AN INFRARED ABSORPTION STUDY OF LITHIUM IN SILICON

by

John Herbert Wood

Thesis submitted to the Graduate Faculty of the
Virginia Polytechnic Institute

in candidacy for the degree of

MASTER OF SCIENCE

in

Physics

APPROVED:  

T. E. Gilmer, Jr., Chairman

R. F. Tiptswood

F. Y. Wu

James A. Jacobs

T. E. Leinhardt

June, 1967

Blacksburg, Virginia
TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>II. REVIEW OF LITERATURE</td>
<td>2</td>
</tr>
<tr>
<td>III. EXPERIMENTAL DETAILS</td>
<td>9</td>
</tr>
<tr>
<td>A. Sample Characteristics</td>
<td>9</td>
</tr>
<tr>
<td>B. Sample Preparation</td>
<td>9</td>
</tr>
<tr>
<td>C. Experimental Procedure</td>
<td>13</td>
</tr>
<tr>
<td>D. Data Reduction</td>
<td>16</td>
</tr>
<tr>
<td>IV. RESULTS AND CONCLUSIONS</td>
<td>27</td>
</tr>
<tr>
<td>V. ACKNOWLEDGEMENTS</td>
<td>33</td>
</tr>
<tr>
<td>VI. BIBLIOGRAPHY</td>
<td>34</td>
</tr>
<tr>
<td>VII. VITA</td>
<td>36</td>
</tr>
</tbody>
</table>
## LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Energy Levels Relative to the Bottom of the Conduction Band</td>
<td>7</td>
</tr>
<tr>
<td>2. Sample Data</td>
<td>10</td>
</tr>
</tbody>
</table>


<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Assembly of Sample, Thermocouple, Sample Holder and Dewar Cold Finger</td>
<td>14</td>
</tr>
<tr>
<td>2</td>
<td>Absorption Spectrum of Sample DC66-1</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>Absorption Spectrum of Sample NASA-1</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Absorption Spectrum of Sample NASA-2</td>
<td>20</td>
</tr>
<tr>
<td>5</td>
<td>Absorption Spectrum of Sample SE-3-C Due to Franks (7), Sample Age 7 Days</td>
<td>21</td>
</tr>
<tr>
<td>6</td>
<td>Absorption Spectrum of Sample SE-3-C Due to Franks (7), Sample Age 14 Days</td>
<td>22</td>
</tr>
<tr>
<td>7</td>
<td>Absorption Spectrum of Sample SE-3-C, Sample Age 3.5 Years</td>
<td>23</td>
</tr>
<tr>
<td>8</td>
<td>Absorption Spectra of Sample SE-1-D Due to Bell (2), Sample Ages 10 and 60 Hours</td>
<td>24</td>
</tr>
<tr>
<td>9</td>
<td>Absorption Spectrum of Sample SE-1-D Due to Franks (7), Sample Age 1 Year</td>
<td>25</td>
</tr>
<tr>
<td>10</td>
<td>Absorption Spectrum of Sample SE-1-D, Sample Age 4 Years</td>
<td>26</td>
</tr>
</tbody>
</table>
I. INTRODUCTION

Lithium, lithium oxide and the group V elements, phosphorus, arsenic, antimony and bismuth, when present in silicon as impurities, act as "shallow" donors (2, 7, 11). These donors have electrons which are bound so loosely that they may be thermally excited into the conduction band at less than room temperature. The excited bound states and, less precisely, the ground states of these electrons are understood within the framework of the shallow donor theory.

At temperatures approaching that of liquid helium only the ground state and other close lying states are highly populated. Infrared radiation may be used to induce transitions from lower to higher energy states. From the resulting peaks in the infrared absorption spectra the relative spacing between energy states and relative transition probabilities can be determined.

