

## Infrared Spectroscopy of Divacancy-Associated Radiation-Induced Absorption Bands in Silicon<sup>†</sup>

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Defect infrared-absorption bands induced by fast neutrons in *n*-type, *p*-type, and intrinsic silicon were investigated by the piezospectroscopic method. The divacancy-associated bands at 1.8 and 3.3  $\mu$  together with two sharp subbands at 3.45 and 3.61  $\mu$  were observed in all types of Si when the measurements were made below 150 °K. When measurements were made at 300 °K the 1.8- $\mu$  band was observed in all samples while the 3.3- $\mu$  band was observed only in *n*-type Si. The 3.9- $\mu$  band which has been identified to be associated with the +1 charge state of the divacancy defect was not observed. Detailed temperature-dependence studies of the fine structures of the 3.3- $\mu$  band give no evidence of phonon structure. The fine structures of the 3.3- $\mu$  band are not associated with a single -2 charge state of the divacancy as previously reported but rather are due to three different optical transitions. We conclude that the charge state of the divacancy defect responsible for the observation of these bands is not the same everywhere in the sample. Detailed low-temperature-stress studies of the absorption bands utilizing polarized light lead to large dichroism and small splitting for the 3.4- and 3.61- $\mu$  sharp bands, with smaller dichroism and large splitting for the 1.8- $\mu$  band. Stress-induced splitting of the bands at 78 °K leads to a confirmation of the model of the divacancy defect deduced from electron-paramagnetic-resonance (EPR) studies by Watkins and Corbett. In terms of a one-electron molecular-orbital model of energy levels the bands at 1.8, 3.45, and 3.61  $\mu$  are identified as associated with the *X*-*Y* dipole-moment transitions. The 3.3- $\mu$  band arises from an optical transition due to ionizations of electrons from the weak-orbital-bonding state to the nearest conduction-band edge.

### I. INTRODUCTION

In the past decade a new and interesting tool has begun to be applied to the study of some of the radiation-induced-defect centers, and has resulted in a considerable increase in the understanding of the symmetry properties of defect centers. The new tool involves the use of the stress-induced realignment and stress-induced splitting in the optical and electron-paramagnetic-resonance (EPR) spectra of the defect centers. The energetic nonequivalence of different orientations of the defect centers whose symmetry is lower than cubic symmetry, the so-called anisotropic centers in the stressed crystal, can lead to a nonuniform distribution (by reorientation) of the centers. This reorientation of either electronic or atomic distributions can lead to an explanation of the configuration of the defect center, and the stress-induced splitting can lead to a determination of the symmetry of the defect in semiconductor crystals. Therefore, the microscopic nature of the defect centers can be understood by studying their response to stress.

Extensive studies of the divacancy defect in silicon have been carried out utilizing EPR,<sup>1</sup> infrared (ir) spectroscopy,<sup>2-6</sup> and photoconductivity<sup>4,7</sup> as the measurement probes. However, there are still several questions left unanswered, especially the correlation of the charge states associ-

ated with the various ir-absorption bands. The 3.3- $\mu$  band which was identified<sup>3</sup> as being associated with the -2 charge state of the divacancy defect actually consists of a broad band with two distinguishable sharp subbands at 3.45 and 3.61  $\mu$ . Cheng and Vajda<sup>6</sup> have reported that they observed different dichroism for these two sharp bands under the effect of polarized light at low temperature. They also observed that the activation energy for the 3.3- $\mu$  band agrees with that of the negative charge state of the divacancy defect reported by Watkins and Corbett.<sup>1</sup> In addition to the different dichroism between two sharp bands, Chen *et al.*<sup>5</sup> have also observed different shifting and splitting of the two sharp bands under the effects of uniaxial compressive stress at 78 °K. This leads us to ask, "Are the broad band and two sharp bands associated with the same charge state and the same defect? If not, what are they?"

According to the photoconductivity study of the divacancy defect using the stress-induced dichroism technique, Cheng<sup>4</sup> has concluded that the 3.9- $\mu$  (0.32-eV) photoconducting band is equivalent to the 3.9- $\mu$  ir-absorption band associated with the "b" transition according to the Watkins-Corbett<sup>1</sup> divacancy model given in Fig. 1. However, the angle  $\theta$  used in both cases is at least 5° different which seems too large according to the calculation cited in Ref. 3. Therefore one may ask, "Are the 3.9- $\mu$  ir-absorption band and the 3.9- $\mu$  photo-

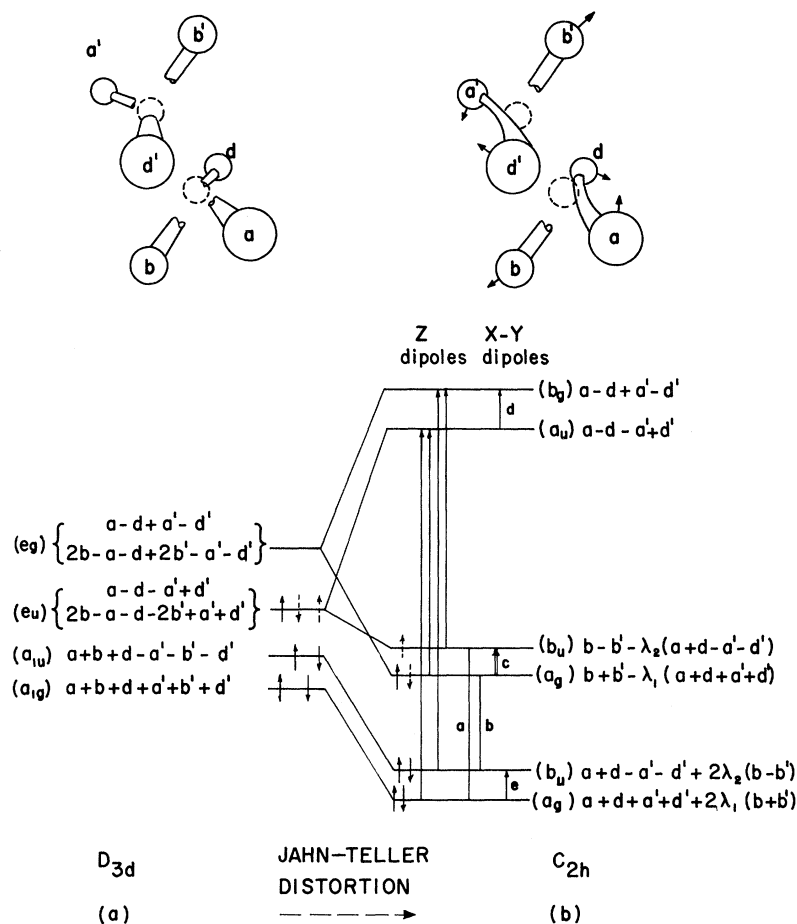


FIG. 1. One-electron molecular-orbital model of energy levels associated with the divacancy proposed by Watkins and Corbett: (a) before Jahn-Teller distortion, (b) after distortion with the allowed electric-dipole-moment transitions.

conducting band associated with the same +1 charge state of divacancy defect?"

In an attempt to answer the above questions, the divacancy-associated ir-absorption bands at 1.8, 3.3, and 3.9  $\mu$  were investigated in both 0.1- $\Omega$  cm *n*-type, *p*-type, and high-purity-intrinsic silicon samples. The effects of various types of impurity in silicon on the divacancy-associated bands, the temperature dependence of the relative intensity of these bands, and the low-temperature (78 °K) stress studies of the bands were carefully investigated to obtain more understanding of the microscopic picture of the divacancy defect in silicon.

#### Divacancy Model

A simple one-electron linear-combination-of-molecular-orbital treatment of the divacancy model deduced from the EPR studies by Watkins and Corbett<sup>1</sup> is shown in Fig. 1. Two vacant lattice sites are designated by the dashed circles *c* and *c'*, and the six nearest-neighbor silicon atoms surrounding the two adjacent vacancies are labeled as *a*, *b*, *d*, *a'*, *b'*, and *d'*. The symmetry of the

divacancy in the undistorted silicon lattice is the  $D_{3d}$  point group. The wave functions are a linear combination of the broken-bond orbitals of a single electron on each of the six neighboring atoms. The filling of the orbitals results in a Jahn-Teller<sup>8</sup> distortion, and the point group symmetry is lowered to  $C_{2h}$ . A model of the divacancy defect for Si is shown in Fig. 2. The order of the energy levels as shown in the figure is determined by the number of the nodes in the wave functions of the orbitals, since the simple group-theoretical treatment does not give any information about the ordering of these orbitals. Since the details of the model including a description of the calculations have been given elsewhere<sup>1,3</sup> we shall not repeat them here.

