomplished by the addition of shallow donors.

The new technique of neutron transmutation doping (NTD) has been shown to be a useful method of producing a controllable and uniform phosphorus dopant.[1]

Reactor facilities provide a source of thermal neutrons, which, by the (n, γ) reaction, produce stable ^{31}P isotope. However, this thermal flux which is always accompanied by a fast neutron component produces radiation damage. The defect structures resulting from irradiation can be healed by heating.

As annealing occurs, the valence electrons of phosphorus are released from defects and the spectra of neutral phosphorus can be excited by far infrared absorption.

The purpose of this research is to investigate the effects of temperature and time of anneal on the healing of defects as determined by the growth of optical activity of neutral phosphorus. These results will be compared with those found by the change of resistivity of NTD silicon with annealing.

In Chapter II the problem will be discussed in detail. The experimental apparatus and procedures will be described in Chapter III. Chapter IV presents the data and analysis and Chapter V gives the results and conclusion.

CHAPTER II

DISCUSSION OF PROBLEM

II.1. Advantage of NTD silicon

Since conventional techniques such as zone leveling[2] and crystal growing[3] require the simultaneous control of several kinetic processes including evaporation, segregation and vapor-liquid reaction, it can be expected that their satisfactory implementation on a routine basis will require considerable ingenuity.

The NTD technique is a different approach to the problem of preparation of uniform resistivity n-type silicon at any desired level. The major advantages of the NTD process are:

1. A real and spatial uniformity of dopant distribution.
2. Precise control of doping level.
3. Elimination of dopant segregation at grain boundaries in polycrystalline silicon.
4. Superior control of heavy atom contaminants.

Figure 1[1] is a schematic representation of spreading resistance traces across a wafer diameter for conventionally doped and NTD silicon. This shows that the homogeneity of resistance in NTD-Si is better than conventionally doped silicon. This homogeneity is a result of a homogeneous distribution of silicon isotopes in the target material and the long range of neutrons in silicon. Doping accuracy is a result of careful neutron flux integration. From

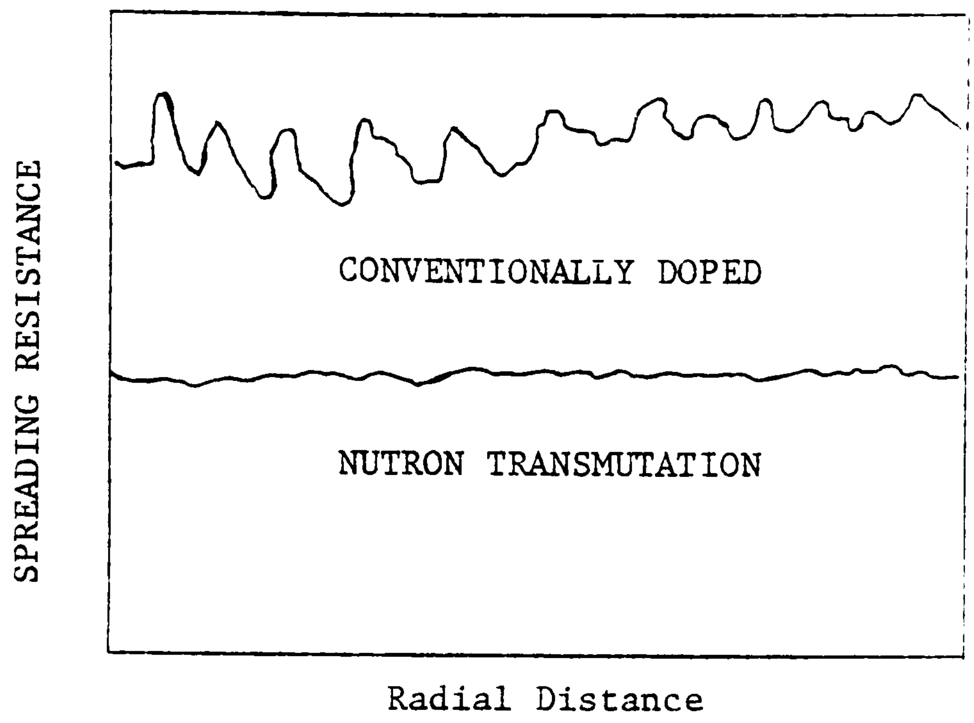

Figure 1

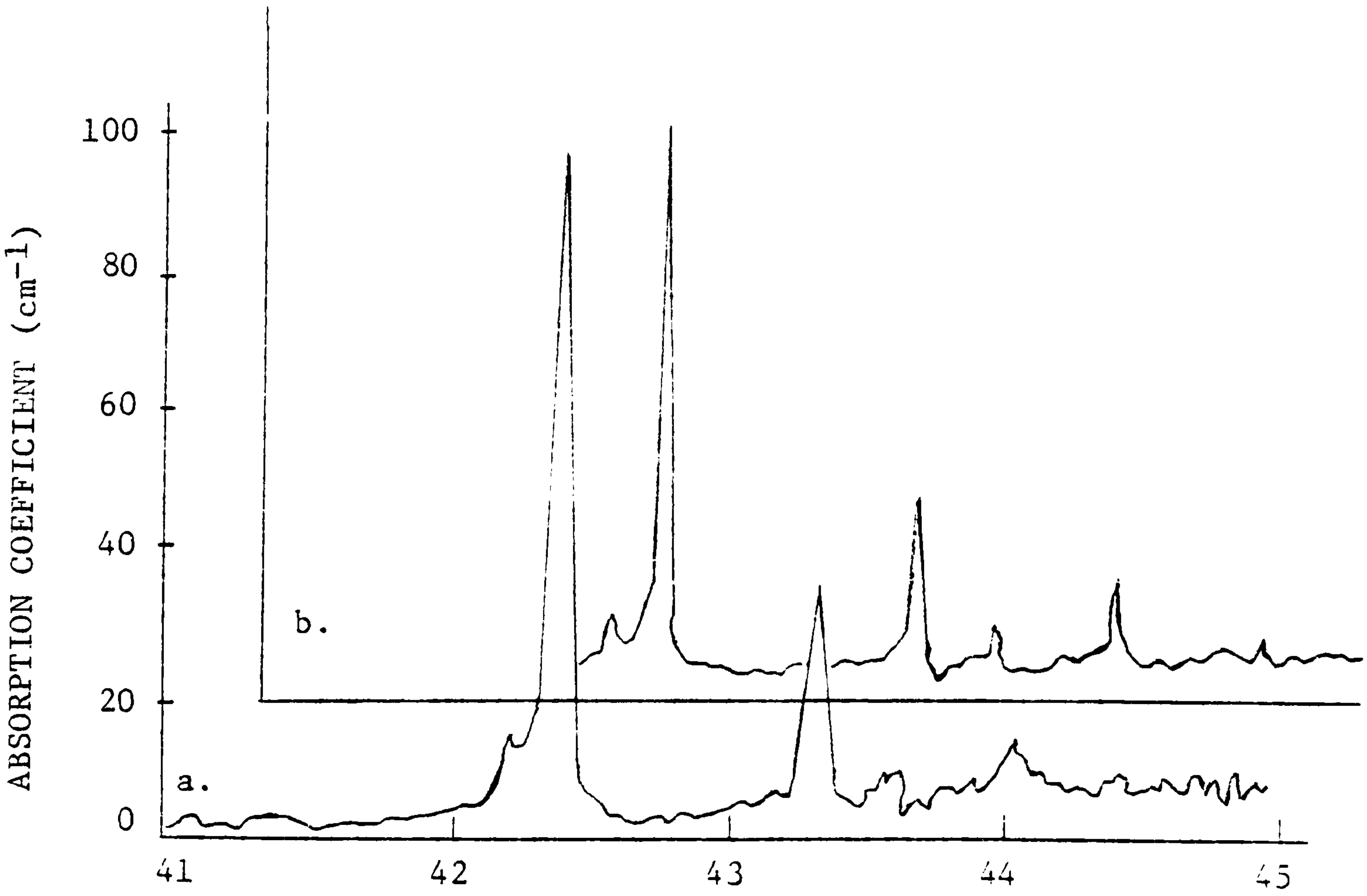

Figure 2. a. Conventionally doped silicon.
b. Neutron transmutation doped silicon.