The spectra of lithium-doped silicon with high oxygen content is complex (1, 2, 7). This investigation was undertaken in an attempt to gain a better understanding of these complicated spectra. In the attempt, information was gained verifying the split in the lithium oxide 1S level, indicating a probable upper bound on the oxygen content of zone refined silicon crystals and a possible splitting of the phosphorus donor states in silicon due to some interaction of phosphorus and lithium.
II. REVIEW OF LITERATURE

The work presented in this paper is described and understood in the framework of the shallow donor theory. Kohn (11) has given an extensive treatment of this theory of which only those points necessary for a qualitative understanding of the theory will be presented here.

A donor state exists in a semiconductor when an electron is localized around an impurity from which it can be released into the conduction band with a small expenditure of energy. A "shallow" donor state is characterized by electron orbits on the order of 50 Å in diameter with binding energies ranging from about 10 to 100 mev (millielectron volts). Consider a neutral impurity atom introduced into a crystal lattice with one of its electrons far removed from the remaining positively charged ion. The ion will polarize the semiconductor so that at large distances it produces an electrostatic potential

\[ U(r) = \frac{e}{K r}, \quad (1.1) \]

where \( K \) is the static dielectric constant of the semiconductor, and \( r \) is the distance from the ion. If it is energetically favorable for the electron to occupy a relatively large orbit over which (1.1) applies, then there exists a "shallow" donor state.

This system may be described by the Schroedinger equation
\[ \left( -\frac{\hbar^2}{2m^*} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \right) F(r) = E F(r) \]  \hspace{1cm} (1.2)

where \( m^* \) is an appropriate effective mass. This equation is identical to the Schroedinger equation for the hydrogen atom except \( m^* \), the effective mass, replaces the free electron mass, \( m \), and \( K \) has been introduced into the potential energy term. The analogy with the hydrogen atom suggests the existence of a ground state and a spectrum of excited bound states of which the allowed energies are

\[ E(n) = -\frac{m^* (e^2/k)^2}{2\hbar^2 n^2} \]  \hspace{1cm} (1.3)

\[ n = 1, 2, 3, \ldots \]

The normalized ground state wave function is

\[ F(r) = \left[ \pi (a^*)^3 \right]^{-1/2} \exp \left[ -r/a^* \right] \]  \hspace{1cm} (1.4)

where

\[ a^* = \frac{\hbar^2 K}{m^* e^2} \]  \hspace{1cm} (1.5)

Using \( K = 12 \) (5) and any reasonable value for a scalar approximation to the anisotropic effective mass \( m^* \), values of \( a^* \), the "effective Bohr radius", greater than 14 Å are found. In comparing these values with the silicon, face-centered cubic lattice constant 5.43 Å, it is seen that the assumption that the electron spends most of its time in the region where (1.1) applies is justified.
In order to provide a detailed picture of donor states in silicon, both the anisotropy of electron effective mass and the detailed structure of the silicon conduction band must be considered. Silicon has six equivalent conduction band minima in k-space located at $(k_o,0,0)$, $(-k_o,0,0)$, ..., $(0,0,-k_o)$. In the region of any one of these conduction band minima the electron energy may be written in the form

$$E = \frac{\hbar^2}{2m_L} (k_z - k_o)^2 + \frac{\hbar^2}{2m_t} (k_x^2 + k_y^2)$$

(1.6)

where the longitudinal and transverse effective mass parameters have the values

$$m_L = 0.98m, \quad m_t = 0.19m.$$  

(1.7)

For the effective Hamiltonian corresponding to (1.6) $F(r)$ is found to satisfy an equation of the type

$$\left( -\frac{\hbar^2}{2m_t} \frac{\partial^2}{\partial z^2} - \frac{\hbar^2}{2m_t} \left( \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} \right) - \frac{e^2}{Kr} \right) F(r) = E F(r).$$  

(1.8)

Solutions to this equation have been found (10,12) using trial wave functions similar to hydrogenic eigenfunctions. The trial function is

$$C \exp \left( -\left( \frac{x^2}{A^2} + \frac{y^2}{A^2} + \frac{z^2}{B^2} \right)^{1/2} \right),$$

(1.9)
where C is a constant and the parameters A and B are used to minimize the energy. It is customary to label the solutions by the atomic notation of the hydrogenic functions into which they go when \( m_e = m_t \). Because of the six equivalent minima of the conduction band in silicon, the solutions exhibit six-fold degeneracy.