#### II. EXPERIMENTAL METHODS

The rectangular-bar samples of dimensions of  $3 \times 3.5 \times 10$  mm<sup>3</sup> were cut and polished with diamond compound and 0.3- $\mu$  alumina abrasive in order to achieve good transmission. We used commercially available silicon single-crystal ingots in the form of cylindrical boules with the [111] direction

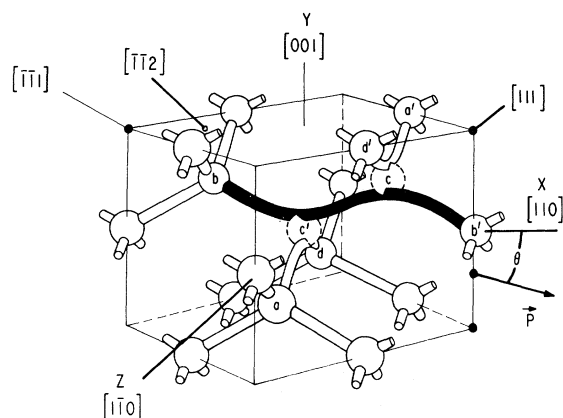


FIG. 2. Model of divacancy defect deduced from EPR studies.

along the axis of the cylinder. The samples were orientated with the long sample dimension in either a  $[111]$ ,  $[110]$ , or  $[100]$  orientation. The orientation was determined either by the x-ray back-reflection Laue technique or by reflection of light from a freshly etched surface.<sup>9</sup> We estimated that the crystal orientation was accurate to  $\pm 2^\circ$ . The silicon single-crystal ingots were floating-zone refined and contained low oxygen concentration ( $\lesssim 10^{16}$  oxygen/cm<sup>3</sup>). The resistivities of the samples before irradiation were 0.1  $\Omega$ cm for  $p$ -type,  $n$ -type, and high-purity-intrinsic ( $> 10^4 \Omega$ cm) silicon crystals. The samples were irradiated to a fluence of  $4-7 \times 10^{16}$  cm<sup>-2</sup> with fast neutrons in a reactor at a temperature below 60 °C.

The measurement of the ir spectra were made at 78 °K using an optical Dewar<sup>10</sup> equipped with a concentric rod and tube to allow one to transmit a known compressive stress on the sample during the optical measurement. A detailed description of the cryostat and stress apparatus has been given elsewhere.<sup>10</sup> Perkin-Elmer model Nos. 621 and 12 ir spectrophotometers were used to record the spectra. Polarized light was obtained using a Perkin-Elmer wire-grid polarizer. The optical spectra are measured with varying and known stress applied to the sample. The dichroism was obtained by taking the ratio of  $\alpha_{\perp}$  to  $\alpha_{\parallel}$ , where  $\alpha_{\perp}$  is the absorption coefficient measured with electric field  $\vec{E}$  polarized perpendicular to stress direction  $E_{\perp}$ ;  $\alpha_{\parallel}$  is the absorption coefficient measured with  $\vec{E}$  polarized parallel to stress direction  $E_{\parallel}$ . The absorption coefficient  $\alpha$  was taken at the wave length of the peak in the band.

### III. EXPERIMENTAL RESULTS

#### A. Effects of Impurities on the Bands

The absorption coefficients of the divacancy-

associated bands at 1.7, 3.45, and 3.61  $\mu$  in silicon samples containing various types of impurity were measured by using the full-beam light (with all wavelengths) of the spectrophotometer and are shown in Table I. We observe the 1.8- and 3.3- $\mu$  bands (actually they are at 1.7 and 3.2  $\mu$ , respectively) and two sharp bands at 3.45 and 3.61  $\mu$  simultaneously in all types ( $n$  type,  $p$  type, and intrinsic) of silicon samples measured at 78 °K. We also observed that the ratio of the absorption coefficients of the 3.61- $\mu$  band to the 3.2- $\mu$  band is different from sample to sample. It is significant to note that we do not observe the 3.9- $\mu$  band in  $p$ -type silicon samples. We also do not observe the 3.9- $\mu$  band (previously observed in  $p$ -type samples in both electrons and fast neutrons irradiation by others<sup>2,3</sup>) even on the samples annealed to 190 °C for 30 min, 200 °C for 20 min, or 230 °C for 30 min.

A 2- $\mu$  filter which cuts out light  $\leq 2 \mu$  and monochromatic light was also used to measure the relative intensity of the bands. Both the 3.45- and 3.61- $\mu$  bands in  $n$ -type samples are not effected by using a 2- $\mu$  filter. However, the intensity of the 3.61- $\mu$  band decreases about 18% in an intrinsic sample and about 20% in a  $p$ -type sample when the 2- $\mu$  filter was placed in front of the sample. The absorption coefficient of the divacancy-associated bands measured by using monochromatic or full-beam light in three different types ( $n$  type,  $p$  type, and intrinsic) of sample is shown in Table II. Clearly, the results of the two measurements (monochromatic and full-beam light) of the 1.8- $\mu$  band in all types of silicon samples and that of the 3.3-, 3.45-, and 3.61- $\mu$  bands in the  $n$ -type

TABLE I. Absorption coefficient (cm<sup>-1</sup>) of the divacancy-associated bands. Note that all types of Si samples become intrinsic after fluences of  $\geq 4 \times 10^{16}$  cm<sup>-2</sup>. However, these samples recover to their original type subsequent to annealing at 190 °C for 30 min. or 200 °C for 20 min.

Type	Sample	$\alpha_{1.7 \mu}$	$\alpha_{3.45 \mu}$	$\alpha_{3.61 \mu}$	$\frac{\alpha_{1.7 \mu}}{\alpha_{3.61 \mu}}$	$\frac{\alpha_{3.61 \mu}}{\alpha_{3.45 \mu}}$
Before annealing						
$p$	Ga doped $[111]$	12.9	0.54	1.2	10.7	2.2
$p$	Al doped $[100]$	13.0	0.60	1.3	10.0	2.2
$p$	B doped $[100]$	11.2	0.41	0.84	13.3	2.1
In.	intrinsic $[110]$	10.7	0.46	0.95	11.0	2.1
$n$	P doped $[111]$	9.6	1.51	3.2	3.0	2.0
$n$	Sb doped $[100]$	9.0	1.69	3.26	2.8	1.9
190 °C anneal for 30 min.						
$p$	Al doped $[100]$	4.3	0.11	0.22	19.6	2.0
$p$	B doped $[100]$	4.2	0.11	0.22	21.0	2.0
$n$	P doped $[100]$	1.2	1.2	2.6	0.46	2.1
200 °C anneal for 20 min.						
$p$	Ga doped $[111]$	4.4	0.11	0.22	20.0	2.0
In.	intrinsic $[110]$	4.1	0.37	0.81	5.1	2.2
$n$	Sb doped $[100]$	0.8	1.2	2.54	0.32	2.1

TABLE II. Absorption coefficient ( $\text{cm}^{-1}$ ) of the divacancy-associated bands in all types of samples measured at 80 and 300 °K. Note that (i) the  $n$ -type sample (P-doped Si) measured in this table is after a 190 °C anneal for 30 min (fluence  $\sim 4 \times 10^{16} \text{ cm}^{-2}$ ); (ii) the  $p$ -type sample (B-doped Si) measured in this table is after a 250 °C anneal for 30 min (fluence  $\sim 3 \times 10^{17} \text{ cm}^{-2}$ ); (iii) all types of Si samples become intrinsic after  $4 \times 10^{16} \text{ cm}^{-2}$  or higher-fluence neutron irradiation. However, these samples recover to their original type subsequent to annealing at 190 °C for 30 min or 250 °C for 30 min. Mon. stands for monochromatic light and full for full-beam light (all wavelengths).

ir bands	80 °K						300 °K					
	$p$ type		Intrinsic		$n$ type		$p$ type		Intrinsic		$n$ type	
	mon.	full	mon.	full	mon.	full	mon.	full	mon.	full	mon.	full
1.8 $\mu^a$	8.5	8.1	10.5	10.0	1.28	1.21	3.9	3.9	5.7	5.8	0.67	0.68
3.3 $\mu^b$	0.50	0.89	0.32	0.59	1.03	1.01	0	0	0	0	0.45	0.45
3.45 $\mu$	0.59	1.1	0.35	0.55	1.21	1.21	0	0	0	0	0	0
3.61 $\mu$	1.1	2.0	0.54	1.12	2.52	2.6	0	0	0	0	0	0
3.9 $\mu$	0	0	0	0	0	0	0	0	0	0	0	0

<sup>a</sup>The 1.8- $\mu$  band becomes sharper and shifts to 1.7  $\mu$  when the measurement was taken at  $T = 80$  °K.