Figures 1 and 2. Comparison of conventionally doped silicon with neutron transmutation doped silicon.

Figure 2[4] one can also see that the conventionally doped silicon has a broader excitation spectrum (a) than NTD-Si (b). It has been suggested that electrically inactive impurities can produce such a broadening.[5]

However, the NTD process also creates damage in silicon and certain defect structures from this damage will trap the phosphorus.

II.2. Radiation damage

The processes of neutron transmutation in silicon are:

$$^{28}Si\ (n,\ \gamma)\ ^{29}Si$$

$$^{29}Si\ (n,\ \gamma)\ ^{30}Si$$

$$^{30}Si\ (n,\ \gamma)\ ^{31}Si \longrightarrow\ ^{31}P + \beta^-$$

The first two reactions produce no dopants, the third reaction produces ^{31}P, the desired donor dopant. In addition to these reactions several radiation damage mechanisms can contribute to the displacement of the silicon atoms from their normal lattice positions. These are[1]:

1. Fast neutron knock-on displacements
2. Fission gamma induced damage
3. Gamma recoil damage
4. Beta recoil damage
5. Charged particle knock-ons from (n,p),(n,α), etc. reactions.

This damage will form many point defect structures. These defects are thought to contain vacancies, for example, the A center vacancy oxygen complex is a single oxygen atom in a lattice vacancy and contains a Si-O-Si and a Si-Si molecule. The defect structure which traps the phosphorus is the E center vacancy-phosphorus pair (Figure 3). Initially there are four broken bonds around the vacancy trapped next to the substitutional P atom impurity. Because of the extra nuclear charge of the P atom two electrons are accomodated in its orbital with opposite spins. Two of the remaining atoms interact via an electron pair bond (Si_2 and Si_3) leaving an unapired electron in the orbital of the remaining Si atom (Si_1).

Since the NTD phosphorus is bound in the E-center after irradiation but before annealing, electronic excitation by far infrared radiation does not occur. As the annealing temperature is increased the E-center defect will change and finally heal with the release of the bonding electron making the phosphorus neutral. As this occurs phosphorus absorption lines will appear in the spectrum and the sample converts from p-type to n-type.

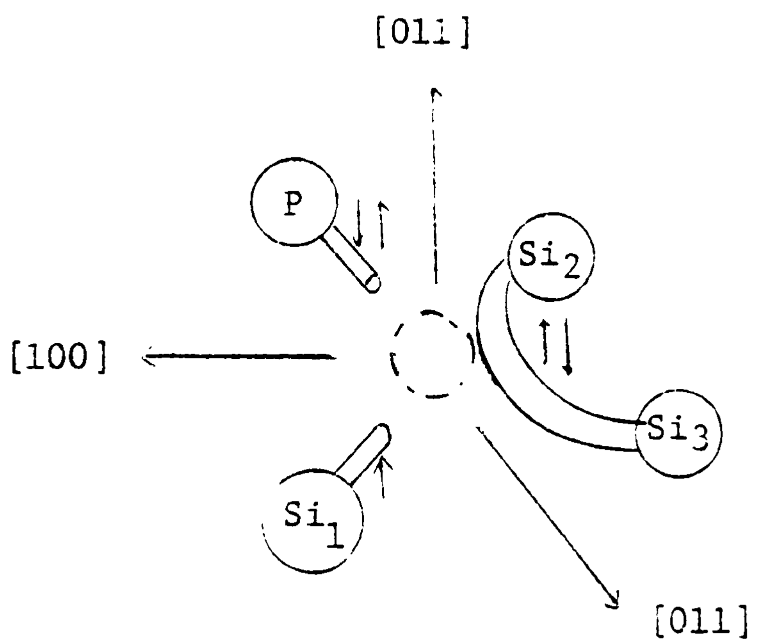

Figure 3. Atomic configuration of the E-center vacancy-phosphorus pair.

II.3. Results of other experiments

Electrical, optical, x-ray and electron microscope techniques have been used to investigate radiation damage and annealing in NTD silicon. For example, M. Tanenbaum[28] after annealing samples at 800° C for 1 hour obtained a predicted resistivity. C. Jagannath[4] annealed NTD silicon at 800° C for 2 hours and obtained an infrared absorption spectrum which is better than for conventionally doped silicon (Figure 2). B. Larson[7] found that annealing of the sample at 800°C for 30 minutes affected the recovery of the electron mobility. Recently, Meese[8] determined the resistivity of NTD silicon for isochronal annealing with a typical result being shown in Figure 4. The samples were annealed at each temperature for only 15 minutes. The conclusions are briefly as follows: the sample was p-type at the start of the anneal and converted to n-type at about 800° C. The large reverse annealing peak from 600°-800° C is primarily associated with the activation of phosphorus resulting in a type conversion from p-type to n-type.

II.4. Optical absorption

The introduction of a group V impurity, such as phosphorus, into a perfect silicon lattice produces an electron loosely bound to the neutral impurity ion. At room temperature electrons are removed from the impurity sites by thermal excitations and exist as free donors in the crystal, while at liquid helium temperature nearly all these electrons are bound to specific impurity sites and occupy the