Kohn and Luttinger (12) have shown that this degeneracy is removed in the case of substitutional impurities (group V elements) by using symmetry arguments along with corrections made to the potential for small \( r \). Their calculations indicate the existence of singly, \( 1S(A_1) \); doubly, \( 1S(E) \); and triply \( 1S(T_1) \) degenerate levels associated with the lowest eigenvalue of (1.8). Recent experimental results (1) have been interpreted to mean that lithium has a tetrahedral site symmetry in silicon with a \( 1S(A_1) \) state lying \( 1.8 \pm .1 \text{ mev} \) above a \( 1S(E + T_1) \) state. The data of Aggarwai, et al., (1) also indicate that for lithium oxide in silicon there is a \( 1S(E + T_1) \) state lying \( 7.7 \pm .1 \text{ mev} \) above the \( 1S(A_1) \) state.

The theoretical predictions for the ground state level do not agree with experimental results for the group V donors. This is probably due to the neglect of effects in the vicinity of the donor nucleus. The agreement for the lithium ground state is much better because the small size of its ion \( (r = .60 \text{ A}) \) (14) and its small atomic number more closely approach the approximations made in developing the shallow donor theory. The observed and the theoretically predicted excited levels are in good agreement. In
Table 1 the donor energy levels theoretically predicted by Kleiner (10) are compared with those observed for arsenic and phosphorus by Bichard and Giles (3), for lithium by Franks (7) and for lithium oxide by Bell (2). For each listed donor, all other energy levels were placed relative to the $3P^\pm$ level ($n = 3$, $\ell = 1$, $m = 1$) for which the shallow donor theory was assumed valid. The relative spacings of the excited donor levels are approximately the same for all "shallow donors".

When lithium is introduced into silicon with a high oxygen content (greater than $10^{17}$/cc), the observed absorption spectrum is different from that of lithium in oxygen-free silicon (2, 7, 1). Pell (15) has determined from lithium precipitation measurements in silicon that lithium-oxygen donor complexes are formed. The model proposed for lithium oxide is described by

$$[\text{LiO}^+] \cdot C = [\text{Li}^+][0]$$

(1.10)

where $[\text{LiO}^+]$, $[\text{Li}^+]$ and $[0]$ are the lithium oxide, lithium and oxygen concentrations in silicon. $C$ is a dissociation constant with a room temperature value of approximately $10^{15}$. The room temperature concentrations are assumed to be frozen in during a rapid cooling to liquid helium temperatures. Although lithium oxide is probably the major product of the lithium oxygen interaction, other complexes may be present.

The group V-like absorption spectrum appearing in lithium-doped,
<table>
<thead>
<tr>
<th>STATE</th>
<th>ENERGY LEVELS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Theoretical</td>
</tr>
<tr>
<td>4P</td>
<td>-1.6</td>
</tr>
<tr>
<td>3P</td>
<td>-2.6</td>
</tr>
<tr>
<td>3P_o</td>
<td>-4.7</td>
</tr>
<tr>
<td>2P</td>
<td>-5.8</td>
</tr>
<tr>
<td>2P_o</td>
<td>-10.6</td>
</tr>
<tr>
<td>Ground State</td>
<td>-28.4</td>
</tr>
</tbody>
</table>

*Due to Aggarwal, et al.,(1)
oxygen rich silicon is assigned to lithium oxide donors (7). There are complex series of absorption peaks which also appear in these spectra that have not been properly explained.

Oxygen is introduced into pulled-from-the-melt silicon crystals by their interaction with the quartz crucible from which they are pulled.
III. EXPERIMENTAL DETAILS

A. Sample Characteristics

The oxygen content, crystal type, impurity concentrations, and thicknesses of the samples after doping are listed in Table 2. A 9μ resonance absorption measurement (9) was made on all samples. This technique is inaccurate for oxygen concentrations of less than 10^{17}/cc in silicon and unusable for concentrations of less than 10^{16}/cc. Only samples SE-1-D and SE-3-C had high enough oxygen concentrations for this technique to be of use. For the other samples estimates of the oxygen concentrations were inferred from the infrared absorption data in the 30 to 54 μ region. Resistivity measurements were made on the silicon samples using the four probe method, due to Valdes (17). Irvin's curves (8) for resistivity versus donor concentration were used to determine the donor concentrations.