<sup>b</sup>The 3.3- $\mu$  band shifts to 3.2  $\mu$  when it is measured at  $T = 80$  °K.

samples are the same. There is a substantial difference between the two measurements of the 3.3-, 3.45-, and 3.61- $\mu$  bands in the intrinsic and  $p$ -type samples. There is still no 3.9- $\mu$  band which is associated with +1 charge state of the divacancy<sup>3</sup> observed when one uses monochromatic light on the sample.

#### B. Temperature Effects

As shown in Table II, the band at 1.8  $\mu$  was observed at both 300 °K and 80 °K in all types of silicon samples. The broad band at 3.3  $\mu$  was observed at room temperature only on the  $n$ -type floating-zone-refined samples. However, it was observed in all types of samples together with the two sharp bands at 3.45 and 3.61  $\mu$  at low temperature. Typical absorption spectra of the 3.3- $\mu$  broad band and two sharp bands are shown in Fig. 3.

The broad band and two sharp bands in an intrinsic sample have been measured at  $T = 68, 78, 82, 100,$  and  $133$  °K. The relative intensities of the 3.45- and 3.61- $\mu$  sharp bands have different temperature dependences and both broad and sharp bands were observed only if the temperature was  $\leq 150$  °K. In addition, the ratio of the integrated absorption in the 3.61- $\mu$  band to the total integrated absorption in the broad band vs  $T^2$  exhibits an exponential rather than a linear temperature dependence. We do not observe shifting of the sharp bands at different temperatures (68–133 °K). On the contrary, the broad band shifts to 3.2  $\mu$  and the half-width also increases when the temperature is changed from 300 to 80 °K.

The isochronal-annealing experiments on the 1.8- and 3.3- $\mu$  absorption bands have been reported by Cheng and co-workers.<sup>3</sup> However, the previous isochronal-annealing experiment<sup>3</sup> did not include a  $p$ -type floating-zone-refined sample, and the 3.3- $\mu$  band which consists actually of a broad

band and sharp bands was considered as a band arising from a single defect.<sup>2,3</sup> Isochronal-annealing experiments have been run on the 3.3- $\mu$  broad band (spectrum measured at  $T = 300$  °K) and also on the 1.8-, 3.45-, and 3.61- $\mu$  bands in both  $p$ - and  $n$ -type samples. We can see from Fig. 4 all these bands anneal out at a temperature of 300 °C (the 3.3- $\mu$  broad band also anneals out at  $T = 300$  °C if the spectrum is measured at  $T = 80$  °K). The annealing behavior of the 1.8-, 3.45-, and 3.61- $\mu$  bands in  $p$ -type silicon is about the same.

In  $n$ -type samples there are three different annealing behaviors. The recovery of the two sharp bands at 3.45 and 3.61  $\mu$  is similar but slower than that of the bands in  $p$  type. The relative amplitude of the 3.3- $\mu$  broad band starts to increase when the annealing temperature is about 160 °C and reaches its maximum point at  $T \sim 190$  °C, whereas the relative amplitude of the 1.8- $\mu$  band decreases sharply in this temperature region (see Fig. 4). This pronounced difference of the annealing behavior between the 3.3- $\mu$  broad band and 1.8- $\mu$  band in  $n$ -type Si may be attributed to the release of the electrons from the  $E$  center since the  $E$  center anneals out at  $T \sim 175$  °C.<sup>11,12</sup>

#### C. Low-Temperature (78 °K) Stress Studies

Low-temperature stress studies on the divacancy-associated bands at 3.45 and 3.61  $\mu$  were first reported by Rao and Ramdas<sup>13</sup> in which they observed splitting and stress-induced dichroism of the bands under the effects of stress in the [111] direction. However, there are no quantitative values reported for either dichroism or splitting when stress is applied to the sample at low temperature. In the previous low-temperature stress measurements,<sup>13</sup> a differential thermal expansion was used to apply the stress and neither the temperature nor the stress values were well defined. In our low-temperature stress studies to be presented here we

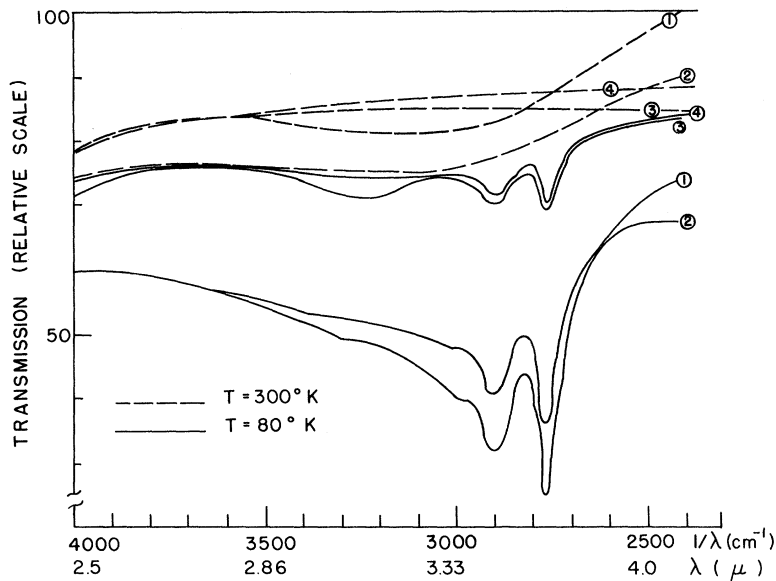


FIG. 3. Typical ir absorption of the 3.2- $\mu$  broad band and two sharp bands at 3.45 and 3.61  $\mu$  measured at 80 °K. (1) P-doped (0.09  $\Omega$  cm) floating-zone (FZ) sample; (2) P-doped (0.1  $\Omega$  cm) FZ; (3) B-doped (100–300  $\Omega$  cm) pulled; and (4) P-doped (40–100  $\Omega$  cm) pulled.

have made a series of measurements under various known stress conditions at constant temperature. Therefore, a good comparison between theory and experimental results can be made.

The application of uniaxial compressive stress to the samples at 78 °K produces a dichroism in three stress directions [001], [110], and [111] for the 1.8- $\mu$  band and the two sharp bands at 3.45 and 3.61  $\mu$ . This stress-induced dichroism for the two sharp bands is much larger than that for the 1.8- $\mu$  band in all three stress directions. The typical measurements of the stress spectra from 1.3 to 2.5  $\mu$  with [110] stress for the 1.8- $\mu$  band, and from 3.23 to 3.85  $\mu$  with [111] stress for the two sharp bands, are shown in Figs. 5 and 6, respectively. We also present our stress-induced dichroism results schematically for all three stress directions in Figs. 7 and 8 for the 1.8- $\mu$  band and for the 3.45- and 3.61- $\mu$  sharp bands, respectively. The stress spectra were also made at room temperature for the 3.3- $\mu$  broad band on Sb-doped silicon samples. There is no other band which interferes with the 3.3- $\mu$  broad band when it is measured at room temperature. A typical measurement of the stress spectra from 2.5 to 5  $\mu$  with stress applied in the [110] direction is shown in Fig. 9. The stress-induced dichroism results for [001], [110], and [111] stress deduced from the data are shown in Fig. 7.

