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Photoconductivity Studies of Radiation-Induced Defects in Silicon[†] [*]

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The annealing behavior and the uniaxial-stress responses of the radiation-induced defect causing the $E_c - 0.75$-, $E_c - 0.54$-, $E_c - 0.42$-, and $E_c - 0.18$-eV photoconductivity energy levels in n-type silicon were studied after 1.5-MeV electron and ^{60}Co γ-ray irradiation at 300 °K. The results suggest that the $E_c - 0.75$-eV level arises from the electronic transition of the neutral charge state of the divacancy to the conduction band. This level also occurs in heavily irradiated p-type silicon when the Fermi level is too high to observe the divacancy-associated 0.32-eV photoconductivity band. The $E_c - 0.75$-eV level is found to be correlated with the 0.32-eV band, indicating that they are due to two different charge states of the same defect. The $E_c - 0.18$-eV level arises from the A-center defect which exhibits only one kind of stress response, i.e., the atomic redistribution among the allowable orientations. No electronic response was observed for the A center in our photoconductivity measurements. Our data fit very well with the A-center model derived from electron-paramagnetic-resonance studies. The $E_c - 0.42$-eV level was quite complicated. Besides the radiation-induced divacancy defect located near this level, we present evidence that some additional trap center inherent as an in-grown defect in the sample also gives rise to this level. The $E_c - 0.54$-eV level anneals out around 150 °C. Whether it really arises from the singly charged state of the divacancy or not is still a question.

I. INTRODUCTION

During the past several years, a new technique of measuring the photoconductivity spectra with polarized light and uniaxial stress has been developed by Cheng[1,2] and Kalma and Corelli.[3] Some important microscopic information on radiation-induced defects in silicon has been obtained using this technique, especially on the divacancy-defect studies. Kalma and Corelli[3] concluded that the $E_c - 0.39$- and $E_c - 0.54$-eV energy levels in the photoconductivity spectra can be correlated with the doubly negative charge state and singly negative charge state of the divacancy, respectively, in n-type Si. Cheng[1,2] showed that the 0.32-eV photoconductivity band can be correlated with the singly positive charge state of the divacancy defect in p-type Si. There have been no definitive results reported on the neutral charge state of the divacancy from photoconductivity measurements. A review of the divacancy-defect properties will not be given here since this can be found in the paper by Cheng *et al.*[4]

As a result of Jahn-Teller distortion the point-group symmetry of the divacancy is lowered from D_{3d} to C_{2h}. The C_{2h} orbitals are shown in Fig. 1. The recent infrared-absorption study by Chen[5] has suggested that the 3.45-μ micron (0.36 eV) and 3.61-μ micron (0.34 eV) absorption bands are mostly due to the transitions from the neutral charge state of the divacancy, i.e., the γ transition.

In this paper, we present the results of similar studies on the $E_c - 0.75$-, $E_c - 0.54$-, $E_c - 0.42$-, and $E_c - 0.18$-eV photoconductivity energy levels in n-type silicon which are produced by 1.5-MeV electron and by ^{60}Co γ-ray irradiation. From the annealing behavior and stress-experiment results, we have assigned the $E_c - 0.75$-eV energy level to the electron transition from the neutral charge state of the divacancy to the conduction band.

The detailed annealing studies on the heavily irradiated p-type samples also will be reported in this paper. The shifting of the Fermi-level positions during the annealing gives us one more piece of evidence supporting our conclusions on the divacancy (see Fig. 6).

The A-center defect was first observed by Wertheim[6,7] and Hill[8] by using minority-carrier-lifetime and electrical-property measurements. They found it had a net acceptor level at $E_c - 0.17$ eV. From electron-paramagnetic-resonance (EPR) studies, Watkins and Corbett[9] concluded that this center is a lattice vacancy trapped by an interstitial oxygen atom. The symmetric A center belongs to the C_{2v} symmetry point group. The one-electron molecular-orbital energy levels associated with the A-center defect are shown in Fig. 2. Spin resonance and electrical activity arise from an additional electron which is trapped in the b_1 orbital state, which is a singlet state having no orbital degeneracy and, therefore, no Jahn-Teller distortion. If all the states are filled with electrons, the electronic configurations cannot redistribute among the particular defect orientations, and no electronic response should be observed under the action of an applied uniaxial stress. The activation energy for the defect reorientation is ≈ 0.40 eV. Therefore, the defects can reorient thermally at room

