Study of Beryllium and Beryllium-Lithium Complexes in Single-Crystal Silicon

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When beryllium is thermally diffused into silicon, it gives rise to acceptor levels 191 and 145 meV above the valence band. Quenching and annealing studies indicate that the 145-meV level is due to a more complex beryllium configuration than the 191-meV level. When lithium is thermally diffused into a beryllium-doped silicon sample, it produces two new acceptor levels at 106 and 81 meV. Quenching and annealing studies indicate that these new levels are due to lithium forming a complex with the defects responsible for the 191- and 145- meV beryllium levels, respectively. Electrical measurements imply that the lithium impurity ions are physically close to the beryllium impurity atoms. The ground state of the 106-meV beryllium-lithium level is split into two levels, presumably by internal strains. Tentative models are proposed to explain these results.

INTRODUCTION

Group-II impurities such as zinc and beryllium have been studied in germanium,[1-3] and have been found to produce acceptor levels which, to a first approximation, can be described by a helium model. The group-II impurities, magnesium and beryllium, have been studied in silicon.[4-8] It is interesting to note that the magnesium produces n-type silicon and occupies an interstitial lattice site, while beryllium produces p-type silicon and is, therefore, believed to occupy a substitutional lattice site. Magnesium introduces two related donor states described by a helium model. Beryllium introduces two independent acceptor states, which are separated by about 40 meV, neither of which seem to have the associated deeper level expected for the helium model. (While it is uncommon for an impurity to produce two independent levels, beryllium is not unique in this respect since sulfur introduces at least two independent donor levels.[9,10]) When lithium is introduced into a beryllium-doped silicon sample, two new series of infrared absorptions are found at energies closer to the valence band edge, indicating lithium forms a complex with the beryllium.

A study of the electrical and optical properties of beryllium and beryllium-lithium complexes in silicon was made to understand better the unusual properties associated with these impurities. The results of this study are presented and discussed in this paper. Tentative models for the two beryllium and the two beryllium lithium impurity sites are proposed.

DESCRIPTION OF EXPERIMENT

Optical Studies

Both Czochralski and floating-zone-refined single-crystal silicon were used in preparing the test samples. Table I lists each sample reported, along with its method of growth, predominant impurity, resistivity prior to and after doping, doping time, and temperature. The samples were polished disks 25.4 mm in diameter, and the thickness varied from about 0.5 up to 3.0 mm. Infrared absorption spectra were obtained over a range from 1.0 to 50 μ using two grating spectrophotometers. A Cary model No. 14 was used for the 1.0–2.5-μ range, and a Perkin-Elmer model No. 621 was used for the 2.5–50-μ range. Both instrument were purged by dry air during all runs.

Sample temperatures during infrared spectroscopy were less than 20 °K unless otherwise noted on the figures. The low temperature of the samples was attained through the use of a liquid-helium Dewar in which a copper sample holder was in contact with the cryogenic liquid. The temperature of the sample was not controlled in most cases and varied from around 8 to 20 °K depending upon the impurity concentration, thickness of the sample, and grade of thermal contact. Sample temperatures were measured with a germanium resistance thermometer.

Absorption spectra are presented in terms of percent transmission rather than absorption coefficient since the absorptions are very strong in most cases, and errors in percent transmission (up to 5 units) would lead to large errors in absorption

TABLE I. General information about samples. Information in columns 3–5 was supplied by manufacturer.

Sample identification	Data presented in figure number	Growth technique	Major impurity prior to doping	Resistivity prior to Be doping (Ω cm)	Be doping Time (h)	Be doping Temp. (°C)	Resistivity after Be doping (Ω cm)
269–4	1, 2	Floating-zone	B	100	1	1300	0.3
X–9	3, 5(b), 6	Floating-zone	P	100	1	1300	0.25
858–13	5(a)	Floating-zone	P	800	1	1300	Could not be measured
Ox–11	7	Czochralski	B	140	2	1320	Could not be measured
X–10	8, 9	Floating-zone	P	100	1	1300	0.2
Ox–4	10	Czochralski	B	140	2	1340	0.4
422–14	11	Floating-zone	B	2600	$1\frac{1}{4}$	1340	0.2
957–23	12	Floating-zone	B	380	1	1300	0.5

coefficient.

Electrical Measurements

Samples for the electrical measurements were cut in the standard bridge shape. Contacts to the samples were made by sputtering aluminum on the tabs and annealing at 600 °C for 15 min to form a eutectic bond between the aluminum and silicon. The leads were soldered to the aluminum-coated tabs with indium solder and a Tesla coil was arced to each tab to help break down any rectifying contacts that still remained. Resistivity and Hall voltage were measured in a manner essentially the same as that described in Ref. 11. The magnetic field used for the Hall measurements was 2740 G.