Similar, but different magnitude, stress-induced splitting and shifting of the bands were observed in all stress directions [001], [110], and [111] for all three bands at 1.8, 3.45, and 3.61  $\mu$  (see Figs. 5 and 6). However, since the band at 3.3  $\mu$  is so broad it is almost impossible to pinpoint any splitting or shifting of the band under the effects of the

stress. The splitting and shifting under the action of stress in [001], [110], and [111] directions are shown in Figs. 10–12 for the 1.7-, 3.45-, and 3.61- $\mu$  bands, respectively. From the stress results, as shown in Figs. 10–12, it is quite clear that the magnitudes of the splitting and shifting are

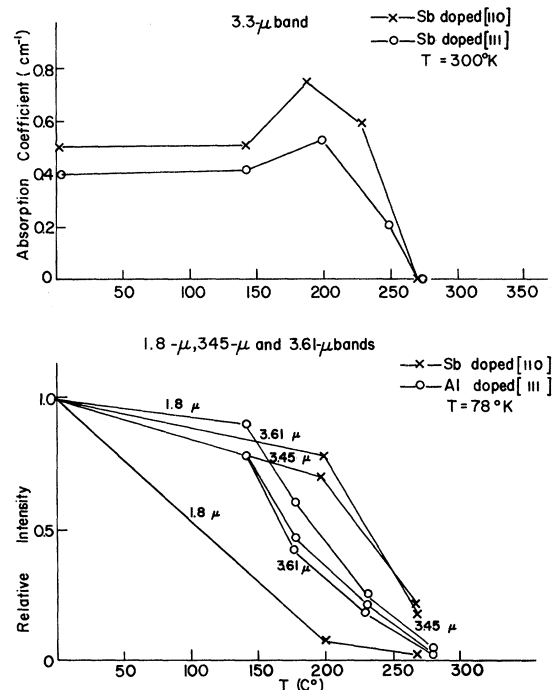


FIG. 4. Isochronal anneal behavior (15 min at each temperature) of the 3.3- $\mu$  band in  $n$ -type Si samples and the 1.8-, 3.45-, and 3.61- $\mu$  bands in both  $n$ - and  $p$ -type Si.

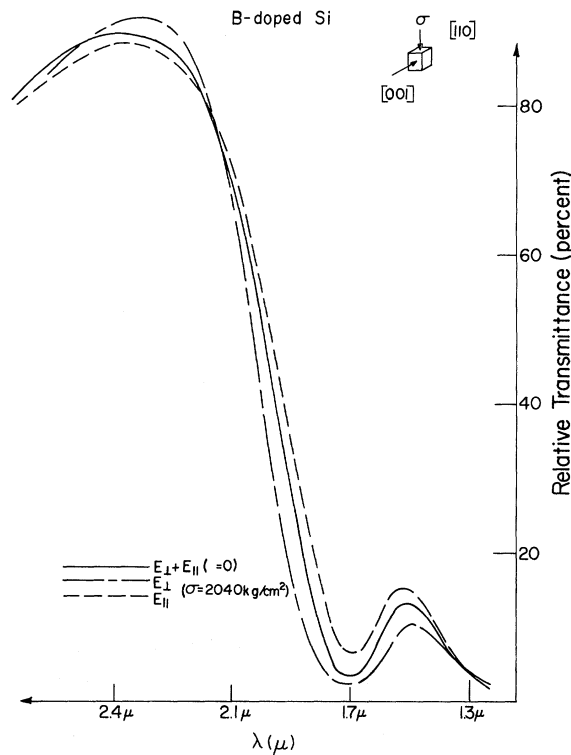


FIG. 5. Typical experimental curves showing the response of the 1.7- $\mu$  band under [110] stress at 78 °K.

all different in each stress direction for all three bands at 1.7, 3.45, and 3.61  $\mu$  and lie outside our experimental error.

#### IV. DISCUSSION

##### A. General

The divacancy-associated bands at 1.8, 3.3, and 3.9  $\mu$  were first observed by Fan and Ramdas<sup>2</sup> in both electron and fast-neutron irradiation of silicon. The 1.8- $\mu$  band was observed in both *p*- and *n*-type samples, and the 3.3- $\mu$  broad band was observed only in *n*-type samples. Both bands were observed at room and low temperature. However, the 3.45- and 3.61- $\mu$  sharp bands were observed together with the broad band only at low temperature, and these bands can be observed only if the Fermi-level position is above  $E_c - 0.21$  eV.<sup>2</sup> In our study, we observed the 1.8- and 3.3- $\mu$  bands and two sharp bands at 3.45 and 3.61  $\mu$  simultaneously in all types of samples at 80 °K using both full-beam (see Table I) and monochromatic light (see Table II). The 3.3- $\mu$  broad band was observed at room temperature only in *n*-type silicon samples.

The simultaneous observation of the 1.8- and 3.3- $\mu$  bands in *n*-type silicon have been reported and interpreted by Cheng and Vajda<sup>6</sup> as due to the inhomogeneity of the neutron damage in the crystal.

The simultaneous observation of the neutral donor, A-center (vacancy-oxygen complex), and -1 charge state of the divacancy defect on the *n*-type crucible-grown silicon in the EPR studies of Daly and Noffke<sup>14</sup> was also interpreted as resulting from the extremely nonuniform distribution of the neutron damage throughout the crystal. However, it seems unlikely that the -2 charge state of the divacancy defect is observable in high-impurity-content *p*-type silicon due to the inhomogeneity of the neutron damage. Therefore, the identification of the 3.3- $\mu$  band as associated with the -2 charge state of divacancy defect by Cheng *et al.*<sup>3</sup> may not be correct, since this identification was based on Fan and Ramdas's observation<sup>2</sup> of the Fermi-level dependence. More evidence to support our view will be given later.

The fact that the intensities of the bands at 3.3, 3.45, and 3.61  $\mu$  were observed to increase when the full-beam light was used to measure the spectra (see Table II) on the *p*-type or intrinsic silicon samples reveals that in *p*-type or intrinsic Si the number of defects present is more than necessary for observation of the defect in its lowest charge state. The higher-energy light seems to create conduction electrons or valence holes which can be trapped metastably at the defect to produce the bands.

The 3.3- $\mu$  band which is identified as associated with the -2 charge state of divacancy defect<sup>3</sup> consists, actually, of a broad band at 3.2  $\mu$  and two sharp bands at 3.45 and 3.61  $\mu$ . From the facts that from sample to sample (i) the ratio of the intensity between 3.2 and 3.61  $\mu$  is different, (ii) the isochronal-annealing behavior (see Fig. 4) between broad and sharp bands is different, (iii) the temperature dependence between the two sharp bands is different, (iv) the stress-induced splitting and dichroism is different (see Figs. 5-12) and that (v) the 3.3- $\mu$  broad band does not exhibit the phonon structure given by Fitchen<sup>15</sup> for *O*-phonon transition since the ratio of the integrated absorption in the 3.61- $\mu$  band to the total integrated absorption in the whole band does not have a linear temperature dependence, we conclude, therefore, that the broad band at 3.2  $\mu$  and two sharp bands at 3.45 and 3.61  $\mu$  are actually not due to the single -2 charge state of the divacancy defect; rather, they are due to three different optical transitions. The temperature dependence of the ratio of the relative intensity of the 3.45- to 3.61- $\mu$  band also rules out the possibility of a single ground state to various excited-state transitions proposed by Fan and Ramdas.<sup>2</sup>

The isochronal-annealing behavior is about the same for all three bands at 1.8, 3.45, and 3.61  $\mu$  in *p*-type silicon samples. This behavior reveals that the relative number of defects responsible