B. Sample Preparation

The diffusion of lithium into the silicon samples was accomplished by submerging the samples with quartz sinkers in a tin-lithium bath at elevated temperatures. A dry helium atmosphere was maintained in the furnace during the diffusion process. Sample SE-1-D was doped by Bell (2). It was submerged in a tin-lithium bath contained in a pyrex glass container at a temperature of 730°K for 23 hours. The bath contained .25% lithium by weight. The sample was then
## TABLE 2
SAMPLE DATA

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal Type</th>
<th>Thickness (mm)</th>
<th>Oxygen Concentrations (cm⁻³)</th>
<th>Donor Concentrations (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S765A-4</td>
<td>Zone Refined</td>
<td>3.04</td>
<td>&lt; 10⁻¹⁴ *</td>
<td>7.5x10¹⁴</td>
</tr>
<tr>
<td>DC66-1</td>
<td>Zone Refined</td>
<td>2.59</td>
<td>&lt; 10⁻¹⁴ *</td>
<td>4.5x10¹⁴</td>
</tr>
<tr>
<td>GD-1</td>
<td>Zone Refined</td>
<td>3.62</td>
<td>&lt; 10⁻¹⁴ *</td>
<td>2x10¹⁵</td>
</tr>
<tr>
<td>NASA-1</td>
<td>Pulled From Melt then Zone Refined</td>
<td>2.46</td>
<td>&lt; 10⁻¹⁴ *</td>
<td>~3x10¹⁴</td>
</tr>
<tr>
<td>NASA-2</td>
<td>Pulled From Melt then Zone Refined</td>
<td>3.22</td>
<td>&lt; 10⁻¹⁴ *</td>
<td>-----</td>
</tr>
<tr>
<td>SE-1-D</td>
<td>Pulled From Melt</td>
<td>3.35</td>
<td>3.5x10¹⁷ **</td>
<td>2x10¹⁵</td>
</tr>
<tr>
<td>SE-3-C</td>
<td>Pulled From Melt</td>
<td>4.32</td>
<td>1.5x10¹⁷ ***</td>
<td>2.5x10¹⁵</td>
</tr>
</tbody>
</table>

* Inferred from infrared data and Pell's value for C in (1.10)
** Bell (2), 9μ technique
*** Franks (7), 9μ technique
submerged in a pure tin bath at the same temperature for 41 hours during which out-diffusion took place. The resulting lithium concentration was judged to be uniform to within 20%. Sample SE-3-C, doped by Franks (7), was submerged in a tin-lithium bath of .004% lithium by weight contained in a fused quartz container at a temperature of 900°C for 37 hours. Lithium was diffused into samples DC66-1, S765A-4 and NASA-1 by submerging the samples in a tin-lithium bath contained in a Vicor (quartz-pyrex mixture) container at 880°C for 50 hours. The lithium concentration was approximately $10^{19}$/cc. In the same manner, sample GD-1 was treated in a bath of lithium concentration of approximately $10^{20}$/cc. Sample NASA-2 contained no lithium. The diffusion times were long enough to assure a variation in uniformity of less than 10% according to calculations made using the method outlined by Boltaks (4). All single crystal silicon samples except for NASA-1 and NASA-2 had high resistivities when received, indicating little contamination. High purity tin and a very small amount of reactor-grade lithium were used. This, coupled with the exceptionally high diffusion rate of lithium in silicon, precluded any contamination of the samples during the lithium doping process.