The resistivity of the optical samples prior to polishing was measured by a four-point probe as explained by Valdes.[12] The resistivity of some optical samples was not measured due to difficulty in establishing good electrical contacts.

Doping Procedures

Beryllium. Beryllium was thermally diffused into the silicon using the "sandwich" method.[4] A layer of beryllium was vapor deposited onto each silicon wafer. Two or more wafers were stacked with the plated sides adjacent and placed in a helium environment at temperatures of 1300 to 1340 °C for 1 to 2 h (see Table I). The wafers were welded together during the doping and had to be sawed apart.

Lithium. The most efficient way to introduce the lithium was to plate a silicon wafer on both sides with lithium and sandwich this wafer between two beryllium-doped wafers. The sandwich was placed in a helium environment and heated to 600 °C for 30 min. The two outer wafers were then turned over and heated for another 30 min. The lithium-

plated wafer was then removed, and the two doped wafers were annealed at 600 °C for 30 min to assure a more uniform doping.

Annealing and Quenching Procedures

Samples to be annealed were placed between two high-purity wafers of silicon in a furnace with a helium environment. This was done to reduce surface chemical reactions between stray impurities in the system and the doped sample.

For quenching, the samples were held against the end of a graphite cylinder by means of a reduced pressure inside the cylinder. A thermocouple was placed against the silicon to monitor temperature. This system was placed in a cylindrical quartz tube with nitrogen gas flowing by the sample. The graphite was heated by means of an rf heater until the wafer reached the desired temperature where it was held for about 3–5 min and dropped into a liquid-nitrogen bath. In all cases the samples were brought back to room temperature before mounting in the cryostat for absorption measurements.

RESULTS AND DISCUSSION

Beryllium

When beryllium is thermally diffused into silicon, the resultant p-type material has an ionization energy of about 170 meV as determined from Hall-effect measurements. The parameter plotted in Fig. 1 is derived from Hall-coefficient calculations and the slope of the curve in the higher-temperature region gives a direct value for the ionization energy. Hall mobility
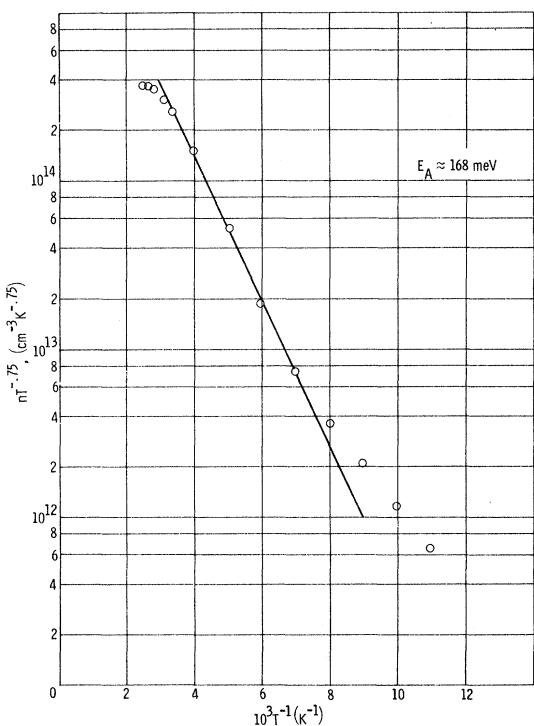
$$\mu_H = R_H/\rho \tag{1}$$

FIG. 1. Parameter involving carrier concentration and temperature as a function of temperature for beryllium-doped silicon.
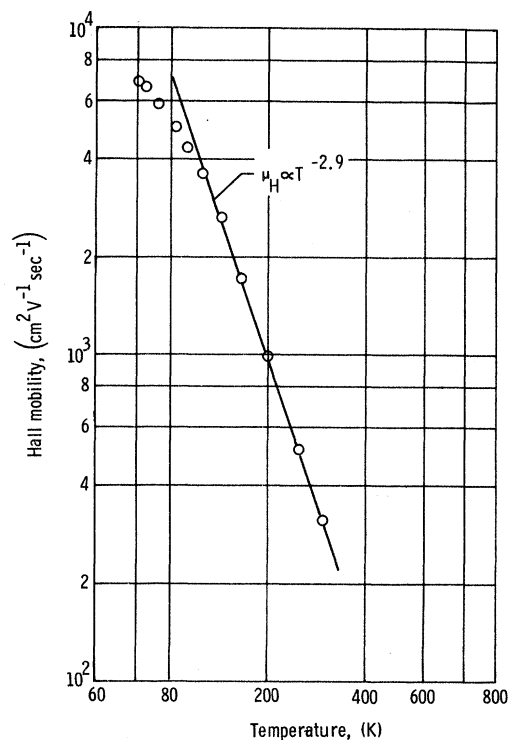
FIG. 2. Hall mobility as a function of temperature for beryllium-doped silicon.