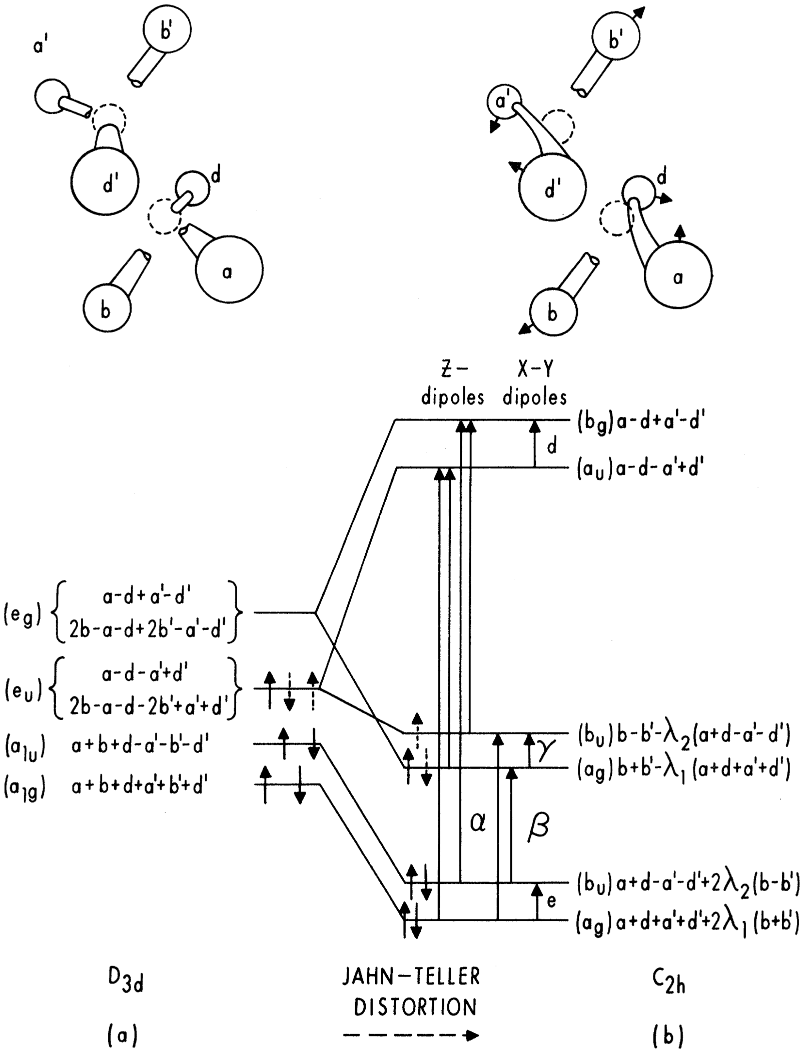

FIG. 1. Simple LCAO molecular-orbital model of the electronic structure of the divacancy: (a) before Jahn-Teller distortion; (b) after distortion with the possible electric-dipole transitions.

temperature. The detailed uniaxial-stress experiments have been done on the $E_c - 0.18$-eV level. The data fit very well with the A-center model given by Watkins and Corbett.[9]

II. EXPERIMENTAL PROCEDURE

All the samples used in this study were cut from commercially available silicon ingots of both crucible-grown (CG) ($\gtrsim 10^{17}$ oxygen atoms/cm^3) and floating-zone-refined FZ ($\lesssim 10^{16}$ oxygen atoms/cm^3) crystals. The sample dimensions were about $3 \times 3 \times 12$ mm. The phosphorus impurity concentrations ranged from 5×10^{13} to 6×10^{15} impurity/cm^3. The Ohmic contacts were made by a hot probe which pressed As-doped gold wire on both ends of one of the polished sample surfaces. The contacts were considered Ohmic if they did not rectify at liquid-nitrogen temperature. The sample surfaces which were exposed to infrared light were polished with diamond abrasive and 0.3-μ alumina abrasive to eliminate spurious surface effects and also to increase the transmission. The ends of the sample were polished flat and parallel to prevent breakage during stressing.