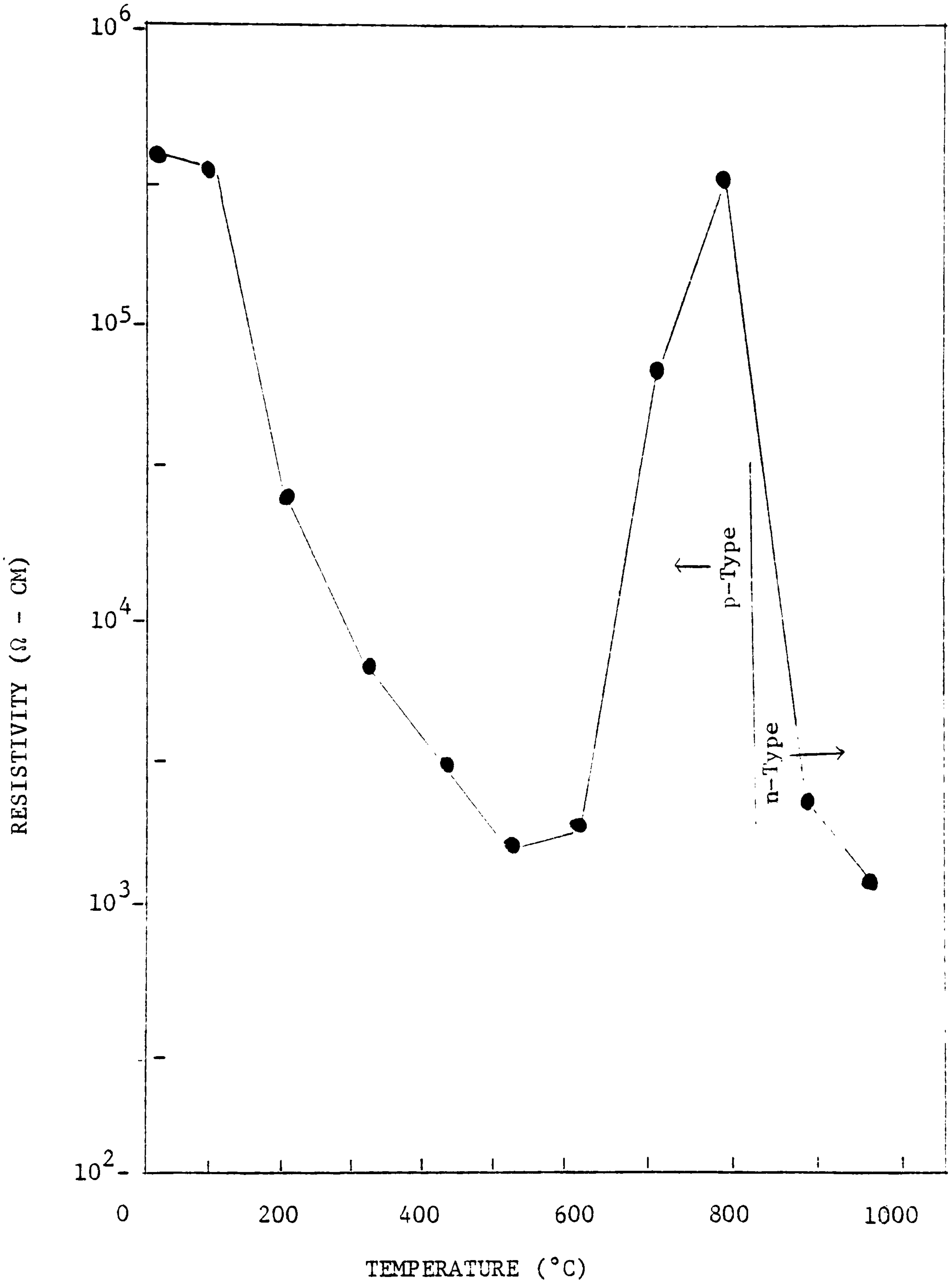

Figure 4. Resistivity measurement.
Vacuum isochronal anneal of phosphorus doped silicon
(Fluence 1.986 x 10^{15} n/cm^2).

lowest energy state. In phosphorus doped silicon, infrared absorption takes place through the excitation of bound electrons from the ground to excited states. This leads to a line spectrum. Table II.1 lists observed phosphorus infrared absorption lines.[9]

After neutron doping, the electrons of phosphorus bond the vacancy centers as previously described. Annealing releases the valence electron from the bond structure and infrared absorption can then take place through the excitation of these electrons. Absorption spectra will be taken for samples with various annealing temperatures and times to determine the rate at which neutral phosphorus is formed which assumed is the rate at which defects involving P (mainly E-centers) are healed.

The samples will be annealed at 200° C intervals until the phosphorus absorption no longer increases.

TABLE II.1

OBSERVED PHOSPHORUS INFRARED ABSORPTION LINES

Identification	Donor Peak Position cm^{-1} $\pm 0.04 cm^{-1}$	Observed Lines
$2P_o$	275.08	$2P_\pm - 2P_o$
$2P_\pm$	315.93	$3P_o - 2P_\pm$
$3P_o$	323.40	$4P^o - 2P_\pm$
$4P_o$	340.87	$3P_\pm - 2P_\pm$
$3P_\pm$	342.38	$4P_\pm - 2P_\pm$
	348.77	$4F_\pm - 2P_\pm$
$4P_\pm$	349.87	$5P_\pm - 2P_\pm$
$4F_\pm$	352.27	$5F_\pm - 2P_\pm$
	354.31	$6P_\pm - 2P_\pm$
$5P_\pm$	355.77	
$5F_\pm$	357.36	
$6P_\pm$	358.78	
	359.80	
$7P_\pm$	360.70	

CHAPTER III

EXPERIMENT

III.1. Apparatus and procedures

Because the apparatus used in this experiment is described in detail in the dissertation of B. Covington,[10] only a brief description of the procedures and apparatus will be presented.

In order to assure that the electrons will be excited from the ground state only and to prevent lattice vibration from affecting the absorption lines, the sample will be held at liquid helium temperature (4.2° K).

The sample, after annealing, was attached to the brass plate of the sample holder on which a calibrated (1.5° to 100° K) germanium resistance thermometer was mounted. The sample holder had a 1.2 x 1.2 cm hole through which the light passed to the sample.

The sample holder with sample was then put into the liquid helium cryogenics dewar one end of which has two windows. The light from the Fourier Spectrophotometer source passed through the window, hit the sample, and the transmitted part was subsequently detected by a Golay cell. The sample was maintained at about 4.2° K by allowing liquid helium gas to pass over it. The transmitted light was detected by a Golay cell which transmitted an electrical signal to the analoque to digital converter. The converter transmitted the digitized signals to the interfacing wave analyzer which performed a Fourier transform of the interferogram. The intensity versus frequency curve was then printed by a standard Teletype machine.

III.2. Preparation of silicon sample

The silicon samples were irradiated in the Omega West Reactor at Los Alamos Scientific Laboratory and prepared from floating-zone refined material.

The sample was cut to 1.5 x 1.5 cm size just larger than the hole of the sample holder and then polished until an acceptable thickness of about 1 mm was reached. The sample was etched in a mixture of 5 parts concentrated HNO_3 to 1 part concentrated HCl, rinsed in deionized water and then placed in a furnace for annealing at various temperatures and times. The samples were annealed in air and were placed on pure silicon blocks to prevent absorption of foreign materials during anneal. After each anneal the sample remained in the furnace for about 1 day to slowly cool before using.

The samples used in this experiment had a phosphorus concentration of about $1 \times 10^{15}/cm.^3$

CHAPTER IV

DATA AND DATA ANALYSIS

The spectral data are displayed in Figures 5-11. The frequency range shown is from 268.5 to 366.2 cm^{-1} because the absorption lines which can be observed (Table II.1) are within this region. All the spectra are taken with the samples at liquid helium temperature.

Figure 5 is the transmission versus frequency curve of the sample before annealing but after irradiation. This curve is the result of averaging many runs and is obtained by drawing a smooth curve through the average value of data points. This seems justified since no absorption lines are expected before annealing and no lines consistent with the resolution are seen. This curve can therefore be used as a background since for every spectrum the sample has the same refraction index, reflection surface and thickness.

Figure 6, a typical result, is the average of 3 transmission spectra of the sample which had been annealed at 800° C for 3 hours. Taking the average of several spectra can eliminate random noise as much as possible. The standard deviation of this average is about 5%. In order to see the absorption lines this curve was subtracted from normalized background (Figure 5). In this way the effects resulting from refraction index, reflection loss and thickness are eliminated and the resulting curves should show the effects due to annealing only. The result for the 800° C, 3 hour anneal is shown in Figure 11. The results shown in Figures 7-10 were obtained in the same way.