as a function of temperature typically looks like that shown in Fig. 2.

The mobility is primarily controlled by phonon scattering down to a temperature around 80 °K. When silicon is heavily compensated (on the order of 10^{16} cm^{-3}), the mobility is primarily controlled by phonon scattering down to temperatures of only 100 °K or greater; therefore, the beryllium is typical of a p-type impurity with low or moderately

low compensation levels. The room-temperature mobility values are typical of p-type material with a resistivity of 0.1–0.4 Ω cm.

Absorption studies in the infrared region of beryllium in silicon at low temperatures show that there are two series of sharp absorptions, located around 1450 and 1080 cm^{-1} (labeled set I and set II, respectively) and a single broad absorption centered on 500 cm^{-1} (see Fig. 3). The spacing be-
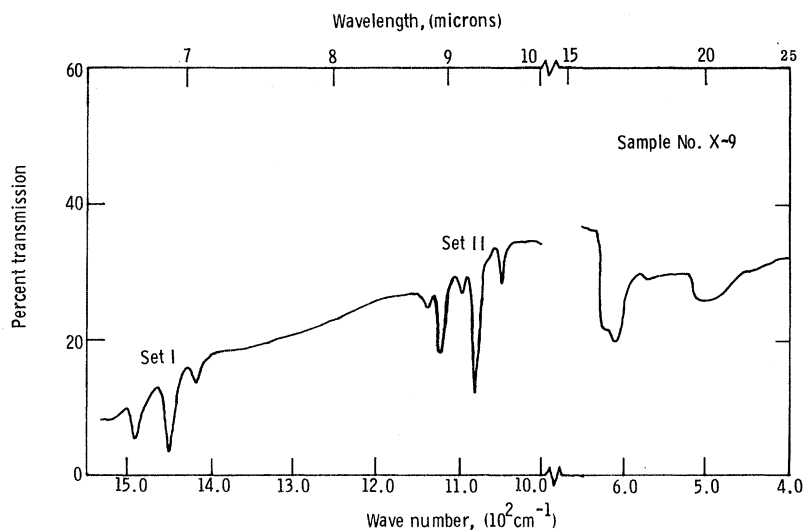
FIG. 3. Typical beryllium spectrum showing set I and set II absorptions and the broad absorption band at 500 cm^{-1}.
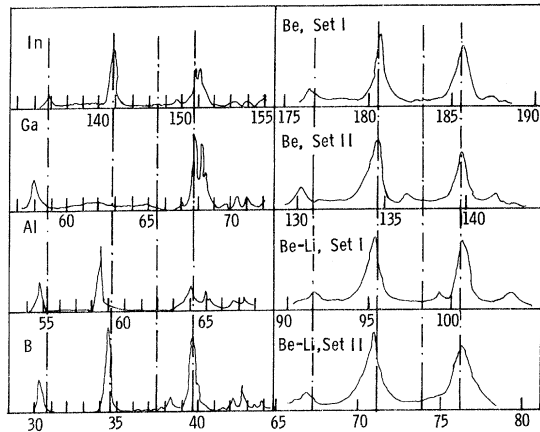
FIG. 4. Absorption spectra of group III impurities and the beryllium-associated impurities. (a) Lines associated with shallow acceptors (Ref. 17); (b) lines associated with beryllium complexes. Vertical lines indicate the predicted location of lines using effective-mass theory. All abscissa values are energy in meV; all ordinate values are schematic representations of relative absorption intensities.

FIG. 5. (a) Temperature dependence of absorptions due to set I beryllium. (b) Temperature dependence of absorptions due to set II beryllium.

tween absorptions is typical of the spacings observed for shallow acceptors in silicon as seen in Table II and Fig. 4. If shallow-acceptor theory is applied, these two series correspond to ionization energies of 191 and 145 meV, respectively. This is in acceptable agreement with the value obtained from the Hall measurements.