The 1.5-MeV electron irradiations were carried

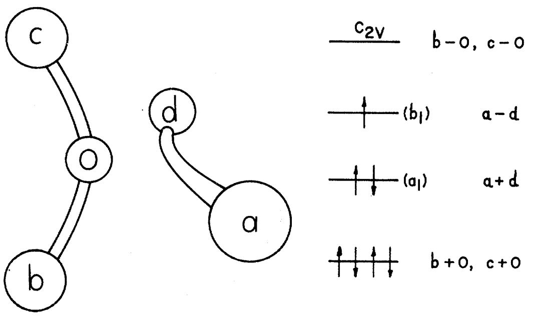

FIG. 2. The one-electron LCAO molecular-orbital energy levels associated with the A-center defect.

out both on the R.P.I. 3-MeV Van de Graaff and the 1.5-MeV cathode-ray accelerator of the General Electric Research and Development Center. The samples were mounted on a thin-walled aluminum box with cold water flowing inside. The sample temperature was $\lesssim 30\,^\circ\mathrm{C}$ during irradiation. The ^{60}Co γ-ray irradiation was performed using facilities and personnel at the Air Force Cambridge Research Laboratories, Bedford, Mass.

The photoconductivity spectra were measured in a standard liquid-nitrogen cryostat. The sample was cooled down to liquid-nitrogen temperature by heat transfer of helium gas. A small hole in the sample holder allowed incoming light to be detected by a thermocouple so that we could obtain the normalized spectra directly, i.e., simultaneous measurement of both the sample signal and light-source signal. For low-temperature stress studies the sample was stressed in the cryostat after the sample was cooled down to liquid-nitrogen temperature, with pressure remaining on the sample during the measurement. For room-temperature stress, the pressure was applied to the sample at room temperature for 1 h, then cooled to liquid-nitrogen temperature and the stress removed for the measurement. In all our experiments the stress was applied by a hydraulic press. A description of the stresser is given elsewhere.[3]

Two different kinds of monochromators were used in this study. A Spex model No. 1500 evacuable grating monochromator was used to measure straight photoconductivity spectra (i.e., without stress) and for detailed annealing measurements. For all the stress studies, a Perkin-Elmer model No. 98 monochromator was used. The energy resolutions of the grating monochromator were better than 0.005 eV and were about 0.02 – 0.005 eV for the prism monochromator throughout the energy region in which the photoconductivity spectra were taken (1.1–0.13 eV). Both systems were purged with dry air to eliminate water vapor and carbon-dioxide absorptions during the measurement. A Perkin-Elmer wire-grid polarizer was placed at the entrance slit of the prism monochromator.

The signal-to-noise ratio is lowest (~2–5) at the photoconductivity cutoff at the lowest energy and is in general 20 or larger at the higher-energy end of the spectrum.

The photoconductivity-signal voltages were measured with two Princeton Applied Research Corporation model No. HR 8 lock-in amplifiers equipped with type-A or type-C preamplifiers. For sample impedance above ~5000 Ω, the type-A preamplifier was used. For low-impedance samples a type-C preamplifier was used. The signals from both amplifiers were fed into a Princeton Applied Research Corporation model No. RC10 ratiometer which yielded the normalized photoconductivity signal at the output.

The annealing was performed in a temperature-controlled furnace with the sample in air.

The infrared light beam was chopped at various frequencies; for high sensitivity we chose 13 Hz for most of the measurements.

III. EXPERIMENTAL RESULTS

A. $E_c - 0.75$-eV Defect Level

In the photoconductivity studies of 1.5-MeV electron and ^{60}Co γ-ray–irradiated *n*-type silicon, we found a defect level located at $E_c - 0.75$ eV in both CG and FZ samples regardless of chemical species of dopant (P, As, and Sb). This level was first observed in irradiated Si by Thackev *et al.*[10] in their photoconductivity measurements but they did not give any interpretations of the defect causing this level. In our work we shall correlate this level with the neutral charge state of the divacancy. Figure 3 presents the isochronal annealing (up to 400 °C) of photoconductivity spectra for a 100-Ω cm FZ sample irradiated with 10^8 rad of γ rays. Figure 4 gives the spectra of a sample cut from the same ingot and irradiated with 1.6×10^{15} e/cm^2. It is obvious that there is no difference in defect levels produced by ^{60}Co γ-ray and 1.5-MeV electron irradiation. This evidence was also found by Saito and Hirata,[11] who used electrical-property measurements to detect defects. In Figs. 3 and 4 we see that three dominant levels are introduced by the irradiation. They are located at $E_c - 0.75$, $E_c - 0.42$, and $E_c - 0.18$ eV. Here we shall consider only the $E_c - 0.75$-eV level. Since the Fermi level is about 0.18 eV from the edge of the conduction band, the contribution to the 0.75-eV energy level by electron transitions from the valence band to this level is automatically ruled out. The only possible transition would be from the $E_c - 0.75$-eV defect level to the conduction band. The results of the isochronal annealing show that this level disappears after 350 °C. This is the temperature at which the divacancy is annealed out. The spectrum after the 400 °C anneal is almost the same as the preirradiation spectrum (shown in Fig. 3), which means all the defects produced by radiation were gone after a 400 °C anneal.