Samples SE-1-D and SE-3-C were pulled from the melt and thus had high oxygen concentrations (greater than $10^{17}$/cc). Samples DC66-1 and S765A-4 were presumably float zone refined, but were expected by their respective suppliers (Dow-Corning and
Monosilicon Inc.) to contain around $10^{15}$/cc. Sample GD-1 was float zone refined in an inert atmosphere, and was expected by the supplier (General Diode Corporation) to have an intermediate oxygen concentration. Samples NASA-1 and NASA-2 were prepared for NASA by the General Diode Corporation. The boule from which they were taken was pulled from the melt and then had one zone refining pass made on it. The sample was doped with a phosphorus concentration of $9 \times 10^{14}$/cc.

Each sample was ground with parallel faces and a good polish. Samples S765A-4, DC66-1, NASA-1, NASA-2 and CD-1 were ground first with number 200-A and 600-A silicon carbide paper with water used as a lubricant. Except for sample S765A-4, these samples were then given a final polish on a buffing wheel using yellow rouge. A flat was ground on each sample for the copper constantan thermocouple used to monitor the sample temperature.
III. EXPERIMENTAL DETAILS

C. Experimental Procedure

The arrangement of sample, thermocouple, and sample holder is shown in Figure 1. A coat of silicone grease was placed between the sample holder and the dewar cold finger, between the sample and sample holder and between the sample and the thermocouple to enhance thermal contact. Sample temperatures as low as 150K were obtained using liquid helium as a coolant. The thermocouple was held in place by a spring as indicated.

A grating spectrometer previously described by Bell (2) was used in this investigation except for the 9μ measurements which were made at room temperature with a Perkin-Elmer Model 13 Spectrometer. The grating spectrometer was calibrated over the energy range 23.0 mev to 45.0 mev using water vapor absorption lines as determined by Randel, Dennison, Ginsburg, and Weber (16). The photon energy was expressed as a fourth order polynomial in terms of the grating drive scale reading with a standard error of .03 mev (2).

An Andonian Associates dewar model No. MHD-3L-15N was used in these experiments. In this dewar the cold finger is not attached to the helium well directly, but to a gas exchange column which runs through the helium well. When attempting to do an experiment at the lowest temperature possible, a quantity of the pressurized helium gas condensed in the gas exchange tube.
FIGURE 1

- Gas Exchange Tube
- Cold Finger
- Sample Holder
- Spring
- Sample
- Thermocouple
The area surrounding the sample was evacuated and the infrared radiation was admitted through cesium iodide windows. The dewar was placed so that the silicon sample faces were perpendicular to the infrared beam of the spectrometer. In order to reduce the effect of the strong water vapor absorption in this wavelength range, the system was purged with dry nitrogen gas (maximum moisture content .0012% by weight) one hour and 45 minutes prior to and during transmission measurements. Transmission measurements were taken first with only the sample holder in place and then with the sample in place.
III. EXPERIMENTAL DETAILS

D. Data Reduction

The intensity, \( I \), of the spectrometer beam after passing through the sample is

\[
I = \frac{I_0 (1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)}
\]  

(1.11)

where \( I_0 \) is the initial beam intensity, \( R \) is the surface reflectivity of the sample, \( t \) is the sample thickness, and \( \alpha \) is the sample absorption coefficient. This equation may be solved for \( \alpha \) yielding

\[
\alpha = \frac{-\ln\left[\frac{-I_0 (1-R)^2}{2IR^2} + \left(\frac{I_0 (1-R)^2}{2IR^2} + \frac{1}{R^2}\right)^{1/2}\right]}{t}.
\]  

(1.12)

The absorption coefficient will have two components, \( \alpha_i \) due to the impurity and \( \alpha_o \) due to the silicon crystal. Bell \cite{2} has found the absorption coefficient due to undoped silicon to be approximately .12/cm throughout the region of interest. This small contribution has not been subtracted from the calculated \( \alpha \)'s. A value of .3 \cite{17} has been used for \( R \) which is essentially constant throughout the region of interest.