Table IV.1 is the relative absorption intensity of the 2P± line at 800° C for varying times of anneal. To find this intensity the area of 2P± line was measured by first subtracting the unsymmetrical region which is due to noise. The error limits are estimated from the intensity of the noise contribution to the spectra. The data of this table are plotted in Figure 12.

TABLE IV.1

THE RELATIVE INTENSITY OF 2P± LINE FOR VARIOUS ANNEALING TIMES AT 800° C

Anneal Time	30 min.	1 hr.	2 hrs.	3 hrs.
Intensity	26 ± 6	42 ± 3	63 ± 3	66 ± 4

CHAPTER V

RESULTS

V.1. Interpretation

Neutron irradiation of silicon produced defects which are effective in trapping carriers. These defects exhibit characteristic annealing behavior which has been investigated by determining the absorption spectra of phosphorus donors in NTD silicon as a function of annealing tempratures and times.

The sample was first annealed at 200° C, 400° C and 600° C for 30 minutes. Spectra taken after each of these annealings show no absorption lines. Spectra for annealing temperatures of 200° C and 400° C are similar to that at 600° C shown in Figure 7, none of which show phosphorus absorption peaks.

Figure 4 shows that for annealing temperatures of 600° C or less the sample is still p-type. Therefore no absorption lines of phosphorus should appear in these spectra in agreement with these results.

As the sample was annealed at 800° C for 30 minutes, absorption lines began to appear but not very clearly (Figure 8). The results of a continued annealing for a total of 1 hour at 800° C are shown in Figure 9. Absorption lines at 275 cm^{-1}, 317 cm^{-1} are clearly seen with lines at 341 and 366 cm^{-1} not clearly resolved. The source of the small peaks between 275 cm^{-1} and 317 cm^{-1} is unknown but they are probably due to noise. The sample was further annealed at 800° C for another 1 hour (Figure 10). In this spectrum, other peaks are formed at 342 cm^{-1}, 350 cm^{-1} and 356 cm^{-1}. These absorption lines are not completely resolved and are still too broad. According to Kogan,[5] the electrically inactive impurities can produce such a broadening indicating that the sample needs to be further annealed. Figure 11 shows the results when the sample was annealed at 800° C for 3 hours. In this spectrum the absorption peaks at 275, 317, 342, 350 and 356 cm^{-1} are very clear which are identified with the $2P_o$, $2P\pm$, $4P\pm$ and $5P\pm$ lines, respectively. The small fluctuations in the spectrum are due to noise.

The growth of absorption by phosphorus as shown in Figures 8-11 corresponds to the reverse annealing peak shown in Figure 4 from 600°-800° C. The increasing intensity of the absorption lines is due to the electrical activation of the phosphorus.

Figure 12 shows that the intensity of the absorption lines increased when the annealing time increased. The results for 2 hours and 3 hours annealing are the same within experimental error. This means that for 3 hours annealing at 800° C the absorption intensity of $2P\pm$ line reaches a maximum so that the defects trapping phosphorus are totally removed.

V.2. Summary

A Fourier transform system was used to determine phosphorus absorption lines as a function of frequency for neutron transmutation doped silicon with phosphorus concentration 1×10^{15} cm^{-3}.

Because of radiation damage, there are many defect structures, some of which trap the phosphorus. At annealing temperatures less than 600° C no absorption lines are seen, therefore no active donors exist. At 800° C the donors become active and the sample begins to be converted from p-type to n-type. After annealing at 800° C for 3 hours all of the defects trapping phosphorus are removed and a uniform n-type silicon results.

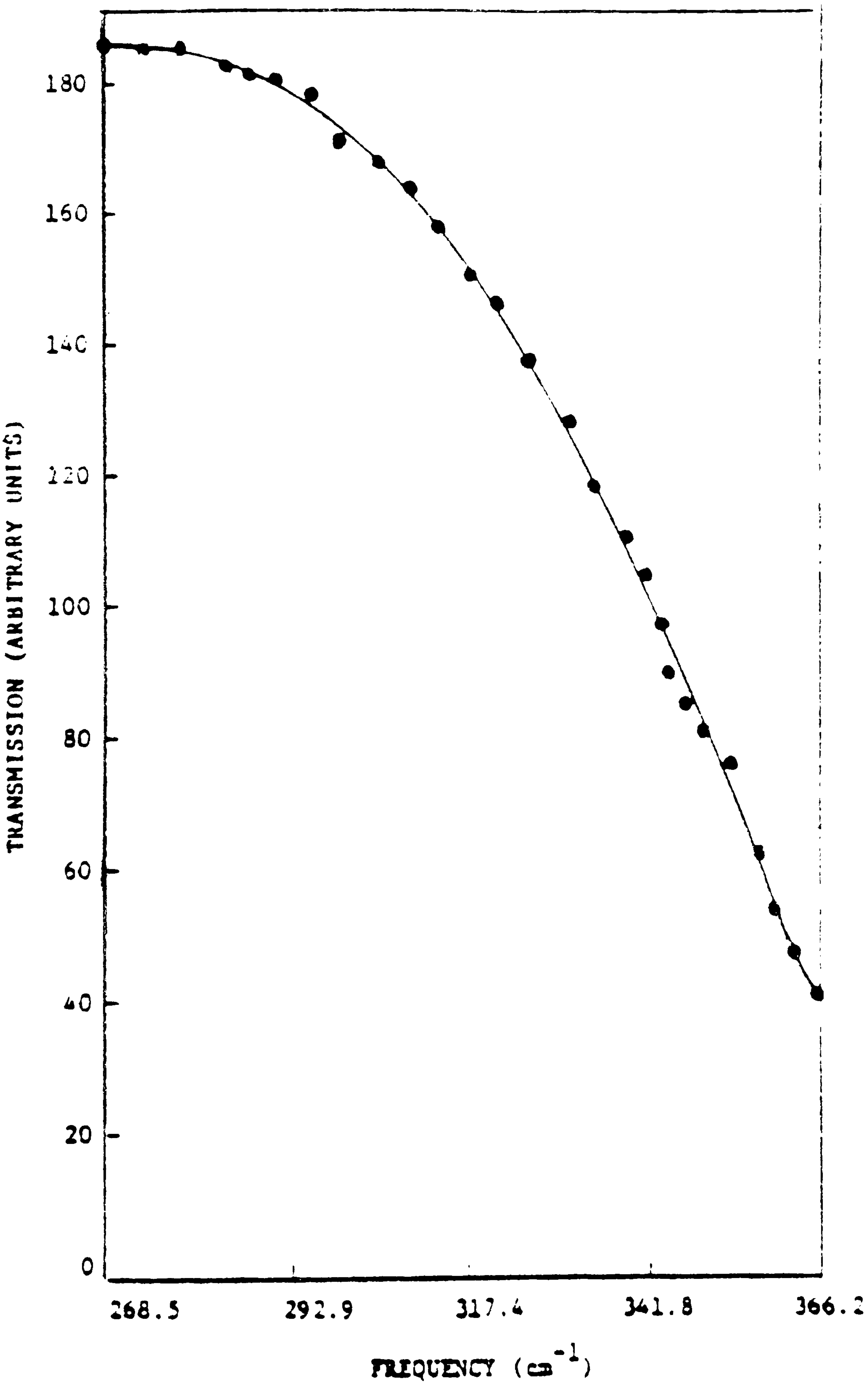

Figure 5. Transmission curve before annealing (4.2° K).