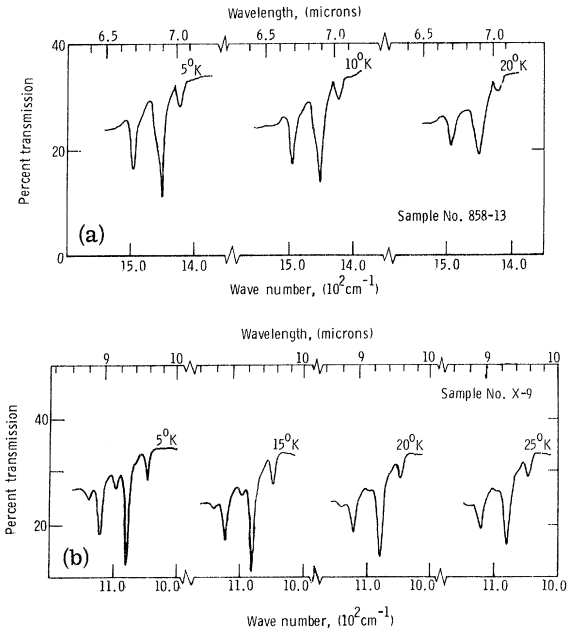As the temperature of the sample is raised, the

set I and set II lines broaden quite rapidly as shown in Figs. 5(a) and 5(b). Resolution of the lines above 100 °K was not possible. However, the broad line at 500 cm^{-1} does not seem to change very much with temperature, indicating that it is probably a localized impurity vibrational absorption associated with one

TABLE II. Energy location and spacings of lines in typical beryllium and beryllium-lithium spectra.

Line number	Boron	Indium	Beryllium, set I[a]	Beryllium, set II[a]	Be + Li, set I[a]	Be + Li, set II[a]
			Energy location of lines for various impurities (meV)			
1	30.38	141.99	176.6	130.2	91.8	67.0
2	34.53	145.79	180.3	134.4	95.1	70.8
3	38.35	149.74		136.4	99.1	
4	39.64	150.80	185.6	139.7	100.4	76.1
	39.91	151.08				
5	41.52	(152.8)				
6	42.50	153.27				
7	42.79			141.9	103.0	
			Energy spacings between lines (meV)			
Δ12	4.15	3.80	3.7	4.2	3.3	3.8
Δ23	3.82	3.95		2.0	4.0	
Δ24	5.11	5.01	5.3	5.3	5.3	5.3
Δ47	3.15			2.2	2.6	

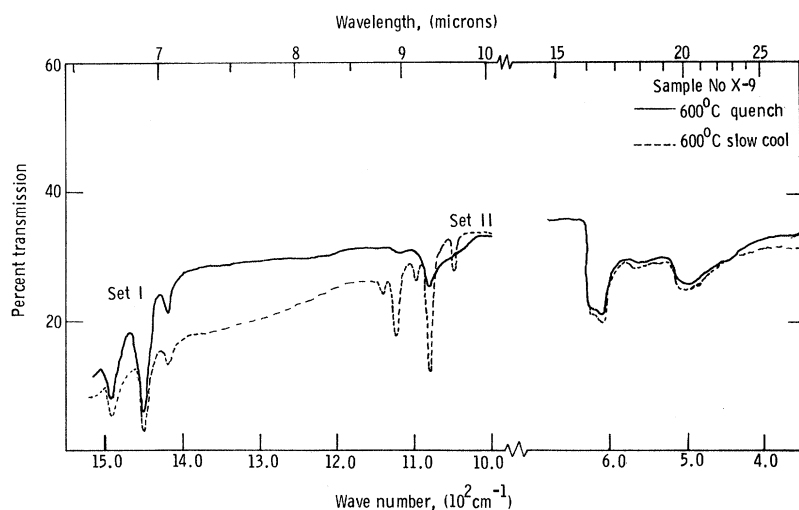[a]Line designations are arbitrary.

FIG. 6. Effects of quenching and annealing on set I and set II beryllium.

of the beryllium centers.

As seen in Table II, the spacings of the major lines in the set I and set II absorptions are quite similar. The set II series is always weaker than the set I, never having an absorption intensity greater than about one-third that of set I. When a beryllium-doped sample is quenched from a temperature greater than about 600 °C, the set II series is drastically reduced or disappears while the set I and 500-cm^{-1} lines increase slightly (Fig. 6). When a sample is slowly cooled (on the order of 2 h) from 600 °C to room temperature, the set II series absorption is increased to its maximum value relative to set I. Set I and the 500-cm^{-1} lines are slightly decreased in strength (Fig. 6).