The absorption coefficients were calculated for energy increments of .1 mev using an IBM 7040 computer. The background conditions were different at essentially every point scanned. This, coupled
with the low signal to noise ratio at absorption peaks, prevented a precise determination of the absorption coefficient \( \alpha \). A high polish is required to insure a sample reflectivity of 0.30. The effective reflectivities of samples SE-1-D, SE-2-C and S765A-4 were found to be .416, .45 and .5 respectively.

The positions of the centers of the absorption peaks are located to within \( \pm .1 \) mev. The relative intensities of the different absorption peaks cannot be known precisely since the magnitude of the absorption coefficient is not well determined.
FIGURE 2  ABSORPTION SPECTRUM OF SILICON SAMPLE DC66-1
FIGURE 5. ABSORPTION SPECTRUM OF SILICON SAMPLE SE-3-C, DUE TO FRANKS (7)

LITHIUM DOPED SILICON

OXYGEN CONCENTRATION $1.5 \times 10^{17}$/CC.
DONOR CONCENTRATION $4 \times 10^{16}$/CC.
TEMPERATURE 16°K.
SAMPLE AGE 7 DAYS
Figure 6. Absorption spectrum of silicon sample SE-3-C, due to Franks (7).
LITHIUM DOPED SILICON
Oxygen Concentration $1.5 \times 10^{17}$/cc
Donor Concentration $25 \times 10^{15}$/cc
Sample Temperature 15°K
Sample Age 3.5 Years

FIGURE 7 ABSORPTION SPECTRUM OF SILICON SAMPLE SE-3-C

Absorption Coefficient ($\text{cm}^{-1}$)

Photon Energy ($10^{-3}$ ev)

2P\text{\raisebox{-1pt}{\tiny$-$}}
2P\text{O}
3P\text{O}
3P\text{$\pm$}
4P\text{$\pm$}
IV. RESULTS AND CONCLUSIONS

The absorption spectra of lithium-doped silicon of high oxygen content are dominated by a group V-like spectrum attributed to lithium oxide. Considering for a moment only the lithium oxide and lithium and utilizing (1.10) and the equations of restraint

\[ [0] + [\text{LiO}^+] = N_o \quad (1.13) \]

\[ [\text{Li}^+] + [\text{LiO}^+] = N_L \quad (1.14) \]

an estimate of the relative amounts of isolated lithium and lithium oxide present in a sample can be made. \( N_o \) is the number of oxygen atoms and \( N_L \) is the number of lithium atoms as determined by resistivity measurements. The room temperature equilibrium concentration values are found using the room temperature value of \( C \) which equals \( 10^{15} \). These concentration values are assumed to be the values seen during a low temperature experiment. For a sample like SE-3-C with \( N_o \) equal to \( 1.5 \times 10^{17} / \text{cc} \) and \( N_L \) about \( 10^{15} / \text{cc} \), a calculation gives on the order of \( 10^{13} / \text{cc} \) for the [Li+]. The most prominent isolated lithium peaks occur at about 26.6 and 29.8 mev as can be seen in Figure 2. The peak appearing at about this point in the spectra due to lithium-doped, oxygen-rich samples (shown in Figures 5-10) is probably due to the isolated lithium transition from \( 1S(E+T_1) \), the ground state (1), to the \( 2P^z \) state. If \( N_o = 10^{15} / \text{cc} \) and
\( N_L = 10^{15} / \text{cc} \), then the \([\text{Li}0^+]\) would equal \(3.8 \times 10^{14} / \text{cc} \) and the 
\([\text{Li}^+]\) would equal \(6.2 \times 10^{14} / \text{cc} \). The spectrum due to both of these 
concentrations would be clearly discernible. For \( N_o = 10^{14} / \text{cc} \) and 
\( N_L = 10^{15} / \text{cc} \), the \([\text{Li}0^+]\) would be \(5 \times 10^{13} / \text{cc} \) which is probably 
detectable. Therefore, if there is oxygen present in concentrations 
greater than \(10^{14} / \text{cc} \), then after doping with lithium the \([\text{Li}0^+]\) should 
be detectable.