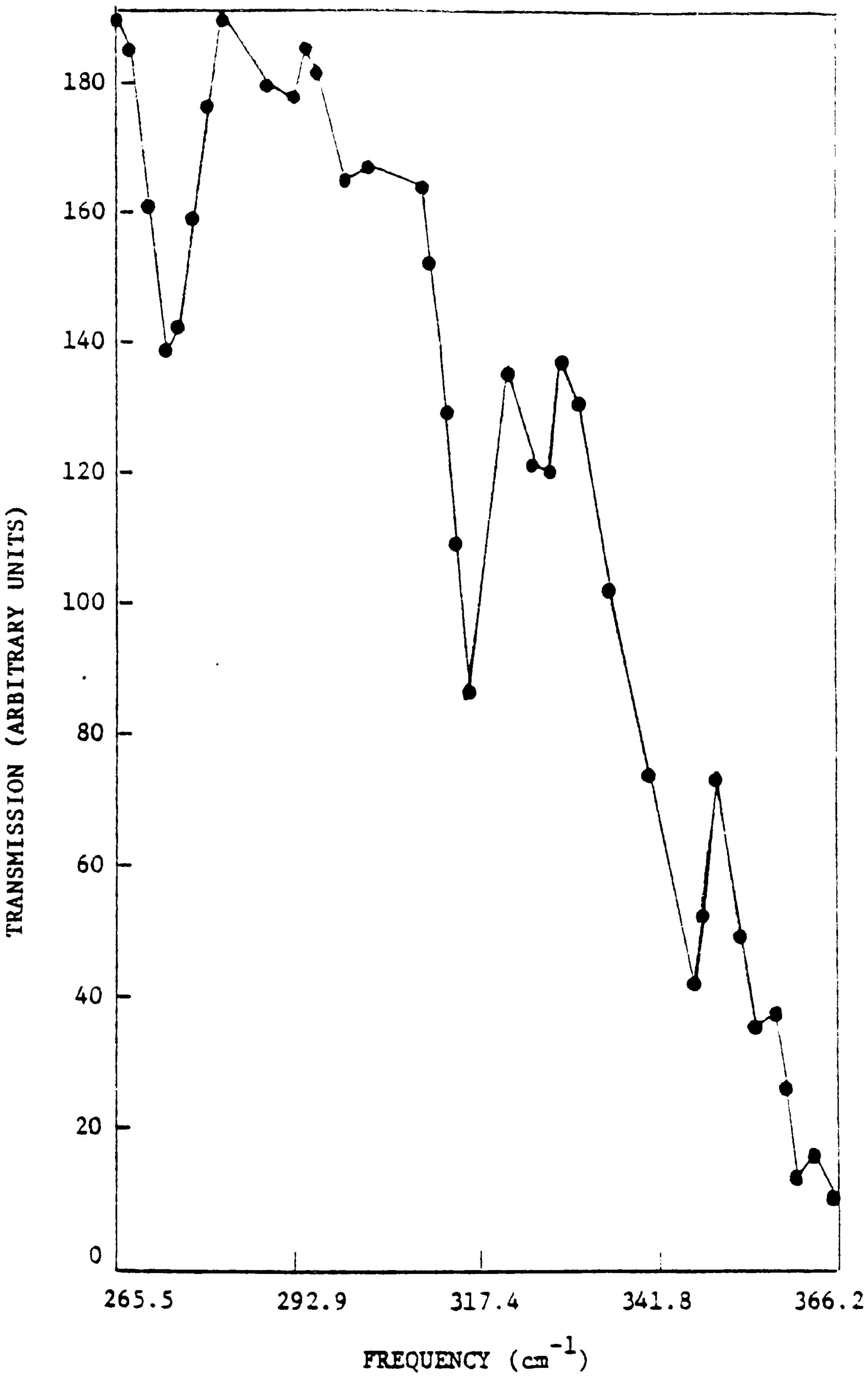

Figure 6. Transmission curve at 800° C for 3 hours (4.2° K).

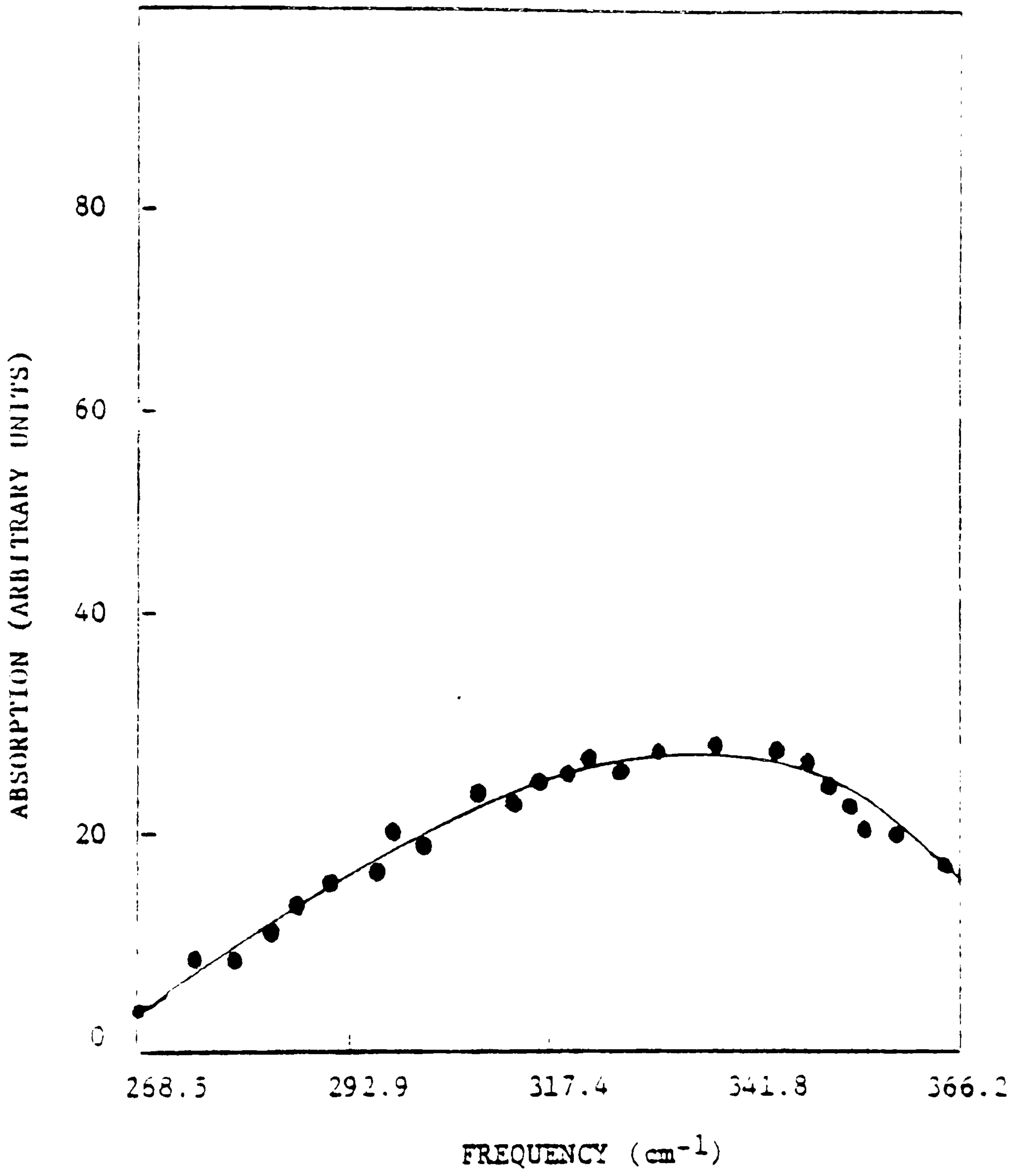

Figure 7. Absorption curve at 600° C for 30 minutes (4.2° K).