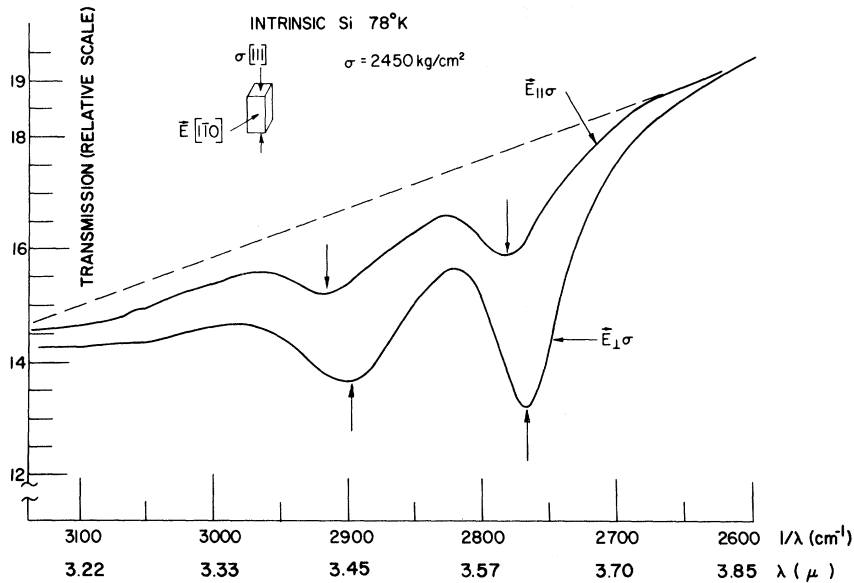


FIG. 6. Typical experimental curves showing the dichroism and splitting of the 3.45- and 3.61- $\mu$  bands under [111] stress at 78°K. Arrows indicate positions of the minima in the peaks.

for these bands does not change much upon annealing. The annealing behavior of the two sharp bands at 3.45 and 3.61  $\mu$  is slightly faster than that of the 1.8- $\mu$  band which may be attributed to the release of the holes from the group-III vacancy-associated defects which have annealing temperature around 300 °C.<sup>16</sup> In *n*-type silicon samples, the annealing behaviors of the 3.3- and 1.8- $\mu$  bands are substantially different in that the relative absorption of the broad band at 3.3  $\mu$  increases and that of 1.8- $\mu$  band decreases quite remarkably upon anneal to a temperature reaching the vicinity of 150 °C (see Fig. 4). From the previous EPR and ir studies, the *E* center (group-V vacancy complex)<sup>11,12,17</sup> and a new defect which is responsible for the 6–10- $\mu$  absorption bands<sup>5,18</sup> are also present in the *n*-type floating-zone-refined silicon. These defects also need donor electrons to give rise to absorption lines in their spectra, and they anneal out around 175 °C. This evidence leads us to conclude that the electrons released during anneal from the *E* center and the new defect reported earlier<sup>5,18</sup> are trapped by the defect center to give an increase of the 3.3- $\mu$  broad band, and also cause a sharp drop of the 1.8- $\mu$  band in the *n*-type silicon sample since according to the atomic re-orientation and annealing experiments<sup>3</sup> and also our low-temperature stress results both bands are associated with the same divacancy defect. Therefore, the difference of the annealing behavior between these two bands is attributed to the change of the Fermi-level position.

#### B. Analysis of Stress Spectra

Since the elastic deformation in the lattice is small (order of  $10^{-3}$ ) the change in the potential at

the defect due to an applied external stress in a cubic crystal can be treated as a perturbation term experienced by the electronic states of the defect. The energy of a defect can be considered as a linear function of the components of the stress

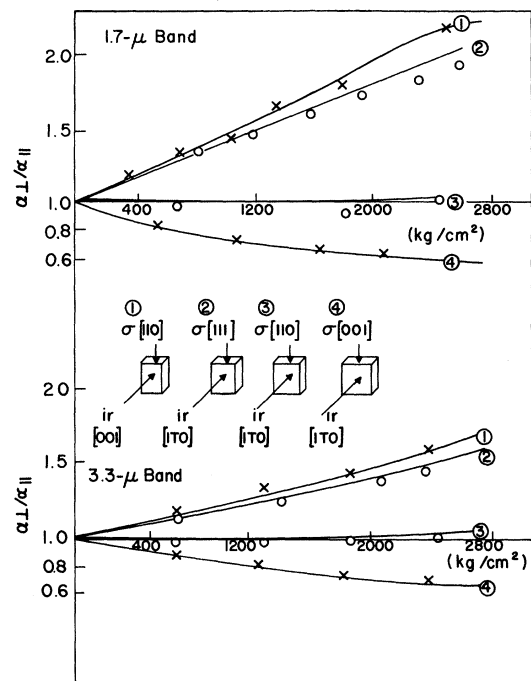


FIG. 7. Dichroism ( $\alpha_{\perp}/\alpha_{\parallel}$ ) exhibited by the 1.7- $\mu$  band vs stress measured at 78°K. The directions of applied stress and incident light are shown in the figure. The solid lines are calculated values using the parameters given in Table III.

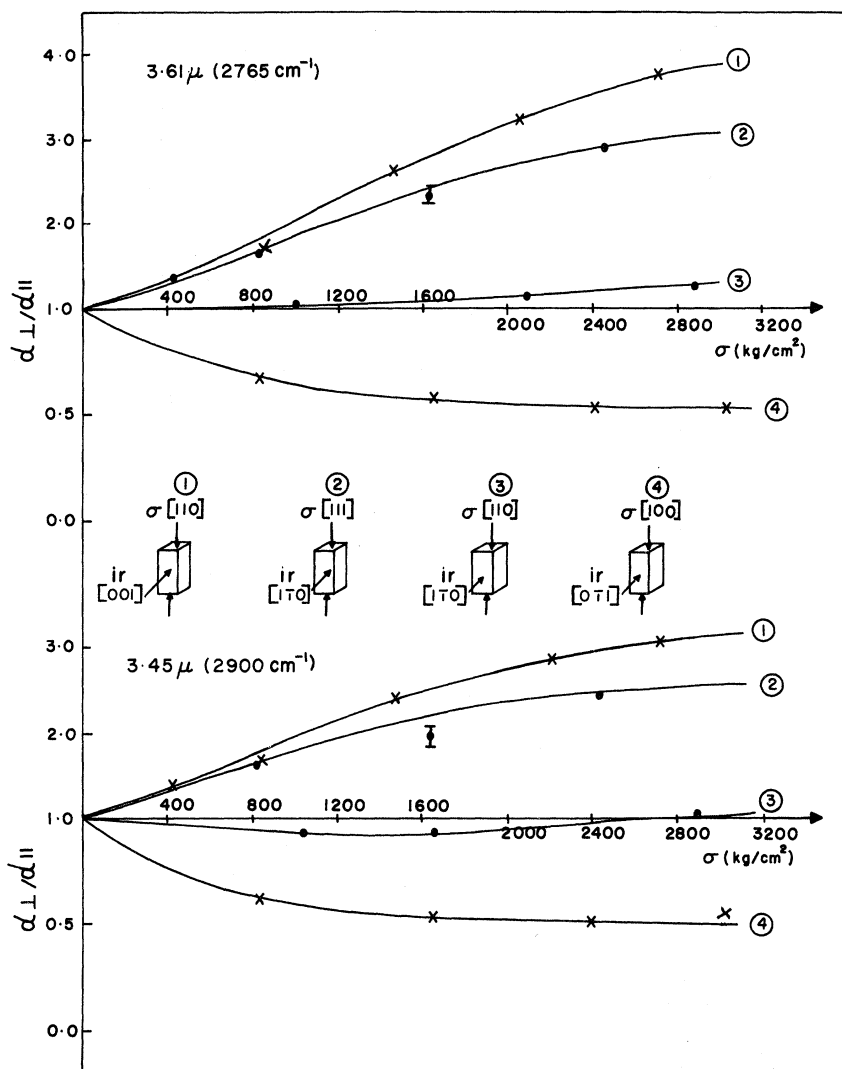


FIG. 8. Dichroism ( $\alpha_{\perp}/\alpha_{\parallel}$ ) exhibited by the 3.45- and 3.61- $\mu$  bands vs stress measured at 78°K. The directions of applied stress and incident light are shown on the figure. The solid lines are the calculated values using the parameters given in Table III.

tensor  $\{\sigma_{ij}\}$  or the deformation  $\{\xi_{ij}\}$  in the lattice:

$$\Delta E = \sum_{ij} A_{ij} \sigma_{ij}, \quad (1)$$

where  $A_{ij}$  are electronic operators.