The spectra of samples S765A-4, DC66-1 and GD-1 showed only 
the absorption peaks due to isolated lithium in silicon. A spectrum 
of sample DC66-1 is shown in Figure 2.

The spectrum of sample NASA-1, shown in Figure 3, does not 
indicate the presence of lithium-oxygen complexes. Therefore it is 
 presumed that none of the oxygen present when this sample was first 
pulled from the melt survived the zone refining process in a form 
suitable for the formation of lithium-oxygen complexes.

The absorption spectrum of phosphorus-doped silicon, sample 
NASA-2, is shown in Figure 4. Samples NASA-1 and NASA-2 were taken 
from the same silicon boule. In Figure 3, the spectrum shown for 
sample NASA-1, which is doped with both phosphorus and lithium, 
seems to indicate a split in the phosphorus peaks normally occurring 
at 34.4 mev, \(2P_o\), and 39.2 mev, \(2P^+\). The split in these peaks 
seems to be \(0.8 \pm 0.1\) mev. These peaks do exhibit a similar splitting 
when subjected to uniaxial stress (l).
From the data on samples DC66-1, GD-1, S765A-4 and NASA-1, it is concluded that all zone refined single crystal silicon probably has an oxygen concentration of less than $10^{14}$/cc.

As indicated by Bell (2) and Franks (7) there is a narrowing of absorption peaks with time. This is especially noticeable over a short time interval after doping as indicated in Figures 5, 6, and 8. The data taken on samples SE-1-D, Figure 10, and SE-3-C, Figure 7, during this investigation do not show any large changes from the data taken several years before. As lithium precipitates into precipitation centers in the silicon, the lithium oxide will tend to dissociate (15) and more lithium will precipitate until equilibrium is reached. This reduction of the overall donor level will reduce concentration broadening. The oxygen concentration affects the solubility of lithium in silicon (15). In sample SE-3-C, with an oxygen concentration of $1.5 \times 10^{17}$/cc, the donor concentration decreased from $4.0 \times 10^{15}$/cc at 7 days, to $3.0 \times 10^{15}$/cc at 14 days (7), to $2.5 \times 10^{15}$/cc at 42 months. The donor concentration of sample SE-1-D with oxygen concentration of $3.5 \times 10^{17}$/cc has remained at $2.0 \times 10^{15}$/cc. This dissociation and precipitation process offers some explanation for the time and oxygen content dependence of the smaller peaks occurring in the spectra displayed in Figures 5-10. These peaks are thought to be due to other more complicated lithium-oxygen complexes.

The peak at 30.4 mev is, in sample SE-3-C, small at 7 days and
extremely small or gone at 14 days and at 3.5 years. In sample SE-1-D, with a higher oxygen content, the peak is very evident at 10 hours, 60 hours, 1 year and 4 years. The peak at 24.2 mev in sample SE-1-D does not appear in sample SE-3-C. As seen in Figure 7, after 3.5 years the peak appearing at 32.4 mev has almost disappeared although it is still present after a longer period of time in sample SE-1-D. The peak present at about 28.7 mev in spectra from sample SE-1-D is much larger than any corresponding peak in spectra due to sample SE-3-C.

It has been proposed \(^{(1)}\) that lithium oxide in silicon has a ground state, \(1S(A_{1})\), and a five-fold degenerate state, \(1S(E+T_{1})\), lying \(7.7 \pm .1\) mev above it. At low temperatures, all similar donors may be treated as a system having highly degenerate discrete energy levels \(^{(7)}\). This system will obey Boltzmann statistics \(^{(13)}\). The ratio of the occupation index of level \(i\) to level \(j\) will be given by

\[
\left( \frac{N_i}{N_j} \right) = \exp \left[ \frac{(E_j - E_i) + kT}{} \right], \tag{1.15}
\]