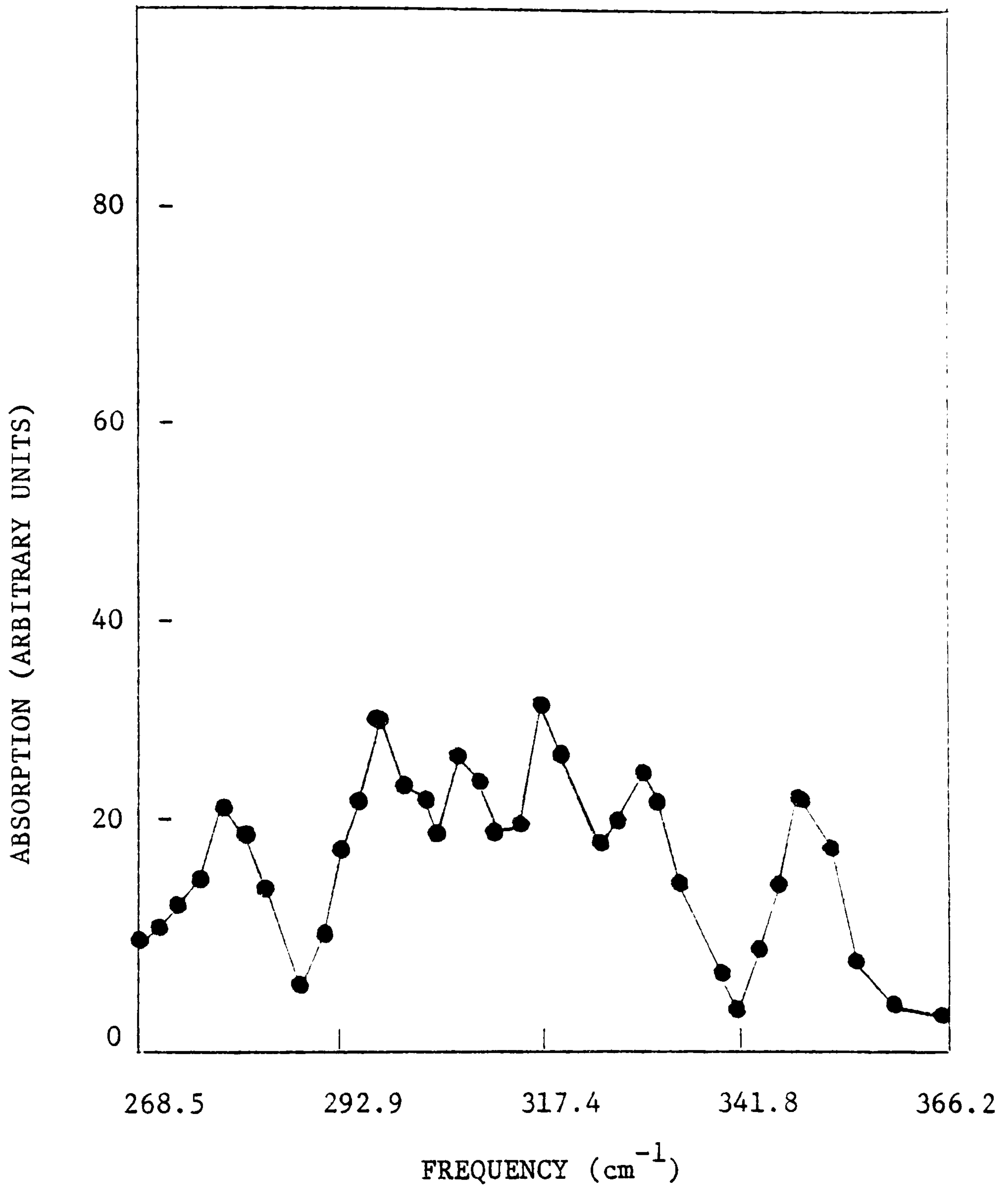

Figure 8. Absorption curve at 800° C for 30 minutes (4.2° K).