In terms of the strain tensor,

$$\Delta E = \sum_{kl} B_{kl} \xi_{kl}, \quad (2)$$

where

$$B_{kl} = \sum_{ij} A_{ij} C_{ijkl}$$

and  $C_{ijkl}$  are elastic constants. According to Kaplyanskii,<sup>19</sup> the symmetry of the divacancy is classified as a type-I monoclinic center, and in the principal-axis system of the defect (see Fig. 2; the  $C_2$  axis of the divacancy defect is in the  $[1\bar{1}0]$  direction), the  $B$  tensor must have the form

$$B = \begin{bmatrix} B_1 & B_4 & 0 \\ B_4 & B_2 & 0 \\ 0 & 0 & B_3 \end{bmatrix}. \quad (3)$$

In previous EPR studies<sup>1</sup> of the divacancy and also in the ir studies<sup>3</sup> of the 1.8- and 3.9- $\mu$  bands, it was found that one parameter sufficed to describe the stress response of dichroism. In terms of the  $B$  tensor, the analysis assumed  $B_1 = B_2 = B_4 = 0$ , and

$$B_3 = M = \left( \frac{dE}{d\xi} \right)_{s_1-s_1} \quad (4)$$

for the change in energy per unit strain along the "bonding"-atom direction associated with Jahn-Teller distortion. The results of a similar analysis<sup>20</sup> for the data of Figs. 7 and 8 are shown by the solid lines in the figures. The values of  $M$  and  $\theta$ , which describes the dipole-moment-transition direction used in the fit for each line, are given in



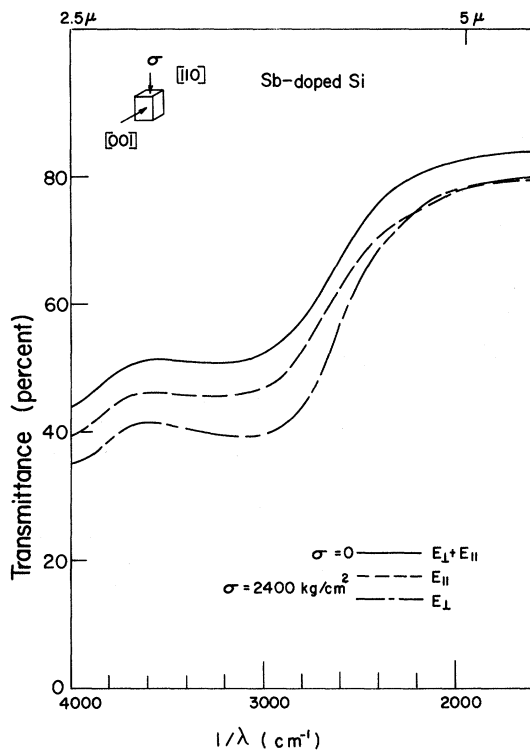


FIG. 9. Typical experimental curves showing the dichroism of the 3.3- $\mu$  broad band in  $n$ -type Si under [110] stress. Spectra were measured at room temperature.

Table III. We see that the theoretical and experimental values are in good agreement in all four stress directions (1-4) for the 1.8-, 3.3-, 3.45-, and 3.61- $\mu$  bands. Therefore, we feel that this close agreement constitutes definitive confirmation of the fact that all these bands are associated with the divacancy defect and the strong bonding between the nearest silicon atoms in the  $Z$  direction of the divacancy in the model of Watkins and Corbett<sup>1</sup> dominates the stress response of dichroism. The values of  $M$  can be compared to 24 eV for the +1 charge state and 32 eV for the -1 charge state of the divacancy as determined by EPR studies,<sup>1</sup> and also to 18 eV,  $\theta = -10^\circ$ , for the 1.8- $\mu$  band and 26 eV,  $\theta = -5^\circ$ , for the 3.9- $\mu$  band as obtained from the ir studies of Cheng *et al.*<sup>3</sup>

Although here the  $M$  value and the angle  $\theta$  for the 1.8- $\mu$  band are quite different from that obtained by previous room-temperature stress-induced-dichroism experiments<sup>3</sup> we find that we are able to fit the Cheng *et al.*<sup>3</sup> experimental result quite well by choosing  $M = 11$  eV and  $\theta = +7^\circ$  instead of  $M = 18$  eV and  $\theta = -10^\circ$ . However, the angle  $\theta$  obtained by atomic reorientation<sup>3</sup> is  $-5^\circ$  which is quite different from the angle determined from our electronic-reorientation experiments

( $+6.9^\circ$  for the low-temperature stress-induced dichroism). The possible explanation of this discrepancy may be due to the vibration states of the defect which make the dipole-moment-transition direction become less well defined<sup>3</sup> at room temperature.

The stress-induced dichroism is attributed to the reorientation of the energetic nonequivalence of the different configurations of the divacancy defect in the crystal, since the 12 different configurations of the divacancy defect<sup>3</sup> are no longer equivalent and the lower-energy ground states will be more populated than the higher-energy ground states under the application of stress to the crystal. Therefore, it is necessary to take into account the relative population of the initial states (or ground states) by the Boltzmann factor. From Table III, we conclude that the 1.8-, 3.3-, 3.45-, 3.61- $\mu$  bands are associated with the  $X$ - $Y$  dipole-moment transitions of the divacancy defect. The different  $M$  value, the energy per unit strain in the "bonding" direction, different annealing behavior between the 1.8- $\mu$ , 3.3- $\mu$ , and two sharp bands in  $n$ -type Si, and different temperature dependence of the two sharp bands at 3.45 and 3.61  $\mu$  lead us to argue that there are four initial states involved for the optical transitions which give rise to the

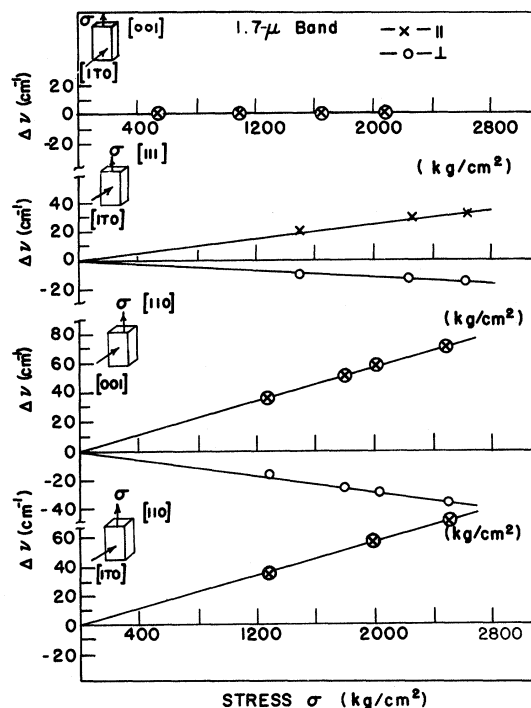


FIG. 10. Splitting and shifting of the 1.7- $\mu$  band vs stress for neutron-irradiated Si measured at 78 °K. The directions of applied stress and incident light are shown on the figure.

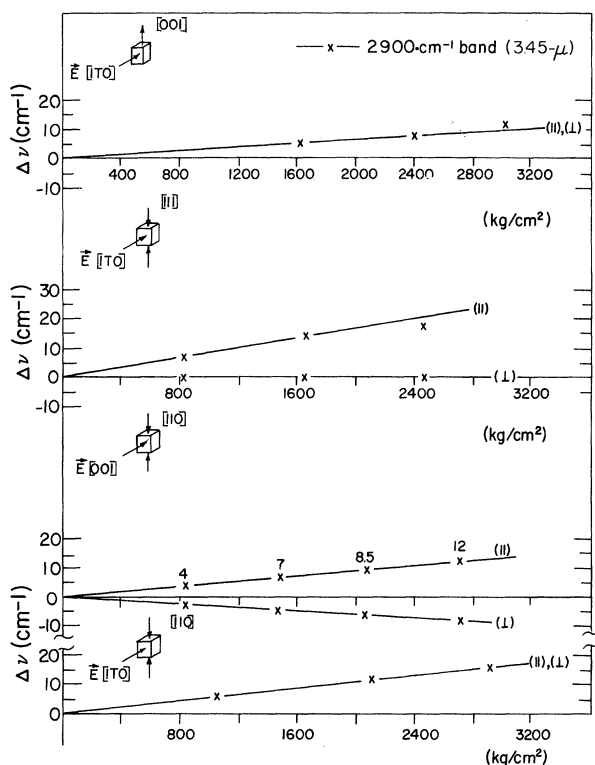


FIG. 11. Splitting and shifting of the 3.45- $\mu$  band vs stress for the neutron-irradiated Si measured at 78°K. The directions of applied stress and incident light are shown on the figure.