It might be noted that beryllium is not unique in introducing more than one independent impurity level spectrum. Sulfur, when introduced into silicon, gives rise to four donor levels, at least two of which are unrelated (i.e., not the second level of a "helium" model), and whose relative absorptions are dependent on temperature histories (Refs. 9 and 10).

Figure 6 indicates that the 500-cm^{-1} band is associated with the set I impurity vibration since it generally tends to follow the behavior shown by set I under quenching and annealing. When a beryllium-doped sample is annealed (held at constant temperature for various times) at temperatures greater than 1000 °C, the set I and 500-cm^{-1} absorptions decrease at about the same rate, so that after about 4 to 6 h they both completely disappear due to out diffusion of the beryllium.

When beryllium is introduced into Czochralski-grown silicon (oxygen content typically 10^{18} cm^{-3}), the 9-μ absorption associated with interstitial oxygen completely disappears (Fig. 7). The beryllium spectra appear to be no different from that for the float-zone silicon (oxygen content less than

10^{16} cm^{-3}). Even after annealing for several hours to remove all the optically active beryllium, the 9-μ oxygen line is never fully recovered (i.e., the interstitial oxygen content in a position giving rise to the 9-μ line remains less than 0.1 its original value).

Beryllium-Lithium Complexes

When lithium is thermally diffused into silicon, it normally occupies an interstitial position and gives rise to a donor level. It is expected that lithium would compensate the beryllium impurities and allow study of the singly ionized beryllium states, expected if beryllium could be described by a helium model. After the lithium was introduced into beryllium-doped silicon by diffusion for 1 h at 600 °C, the samples were still p type. Calculations from Hall data (Fig. 8) indicated that the holes were
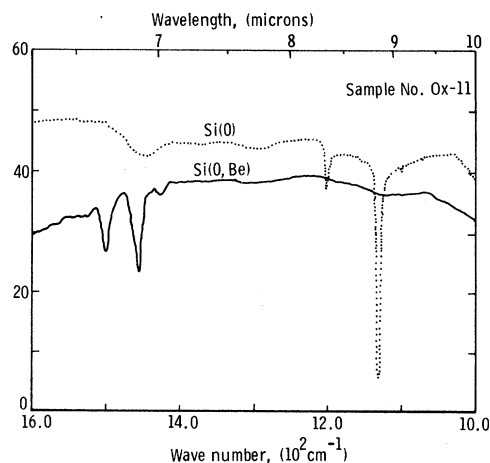

FIG. 7. Effect of beryllium on oxygen in Czochralski-grown silicon.
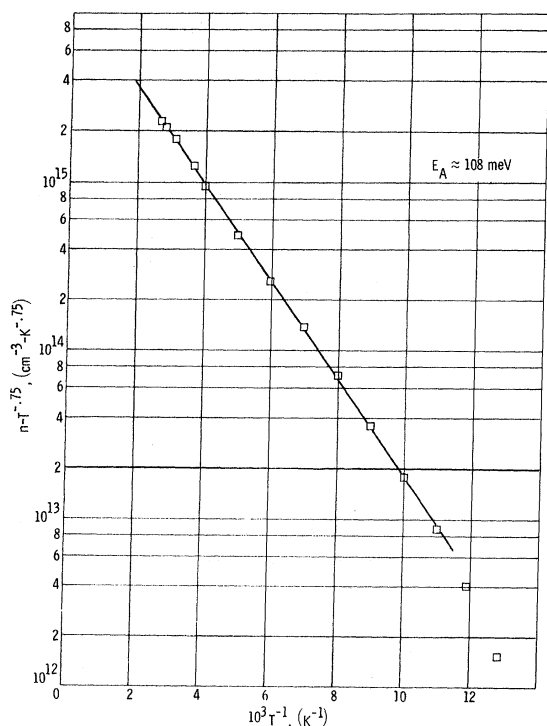
FIG. 8. Parameter involving carrier concentration and temperature as a function of temperature for beryllium–lithium doped silicon.