with \(N\), \(E\), \(k\) and \(T\) being the level degeneracy, level energy, Boltzmann's constant and the sample temperature, respectively. For \(E_j - E_i = 7.7\) mev and \(T = 20^\circ\)K the ratio is 17.6, at \(30^\circ\)K it is 3.94 and at \(40^\circ\)K it is 1.88. The peak occurring at 25.1 mev in sample SE-1-D and at 25.5 mev in sample SE-3-C is assigned to a \(1S(E+T_{1})\) to \(2P^\pm\) transition. Transitions from the \(1S(E+T_{1})\) state to excited
states are denoted in Figures 5-10 by underlined captions. For sample SE-3-C the ratios of the peak height at 25.5 mev to one at 23.7 mev, which does not vary much with temperature, are about one to two, one to one, and two to one at temperatures 160K, 200K, and 330K, respectively, as seen in Figures 5, 6, and 7. In sample SE-1-D, the ratio of the peak height at 25.2 mev to one at 24.2 mev at temperatures 200K and 300K are about one to one and two to one, respectively, as seen in Figures 8 and 10. This is about the temperature dependence expected if the peaks at 25.1 mev and 25.5 mev resulted from a $1S(E+T_1)$ to $2P^+$ transition. A transition from $1S(E+T_1)$ to $3P^+$ would fall slightly higher than the center of the $1S(E_1)$ to $2P_0$ peak at 28.1 mev and be superimposed on it.

The peak occurring at about 39.0 mev in Figures 5-10 is probably due to a small amount of phosphorus contamination.

It is not possible at this time to make definite assignments to the remaining peaks in the complex spectra resulting from lithium-oxygen complexes in silicon.

In order to observe unambiguous spectra from both isolated lithium and lithium oxide in the same sample, it will be necessary to obtain silicon with an oxygen concentration of about $10^{15}$/cc. Single crystal silicon with this oxygen concentration is not readily available. It could be prepared by introducing oxygen into the furnace while a silicon boule is being zone refined. To develop the technique needed for this process would probably require
extensive experimentation on the part of the supplier. It should
be noted that a comparison of the relative intensities of the ab-
sorption peaks due to the isolated lithium and lithium oxide would
provide a test for the oxygen content of silicon in a range from
$10^{14}$/cc to $10^{17}$/cc.

The indicated splitting of the phosphorus peaks in sample
NASA-1 suggests other experiments. Absorption spectra of lithium-
doped and phosphorus-doped zone refined silicon with various ratios
of lithium to phosphorus should be taken along with spectra for
silicon doped with lithium and other group V elements.
V. ACKNOWLEDGEMENTS

The author would like to express his appreciation to the many persons who contributed to this research. Dr. T. E. Gilmer, Jr., guided the author in all phases of the study, Dr. T. E. Leinhardt supplied the necessary refrigerants, R. J. Dexter provided laboratory assistance and C. J. Whidden prepared many of the figures.

The author wishes to express his gratitude to his wife, Lynne, without whose help this work could not have been completed.
VI. BIBLIOGRAPHY


VII. VITA

The author was born in Washington, D. C. on May 16, 1941. He graduated from Washington-Lee High School, Arlington, Virginia, in 1959. In June, 1963 he received the B.S. degree in physics from Virginia Polytechnic Institute where he then began his graduate study.

[Signature]

[Signature]

[Signature]
AN INFRARED ABSORPTION STUDY OF LITHIUM IN SILICON

by

John Herbert Wood

ABSTRACT

Lithium, lithium oxide and the group V elements, phosphorus, arsenic, antimony and bismuth, when present in silicon as impurities, act as "shallow" donors (2, 7, 11). These donors have electrons which are bound so loosely that they may be thermally excited into the conduction band at less than room temperature. The excited bound states and, less precisely, the ground states of these electrons are understood within the framework of the shallow donor theory.

A transition from the 1S(E+T1) state of lithium oxide, which lies 7.7 ± 0.1 mev above its ground state, to the 2Pz state was observed. When phosphorus and lithium were both present as donors in silicon, the phosphorus peaks normally occurring at 34.4 mev, 2P0, and 39.2 mev, 2P+, seemed to be split by 0.8 ± 0.1 mev. An upper limit of 10^{14}/cc was observed for the oxygen content of zone refined silicon using Pell's (15) value for the dissociation constant, C.