Low-temperature stress experiments were performed on the $E_c - 0.75$-eV level for samples of three different orientations. Figure 5 presents the stress results of a 100-Ω cm phosphorus-doped sample irradiated with 3×10^{15} e/cm^2. The stress and infrared beam directions are shown in the figure. The stress magnitude was 2050 kg/cm^2. Before stress, this sample was annealed at 160 °C for 15 min in order to get rid of those defects which can be annealed out at lower temperature. Since uniaxial stress also can give an effect on other de-

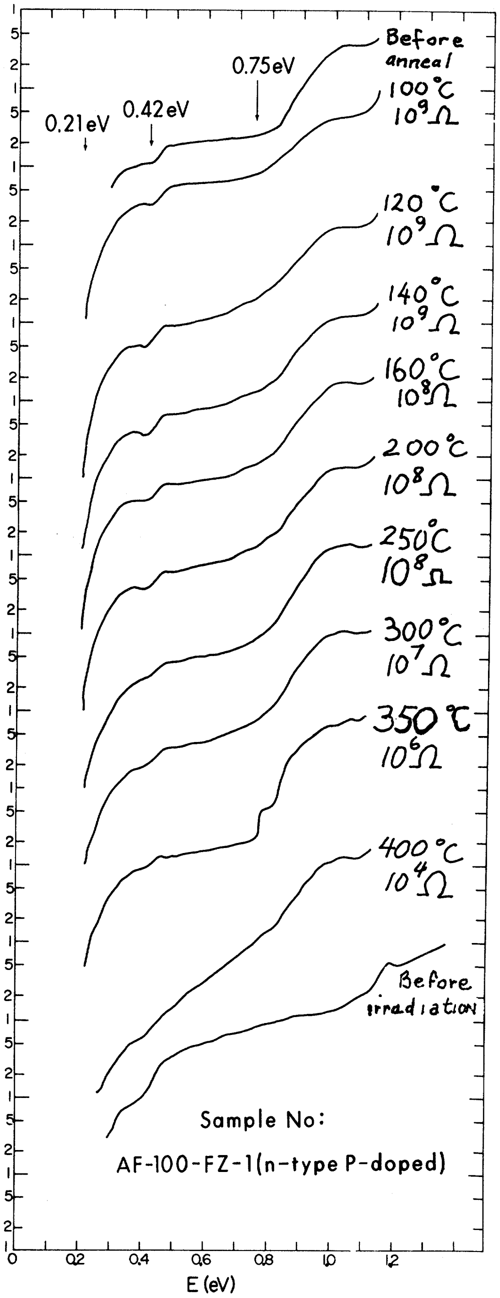

FIG. 3. Isochronal annealing of phosphorus-doped 100-Ω cm FZ silicon irradiated with 10^8 rad of ^{60}Co γ rays. Experimental errors are within width of line drawn through points. Radiation source: Co^{60} γ radiation 10^8 rad; measuring temperature: 78 °K; initial resistivity: 100 Ω cm; initial resistance: 130 Ω (78 °K).

fect levels, thus causing the background (Bkg) itself to exhibit dichroism masking the dichroism of the level under study, it was necessary to perform the 160 °C anneal. Therefore, we must consider both Bkg ⊥ and Bkg ∥. The measured dichroism[12] is 1.20 for the results given in Fig. 5.

Table I presents results of liquid-nitrogen-temperature stress on samples with different orientations. The comparisons of the magnitudes of the dichroisms obtained experimentally with theory are probably of little use as discussed by Kalma and Corelli,[3] but the sense of the dichroism should fit with the theory quite well.

When the stress was removed at liquid-nitrogen temperature, we found the dichroism disappeared very rapidly. This is because the electronic reorientation of the divacancy is not frozen in until temperatures below ~20 °K are reached.