bound in a level with an ionization energy E_A of about 110 meV. This may be compared with ionization energies which would be expected from com-
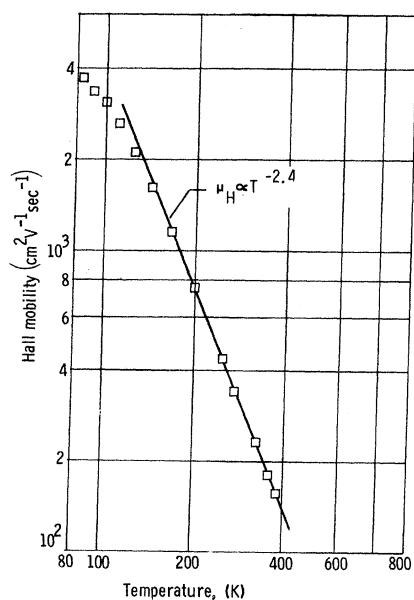

FIG. 9. Hall mobility as a function of temperature for a beryllium–lithium sample.

pensation of the helium model, viz., energies about 4 times deeper than the first level or around 800 meV. The mobility data shown in Fig. 9 exhibited very little of the ionized impurity scattering which would be expected for a highly compensated sample; in fact, the mobility in Be + Li samples was essentially the same as for comparably doped beryllium samples.

The suspicions that the introduction of lithium had not merely compensated the beryllium were verified when the infrared spectrum of a beryllium-lithium-doped sample was observed. As shown in Fig. 10, two new series of acceptorlike absorptions were observed at ionization energies corresponding to 106 and 81 meV, respectively. The previously observed Be spectra were still there. In addition, the absorption around 500 cm^{-1} was asymmetric and had its minimum value at about 516 cm^{-1}.

The spacings between the lines of all four excited-state series are almost identical (cf. Table II). After quenching a Be + Li sample from 600 °C or greater, the set II absorptions are greatly reduced while the set I Be + Li absorptions increase a little (see Fig. 11). Similarly, with a slow cool from 600 °C, the set II Be + Li absorptions are increased while the set I decreases very little.

As with the beryllium samples, the absorptions associated with Be + Li broaden rapidly with increasing temperature and are unresolvable at temperatures greater than about 60 to 70 °K. However, as the sample temperature is increased, another series of lines appears which is displaced from the set I Be + Li series by about 1.2 meV (see Fig. 12). The absorptions associated with set II Be + Li do not seem to broaden as rapidly and do not show the second series. The appearance of the small absorptions in the set I Be + Li is consistent with what would be expected if the fourfold
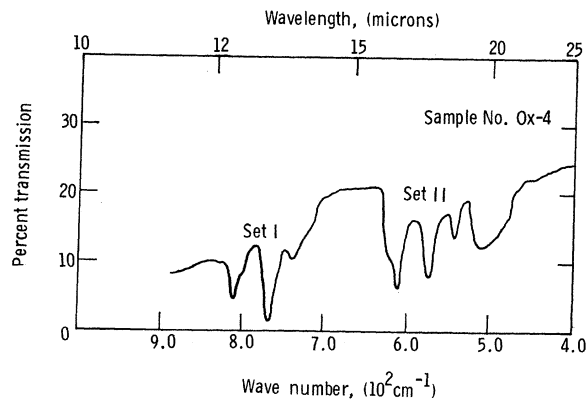

FIG. 10. Typical spectrum showing set I and set II beryllium–lithium absorptions. Czochralski-grown silicon sample.
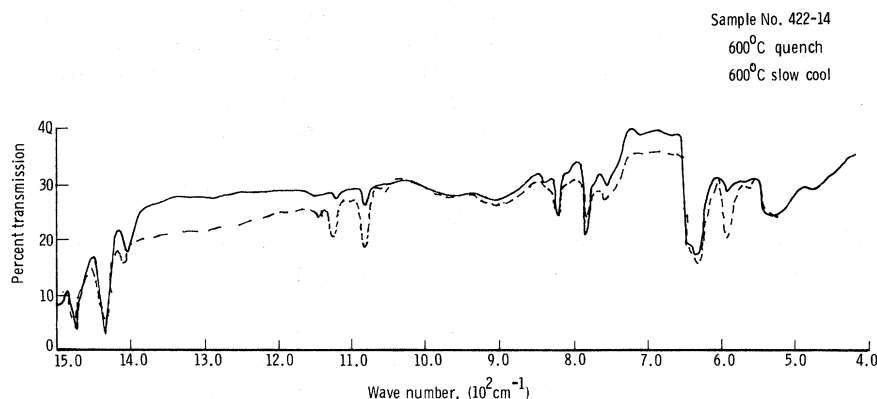
FIG. 11. Effects of quenching and annealing on set I and set II beryllium-lithium absorptions.

degenerate ground state were split into two levels separated by 1.2 meV. As the temperature is raised, the upper level is populated by thermal excitation of the holes, and the transitions to the excited states can then be observed.