1.8-, 3.3-, 3.45-, and 3.61- $\mu$  bands.

The splitting of the bands under the action of stress also must be expressible in the form of Eqs. (1) or (2). However, the  $A$ 's and  $B$ 's in Eqs. (1) and (2), respectively, are different from those used to calculate the dichroic ratio, because in the calculation of the dichroic ratio we considered only the initial state. In the case of shifting and splitting of the band, both the initial and final states must be considered since we are concerned with the energy difference between the initial and final states and the application of the stress to the crystal can shift energy in both initial and final states. The piezospectroscopic tensor  $B'$  used to calculate splitting is the same form as Eq. (3). However, the components  $B'_i$  are actually  $(B_i^e - B_i^g)$ , where  $B_i^e$  and  $B_i^g$  are the components of the piezospectroscopic tensor of the excited state and ground state, respectively. Based on the characteristics of the ground state (or initial state) obtained from the results of the dichroic ratio under the effect of stress, assignment of all possible transitions for the various orientations, and consideration of the possible transitions which may vanish due to re-orientation of the defect by the Boltzmann population factor, we obtained the values of the com-

ponents of the piezospectroscopic tensor  $B'_i$  from our splitting results (see Figs. 10-12) for the 1.8-, 3.45-, and 3.61- $\mu$  bands, as shown in Table IV.

The magnitudes of the components of the piezospectroscopic tensor for the 3.45- and 3.61- $\mu$  bands are clearly an order of magnitude smaller than those of Table III, and that of 1.8- $\mu$  band, on the contrary, is larger than the magnitude of those given in Table III. From this we must conclude that the Jahn-Teller distortion in the excited state is very similar to that of the ground state for the 3.45- and 3.61- $\mu$  bands so that both states couple almost identically to the stress field. On the other hand, the initial-state response for the 1.8- $\mu$  band is much less affected by the stress field than the excited state; therefore, the ground and excited states do not exhibit the same Jahn-Teller distortion. The difference in magnitude of the components of the piezospectroscopic tensor between the 3.45- and 3.61- $\mu$  bands also leads us to conclude that both bands arise from two different transitions. An identification of the 1.8-, 3.3-, 3.45-, and 3.61- $\mu$  bands associated with the possible transitions in terms of one-electron molecular-orbital model of Watkins and Corbett (see Fig. 1) will be attempted in Sec. IV C.

#### C. Nature of Optical Transitions and Possible Charge States

According to the one-electron molecular-orbital model of energy levels associated with the divacancy, a model first proposed by Watkins and Corbett,<sup>1</sup> there are five  $X$ - $Y$  dipole-moment transitions  $a$ ,  $b$ ,  $c$ ,  $d$ , and  $e$  possible, as shown in Fig. 1. As pointed out by Cheng *et al.*,<sup>3</sup> the transitions such as an electron removed from the strong-bonding states between atoms  $a$ ,  $d$ , and  $a'$ ,  $d'$  and transferred to the nonbonding state will be associated with a broad absorption band, since the ground and excited states do not have the same equilibrium "configurational" coordinates. The splitting or shifting of the absorption band under the effect of stress must be large because of the different equilibrium Jahn-Teller distortion between ground and excited states. Therefore, from our stress results we confirm the identification of the 1.8- $\mu$  band as associated with the  $a$   $X$ - $Y$  dipole-moment transition, i. e., the  $a_g$  to  $b_u$  molecular-orbital states given by Cheng *et al.*<sup>3</sup> Since the value  $M$  (the energy per unit strain along the bonding-atom direction) can only give us information about the ground state (or initial states) involved, we are unable to obtain information concerning what charge state is involved in the observation of the 1.8- $\mu$  band from our stress results. However, from the correlation between other absorption bands it is most likely that the 1.8- $\mu$  band is associated with the neutral charge state of the divacancy defect which agrees with the observation of Cheng and

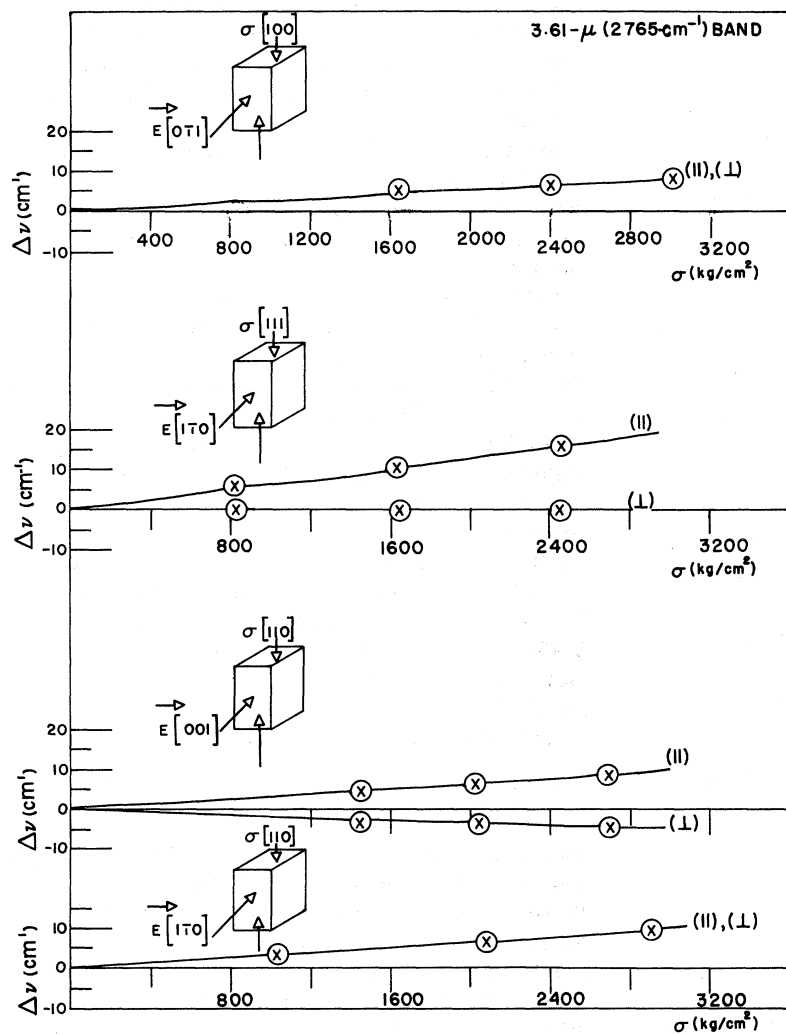


FIG. 12. Splitting and shifting of the 3.61- $\mu$  band vs stress for neutron-irradiated Si measured at 78°K. The directions of applied stress and incident light are shown on the figure.

Vajda.<sup>6</sup>

Since the transitions such as  $c$ ,  $d$ , and  $e$  in the X-Y dipole do not disturb the electrons in the Jahn-Teller bonding orbitals, a sharp absorption band and a small splitting or shifting of the band under the action of stress will be expected because of the nearly equal coupling of the ground and excited states to the stress field. Therefore, it is quite reasonable to assign the 3.45- and 3.61- $\mu$  bands to the  $c$  transition of the X-Y dipole since the  $d$  and  $e$  transitions become possible only if the sample is in the  $-3$  and  $+3$  charge states, respectively. The different temperature dependence, stress-induced dichroism, and stress-induced splitting between the two sharp bands which reveal that they do not exhibit the same optical transition can be explained by the simultaneous presence of two different charge states throughout the crystal. The  $c$  transition becomes possible if the  $b+b'$  orbital state ( $A_g$ ) is occupied by either one electron ( $+1$  charge state) or by two electrons. In the sec-

ond case, we may have a neutral charge state if the  $b-b'$  orbital state ( $b_u$ ) is empty, or a  $(-1)$  charge state if the  $b-b'$  state is half-filled. Therefore, based on our observation of the relative intensity of the divacancy associated bands, we conclude that the charge states responsible for the observation of the two sharp bands at 3.45 and 3.62  $\mu$  must be in either  $-1$  or neutral charge states.