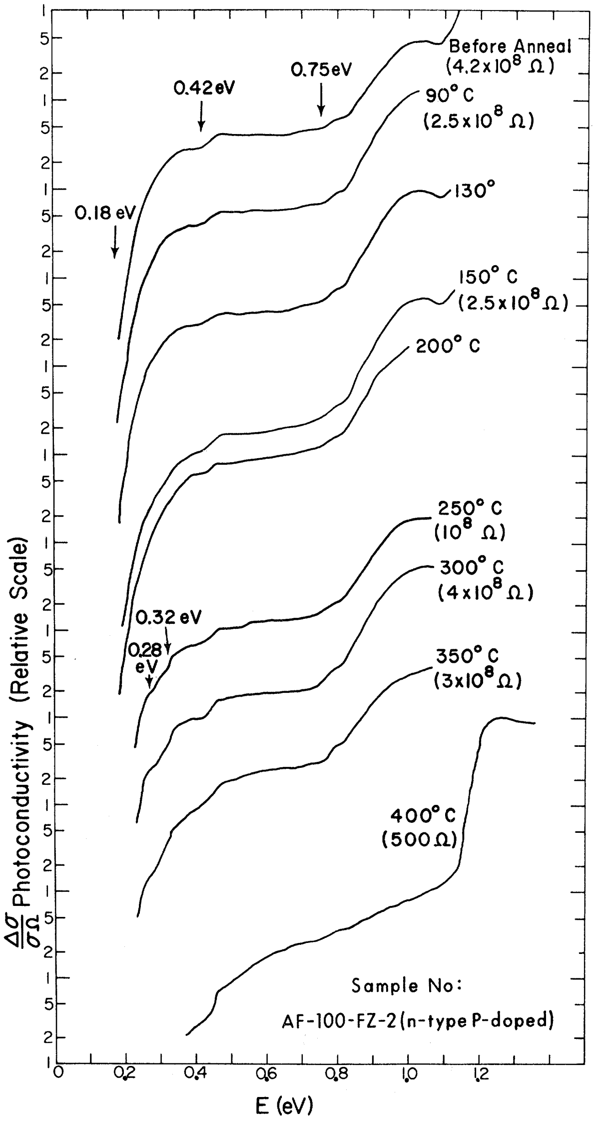

FIG. 4. Isochronal annealing of phosphorus-doped 100-Ω cm FZ silicon irradiated with 1.6×10^{15} e/cm^2 at 1.5 MeV. Experimental error as in Fig. 3. Radiation source: 1.5-MeV electrons 1.6×10^{15} e/cm^2; measuring temperature: 78 °K; initial resistivity: 100 Ω cm; initial resistance: 420 Ω (78 °K).