When lithium is introduced into a beryllium-doped Czochralski silicon sample, the Be + Li spectra are essentially the same as for the floating-zone-refined material. The spectra for a Czochralski sample are shown in Fig. 10. The set II Be + Li lines are broad and are in the vicinity of strong lattice absorptions which make accurate determination of the spacings very difficult.

PROPOSED MODELS

Beryllium

The very fast diffusion rate of beryllium in silicon indicates interstitial diffusion and leads one to expect beryllium to be an interstitial impurity. However, the addition of beryllium produces p-type silicon which indicates that the electrically active beryllium is in a substitutional position. Mass-spectroscopy data shows that only about 10% of the beryllium contributes to the change in electrical and optical properties (Ref. 13). It is believed that the other 90% of the beryllium is located in neutral sites, most likely close substitutional-interstitial beryllium pairs which would behave as neutral impurities. It appears that the beryllium diffuses interstitially but is trapped in the vacancies which are abundant at the doping temperature of 1300 °C. When the beryllium is introduced into Czochralski-grown silicon, the interstitial beryllium interacts with the interstitial oxygen to form an interstitial BeO molecule. The bond energy of the BeO and the Si-Si bonds exceeds that of the Si-O-Si bonds making the formation of the interstitial BeO energetically favorable.

Set I. If a beryllium impurity atom were located on a substitutional lattice site, it would satisfy two of the covalent bonds with nearest-neighbor silicon atoms. The remaining covalent bonds would capture electrons, but the entire center would remain neutral by binding two holes to the Be⁻⁻ center on the lattice site. The holes would be several atomic diameters away and would be described in a simple way by effective-mass theory for a helium model. Therefore, when one of the holes is raised to an excited state, the absorption spectra should look essentially like that of a group III shallow acceptor. This is presumably what gives rise to the set I absorptions. In the present context, the beryllium atom is significantly smaller than the silicon atom. According to the theory of Morgan (Ref. 14), this smaller atom will have a large local strain field associated with it which produces ground states much deeper than predicted by effective-mass the-
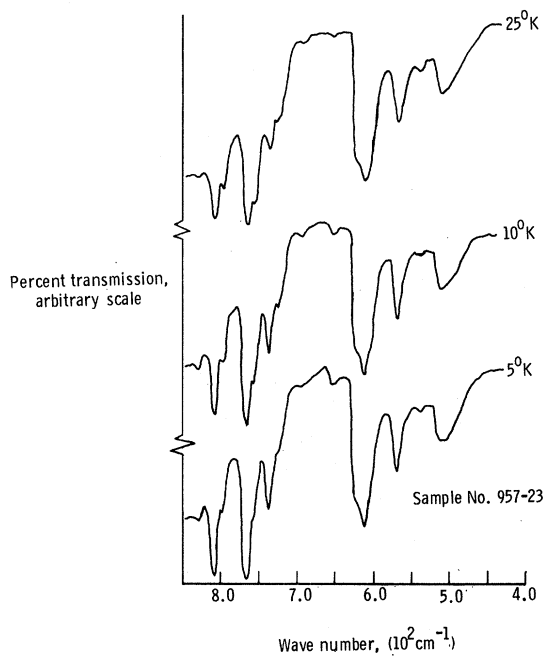

FIG. 12. Temperature dependence of set I and set II beryllium-lithium absorptions.

ory.

When one of the holes is freed, leaving an ionized center, simple theory would predict that the second hole should be observable at an energy somewhere around 4 times that required to free the first hole. This type of behavior has been observed for the donors magnesium (Ref. 7) and sulfur (Refs. 9 and 10) in silicon and the acceptor zinc in germanium (Ref. 2). In the case of beryllium, however, no such second level has been observed in this region. However, one can explain the absence of the second series of absorptions associated with the set I as follows. When the first hole is freed from the heliumlike model, the second hole will be pulled into a smaller orbit. When the orbit becomes smaller, the concept of a dielectric continuum used in effective-mass theory becomes inaccurate. The screening now seen by the hole is much less than before, resulting in a much more tightly bound hole than predicted by effective-mass theory. In addition, a short-range potential, "central-cell potential," would be much more effective for a hole located close to the impurity site, and large values of this potential would result in more tightly bound holes. In a theoretical paper, Ryabokon and Svidzinskii (Ref. 15) state that for group II impurities, "... the effective short-range potential turns out to be more effective in them and leads to quite large level shifts.... Furthermore, some of the deep impurity levels in silicon fall inside allowed energy bands." Thus, it seems possible for beryllium to be in a substitutional site, even though the second hole is not observed as predicted by the helium model.