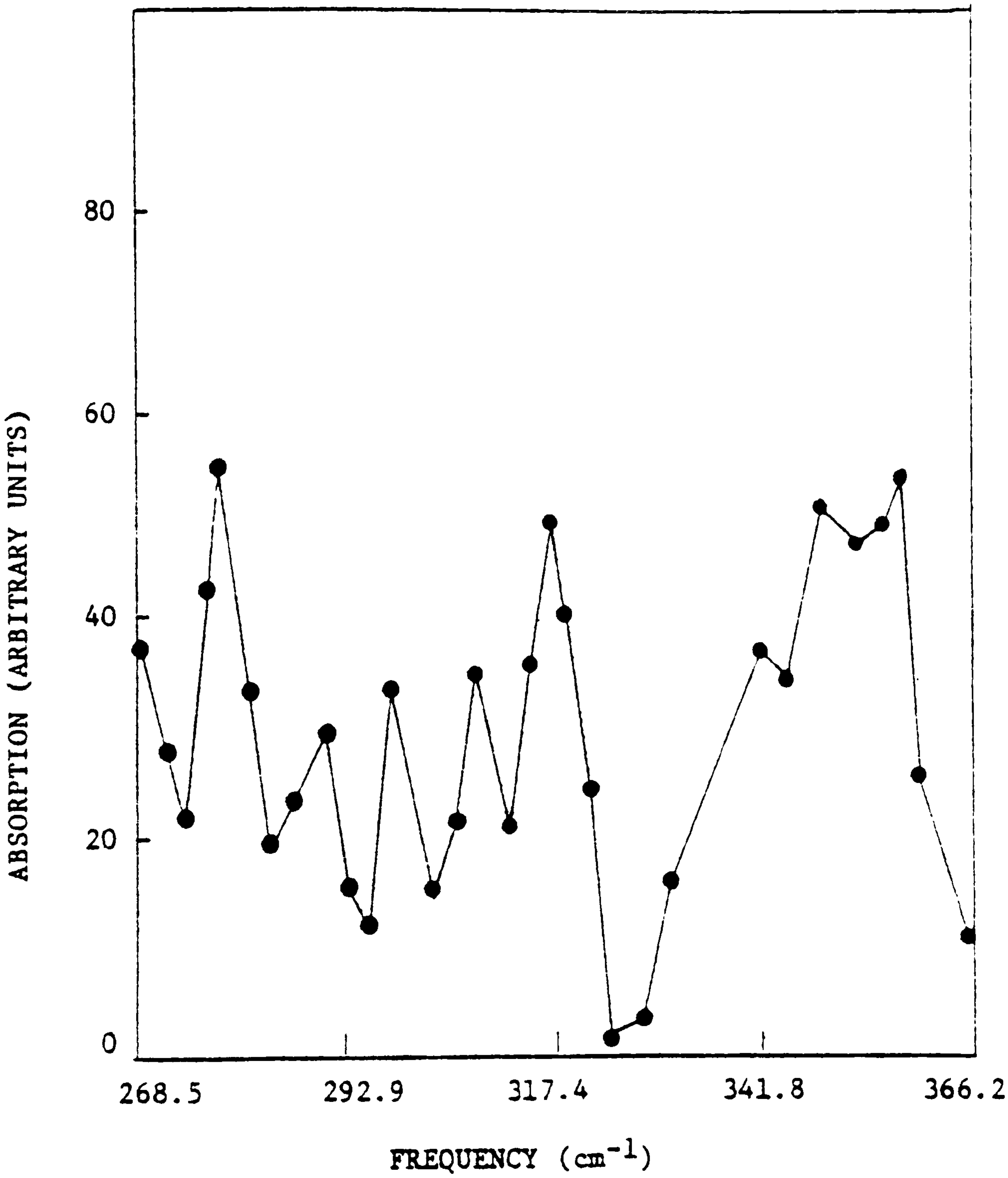

Figure 9. Absorption curve at 800° C for 1 hour (4.2° K).

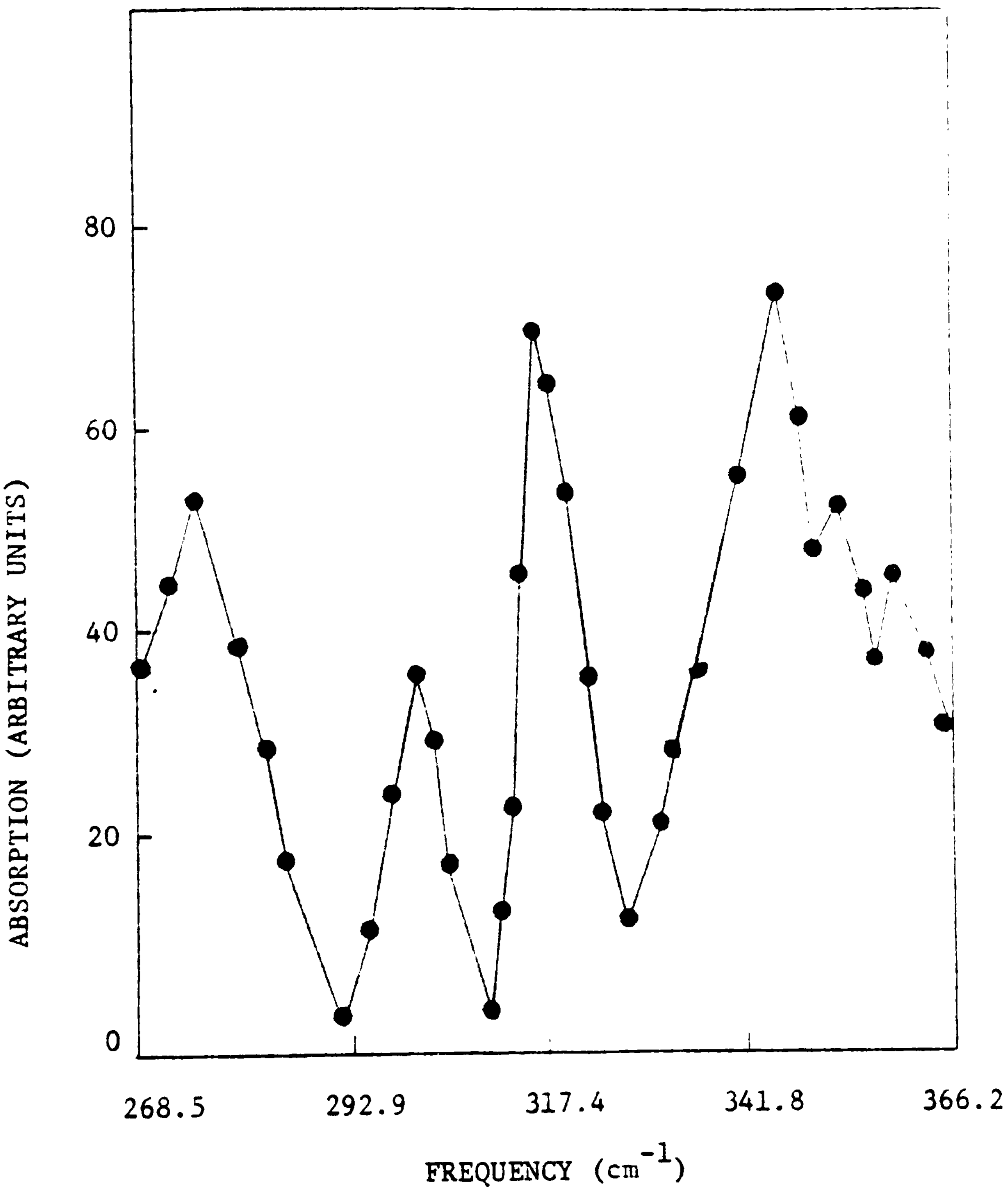

Figure 10. Absorption curve at 800° C for 2 hours (4.2° K).