According to our observed annealing behaviors of the 1.8- and 3.3- $\mu$  bands (see Fig. 4), we believe that the final orbital state of the 1.8- $\mu$  band must be the initial orbital state for the 3.3- $\mu$  band.

The defect responsible for the 3.3- $\mu$  absorption band observable together with the 3.61- $\mu$  band must be in the  $-1$  charge state since based on our identification of the 3.61- $\mu$  band with the X-Y dipole-moment transition between two weak-bonding orbital states  $b+b'$  and  $b-b'$  it is impossible to observe the 3.61- $\mu$  band while two electrons are in the  $b-b'$  orbital state. Therefore, we must conclude that the charge state of the divacancy defect

TABLE III. Defect piezospectroscopic-tensor components (eV) and transition dipole-moment angle  $\theta$ .

Band ( $\mu$ )	$B_1$	$B_2$	$B_3(=M)$	$B_4$	$\theta$
1.8	0	0	9.6	0	+6.9°
3.3	0	0	19.7	0	+9.0°
3.45	0	0	21.3	0	+2.1°
3.61	0	0	18.6	0	+10.0°

in our sample condition is not unique since the 1.8- $\mu$  band associated with the neutral charge state and the 3.3- $\mu$  band associated with the -1 charge state of the divacancy defect were observed simultaneously on the  $n$ -type silicon sample. Upon annealing of the silicon sample, the electron released from other deep acceptor levels are trapped by the divacancy to give most of the divacancy in its -1 charge state and this resulted in a striking difference in annealing between the 1.8- and 3.3- $\mu$  bands.

Although the photoconductivity levels at  $E_c - 0.39$  eV (defined as  $E_c - 0.42$  eV by Young<sup>21</sup>) and  $E_c - 0.54$  eV have been observed and identified as associated with the -2 and -1 charge state of divacancy defect, respectively, by Kalma and Corelli,<sup>7</sup> these identifications are quite ambiguous since there is no definitive correlation in stress-induced dichroism between the photoconductivity, ir, and EPR studies. Therefore, from the broadness of the 3.3- $\mu$  ir band and the observation of the photoconductivity level at  $E_c - 0.4$  eV, we strongly suggest that the 3.3- $\mu$  ir band is due to the ionization of the electrons from the  $b - b'$  orbital state to the nearest conduction-band edge. The defect responsible for this optical transition is most likely in the -1 charge state since from the electrical-property measurements by Wertheim,<sup>22</sup> the EPR studies by Konozenko *et al.*,<sup>23</sup> and also our observation in neutron-irradiated Si, it was found that the Fermi-level position of either  $p$ - or  $n$ -type Si is in the vicinity of the middle of the energy gap. However, the  $M$  value obtained from the room-temperature stress-induced dichroism of the 3.3- $\mu$  band is 19.7 eV which is small compared with the  $M$  value of 32 eV obtained by EPR studies,<sup>1</sup> and the observation of the 3.2- $\mu$  band in low-resistivity  $p$ -type Si at low temperature gives rise to some uncertainty in this identification.

#### V. SUMMARY

The studies on the divacancy-associated bands in various types of neutron-irradiated silicon show that the bands at 1.8 and 3.3  $\mu$  together with two subbands at 3.45 and 3.61  $\mu$  are observed in all types of samples ( $n$  type,  $p$  type, and intrinsic) at temperature  $\lesssim 150$  °K. The 3.3- $\mu$  band is observed only in the  $n$ -type silicon at room temperature and

the 1.8- $\mu$  band is observed in all types silicon at room temperature. The 3.9- $\mu$  band which is identified as associated with the +1 charge state of the divacancy is not observed. Temperature-dependence studies of the broad band at 3.3  $\mu$  and two sharp bands at 3.45 and 3.61  $\mu$  give no evidence of phonon structure in our spectrum. In addition, the different ratio of the band intensity from sample to sample, different isochronal-annealing behavior, and different stress-induced dichroism and splitting between the broad band and two sharp bands lead to the conclusion that the fine structures of the 3.3- $\mu$  band are not associated with a single -2 charge state of the divacancy defect as reported previously,<sup>3</sup> but rather are due to three different optical transitions.

The low-temperature (78 °K) stress-induced dichroism of the bands leads us to confirm that the strong bonding between the nearest-neighbor silicon atoms in the  $Z$  direction of the divacancy in the model of Watkins and Corbett<sup>1</sup> dominates the stress response of dichroism. In addition to the stress-induced dichroism of the bands, the stress-induced splitting of the bands at 78 °K also leads us to confirm the symmetry and model of the divacancy defect deduced from EPR studies by Watkins and Corbett.<sup>1</sup>

In terms of the one-electron molecular-orbital model of energy levels (see Fig. 1) the bands at 1.8, 3.45, and 3.61  $\mu$  are identified as associated with the  $X$ - $Y$  dipole-moment transitions between the strong-bonding and the weak-bonding states ( $a_g \rightarrow b_u$ ), and the two weak-bonding  $b + b'$  and  $b - b'$  orbital states ( $a_g \rightarrow b_u$ ), respectively. The 3.3- $\mu$  band was suggested as an optical transition due to the ionization of the electrons from the  $b - b'$  orbital state to the nearest conduction-band edge.

According to our results on the absorption coefficient of the divacancy-associated bands in Si containing various impurities, it is quite obvious that the impurity plays an important role in the formation of divacancy defect. However, the precise mechanism by which impurities affect the formation of the divacancy is still a question to be answered. In addition, the observation<sup>24</sup> of the several new absorption bands in the 8- to 10- $\mu$  wavelength region on the high-purity intrinsic Si sample after 350 °C annealing reveals that an unknown defect center is still present after the dis-

TABLE IV. Defect-piezospectroscopic-tensor components (eV)  $B_i^j$  for splitting of the divacancy-associated bands.

Band ( $\mu$ )	$B_1^j$	$B_2^j$	$B_3^j$	$B_4^j$
1.8	7.0	11.6	1.7	0
3.45	2.67	1.9	0.23	0
3.61	2.2	1.24	0.28	0

appearance of the divacancy defect. The absence of the 3.9- $\mu$  band which was observed previously on the same sample and dose condition<sup>6,25</sup> and identified as associated with the +1 charge state of divacancy defect, is also not understood. However, from the fact that the Fermi-level position of our neutron-irradiated Si samples is in the vicinity of the middle of the energy gap and the observation of the 1.8-, 3.3-, 3.45-, and 3.61- $\mu$  bands in all types of Si we conclude that the charge states of

divacancy defects responsible for the observation of these bands are not unique, but rather are mostly in the neutral charge state.

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## Short-Range Order and Pseudogaps in Elemental Amorphous Covalent Semiconductors\*

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The role of short-range order in producing a pseudogap in the density of states  $\rho(E)$  of an elemental amorphous material is investigated. An approximate expression for  $\rho(E)$  which emphasizes short-range order and neglects all long-range order is derived from multiple-scattering theory. This expression is used to study the influence of short-range order consisting of two atoms, a single bond, and eight atoms in the staggered and eclipsed bonding configurations on  $\rho(E)$ . The results of numerical calculation for amorphous  $sp^3$ -bonded C, amorphous Si, and amorphous Ge are reported. These results suggest that the pseudogap in  $\rho(E)$  may be attributed to the short-range order.

### I. INTRODUCTION

Recent widespread interest in amorphous Si and

Ge has led to extensive experimental investigations of the properties of these materials.<sup>1</sup> One of the interesting results of these experimental investi-