Set II. When beryllium-doped silicon is quenched from high temperatures, the set II absorptions are greatly reduced or disappear, and the set I absorptions are enhanced. After a slow cool, the set II absorptions are much stronger, and the set I are slightly reduced. This seems to indicate that the set II absorptions result from a more complex arrangement than set I, and that set I absorptions are due to a component of impurities giving rise to set II. It seems that the simplest model for the set II absorptions are two beryllium atoms on nearest-neighbor lattice sites. This configuration would be somewhat similar to the divacancy bonding configurations, but less complex. As the temperature of the sample is raised, the thermal energy of the impurity is such that the set II sites are broken up into two set I sites, that is, two substitutional beryllium sites. This causes the weaker set II and stronger set I absorptions after a quench. When the sample is slowly cooled, the beryllium atoms presumably tend to aggregate to relieve crystal stresses around the small beryllium impurity; thus, more pairs are formed, and set II absorptions are stronger after a slow cool. Again, the

second hole associated with this model might not be observable in the band gap.

These two models seem to be consistent with the optical and electrical data.

Beryllium and Lithium

Set I. When lithium is introduced into beryllium-doped silicon, an acceptor level with almost identical spacings to the set I beryllium spectrum is observed, but with the binding energy of the hole reduced by about 80%. It is believed that the lithium goes into one of the nearest-neighbor-interstitial tetrahedral sites (Ref. 16), and its valence electron satisfies one of the unsatisfied covalent silicon bonds. The lithium in this position would reduce the local strain field thus resulting in a lower ionization energy (Ref. 14). While the short-range effects of the lithium are apparently large, the long-range effects should be quite small; therefore, the excited-state spectra should be essentially unaffected. Similarly, if the lithium is located in the immediate vicinity of the beryllium impurity, the ionic scattering from the complex center would be less than if the spacing were large. That is, the beryllium + lithium center would be essentially a monovalent acceptor site.

As pointed out earlier, there is an apparent splitting of the ground state for the loosely bound hole in Be + Li samples. If the lithium is in the immediate vicinity of the beryllium, the interaction between the beryllium and lithium ions would most likely be directed along a bond or $\langle 111 \rangle$ axis. In effect, this would be equivalent to a uniaxial stress applied in the $\langle 111 \rangle$ direction. As reported by Onton *et al.*, a $\langle 111 \rangle$ stress causes the ground state for a monovalent impurity with T_d symmetry to split into two levels (Ref. 17). Since these stresses are local, the excited states would not be split. This model is in agreement with observations.

Set II. When lithium comes into the vicinity of the set II beryllium, its valence electron again goes into one of the unsatisfied silicon convalent bonds, removing what would correspond to the deep hole. The result, as before, would be to reduce the binding energy of the remaining hole. The mobility would not be affected by this configuration because no new ionic scattering centers have been introduced.

SUMMARY

Beryllium as an impurity in silicon gives rise to two acceptor levels with associated excited states, referred to as set I and set II. The ratio of the absorption coefficients between set I and set II can be changed by quenching or annealing. Analysis of these studies indicates that the set II absorptions are due to an impurity complex, and that the set I

absorptions are due to a component of the set II complex.

When lithium is introduced into the beryllium-silicon system, it gives rise to two new acceptor levels. These levels behave under quenching and annealing just like the set I and set II beryllium levels. The set I Be + Li ground state is split into two levels.

The following models, which seem to be the simplest impurity configurations that agree qualitatively with all the observations, are proposed for these four defects:

(a) *Beryllium—Set I*. This defect is a single substitutional beryllium impurity. The second hole of a heliumlike model is so deeply bound that it is not found in the region predicted by shallow acceptor theory.

(b) *Beryllium —Set II*. This defect is made up of two beryllium atoms on nearest-neighbor substitutional sites. Again, a deep hole may be associated with the level; but the hole could be so deeply

bound that it falls inside the allowed energy bands.

(c). Be + Li—*Set I*. The lithium ion is trapped in the immediate vicinity of the set I beryllium and removes the deep hole. The symmetry of the impurity site is reduced, resulting in the reduction of the degeneracy of the ground state and the splitting of this level.

(d). Be + Li—*Set II*. The lithium is trapped in the immediate vicinity of the set II beryllium site and removes the deep hole as in set I, but the ground-state degeneracy is not reduced due to the different symmetries associated with the set I and set II beryllium sites.

ACKNOWLEDGMENTS

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