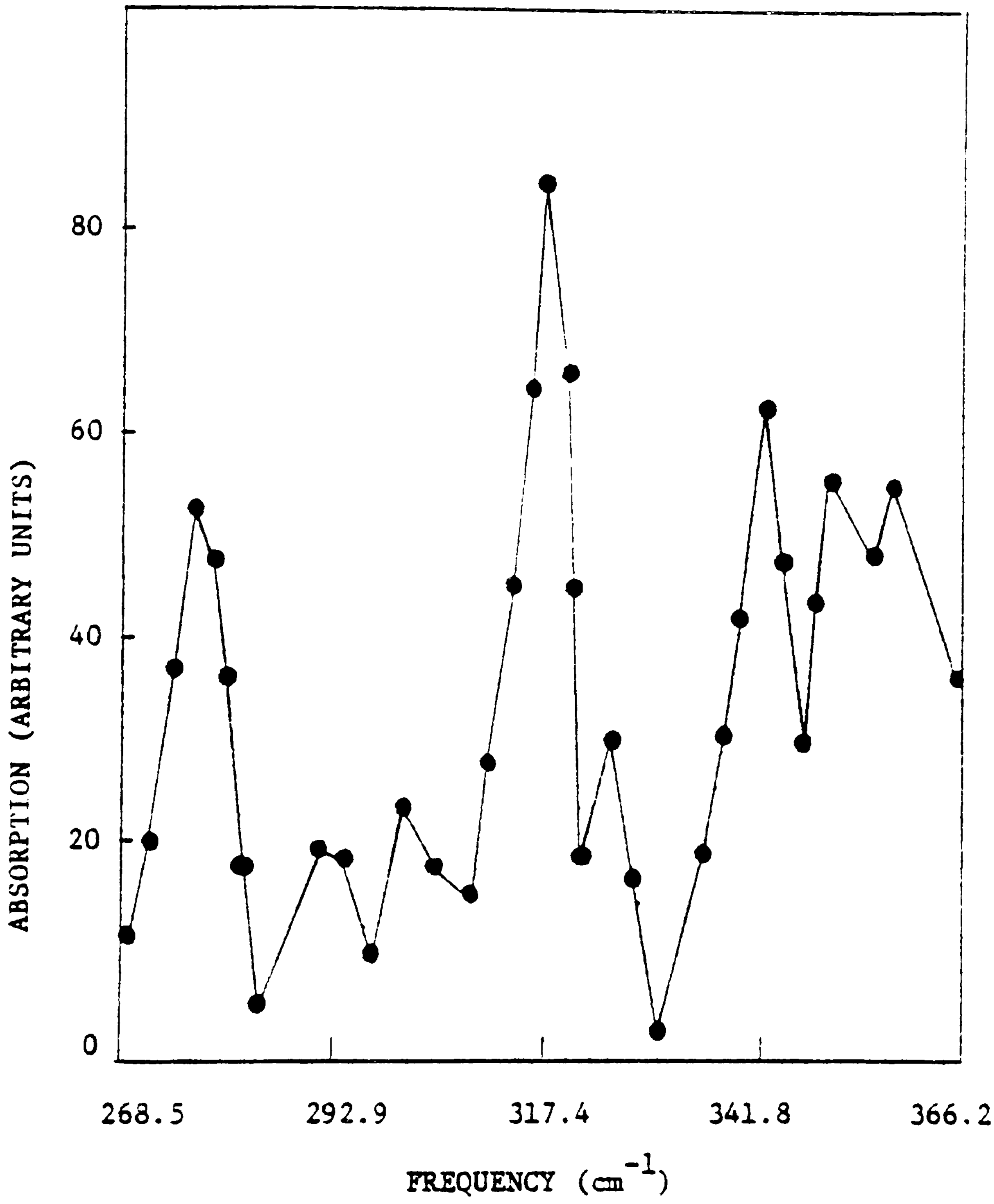

Figure 11. Absorption curve at 800° C for 3 hours (4.2° K).

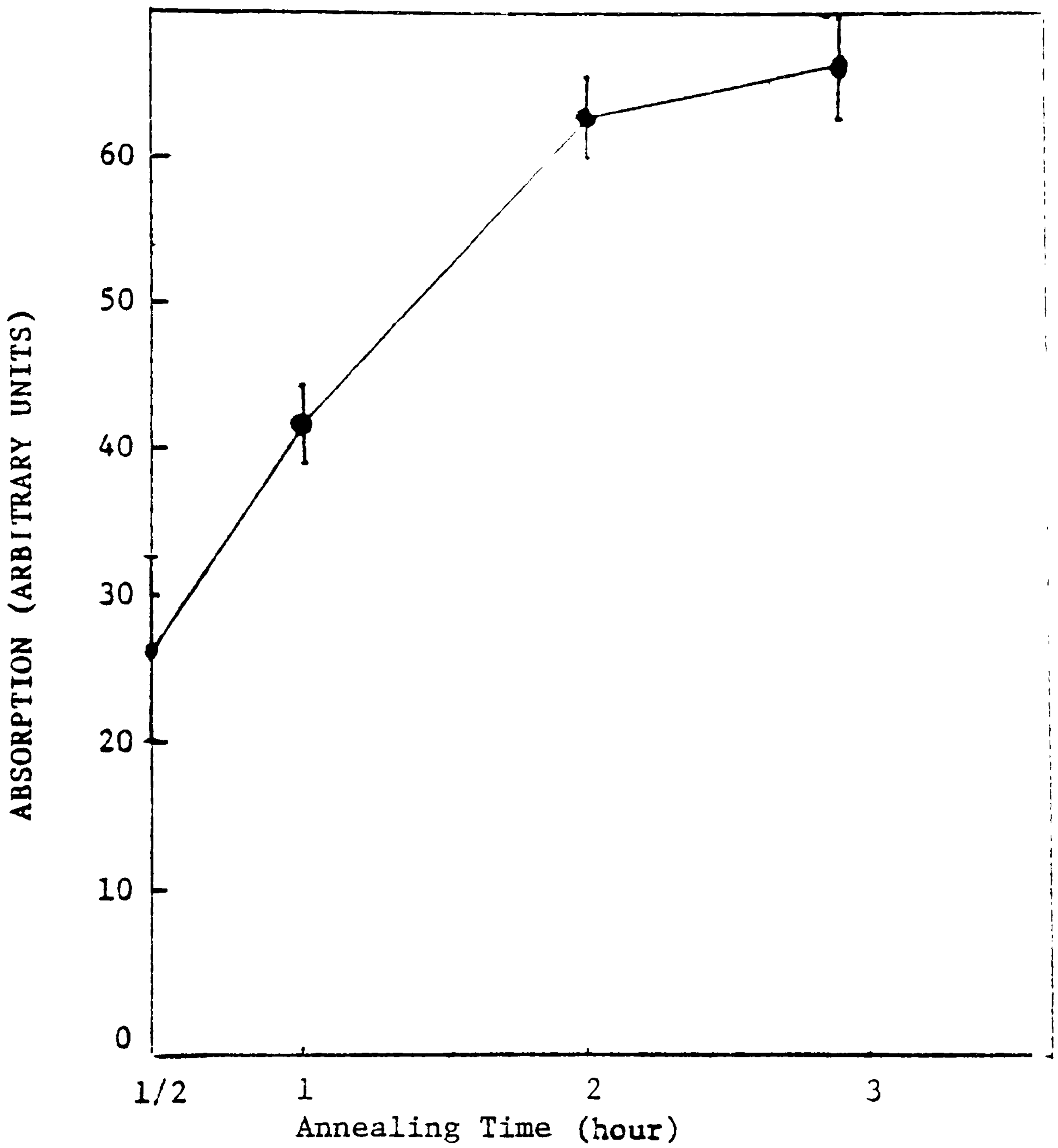

Figure 8. The relative intensity of 2P: line at 800° C anneal vs. annealing time.

LIST OF REFERENCES

1. J. M. Meese, Neutron Transmutation Doping in Semiconductors, Plenum Press, (1979).

2. S. E. Bradshaw and A. Mlavasky, J. Electronics 2, 134 (1956).

3. M. Tanenbaum and A. D. Mills, J. Electrochemical Soc., 108, 171 (1961).

4. C. Jagannath, Z. W. Grabowski, and A. K. Ramadas, Solid State Communication, 29, 355 (1978).

5. Kogan and Lifshits, Phys. Stat. Solidii (a) 39, 11 (1977).

6. J. M. Meese, Advance Techniques for Transmutation Compensation of Extrinsic Silicon Detectors, University of Missouri (1979).

7. B. C. Larson, R. T. Young and J. Narayon, Defect Annealing Studies in Neutron Transmutation Doped Silicon, second international conference on NTD in semiconductor, April, 1978.

8. J. M. Meese, Silicon detector compensation by nuclear transmutation, University of Missouri (1979).

9. M. S. Skolnick, L. Eaves and R. A. Strattling, Solid State Communication, 15, 1403 (1974).

10. B. Covington, A Far Infrared Study of Transmutation-Doped Germanium, Dissertation of Texas Tech University, 1978.