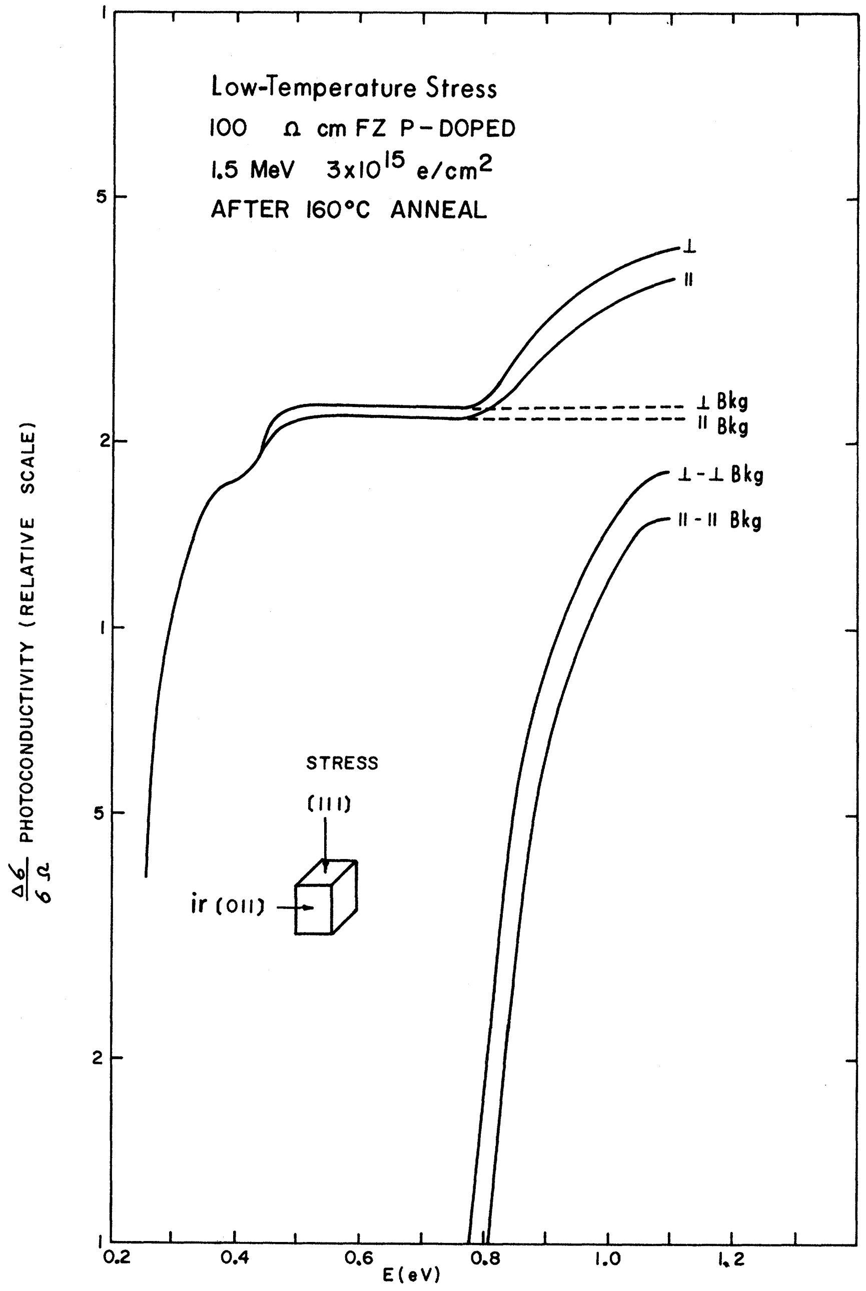

FIG. 5. Dichroism after stress of 2050 kg/cm^2 at 78 °K exhibited by 100-Ω cm phosphorus-doped FZ silicon irradiated with 3×10^{15} e/cm^2 at 1.5 MeV. The sample was annealed to 160 °C for 15 min before the stress was applied. The ⊥ and ∥ denote the photoconductivity signal with the incident light polarized with $\vec{E}$ perpendicular to the stress direction and with $\vec{E}$ parallel to the stress direction, respectively.

In the photoconductivity studies of electron-irradiated p-type silicon samples, we found there is an energy level located at 0.72 eV when the Fermi level is too high to observe the 0.32-eV photoconductivity peak which has been identified with the singly positive charge state of the divacancy.[1,2] Figure 6 presents the spectra of 100-Ω cm B-doped silicon irradiated with 4.6×10^{16} e/cm^2 at 1.5 MeV. With such high doses, the Fermi level is located around the middle of the gap after the irradiation, i.e., above the $b + b'$ orbital state (see Fig. 1). The results show that as the 0.72-eV level anneals out the 0.32-eV peak comes in. This gives us strong evidence that these two levels arise from the transitions from the same orbital with different charge states. Before the 120 °C annealing, the $b + b'$ orbital state is filled with electrons because the Fermi level is above this state, and we observe the transitions from the neutral charge state of the divacancy. After the 120 °C annealing, the Fermi level shifts down, the $b + b'$ state is emptied of electrons, and we should expect to see the transitions associated with the valence band to this empty state which gives rise to the 0.32-eV photoconductivity

TABLE I. Dichroism results on $E_c - 0.75$-eV level for 100-Ω cm phosphorus-doped FZ silicon stressed at 78 °K.

Stress (kg/cm^2)	Stress direction	Infrared direction	D (measured)	D (theory)
2050	[111]	[1$\bar{1}$0]	1.2	> 1
2050	[011]	[100]	1.3	> 1
2050	[100]	[011]	0.81	< 1

peak. The slight energy difference between the n-type and the p-type samples (0.75 eV in n-type and 0.72 eV in p type) is probably due to the disordered regions produced in the p-type sample as a result of the heavy radiation dose.[3,13]

B. E_c-0.18-eV Defect Level

The photoconductivity studies of 1.5-MeV electron-irradiated CG or low-impurity-doped (~ 100 Ω cm) FZ crystals after room-temperature irradiation showed that there is a defect level located at $E_c - 0.18$ eV no matter what species of chemical dopant was in the sample. We also found that the production of this defect level is impurity concentration dependent. For the high-purity CG samples, this level can not be observed because of the unavailability of electrons. Figure 7 presents the photoconductivity spectrum of 1-Ω cm phosphorus-doped CG sample irradiated with 8×10^{16} e/cm^2. In order to identify the $E_c - 0.18$-eV level with the A-center defect (oxygen-vacancy pair), the location of Fermi level in the forbidden gap is very

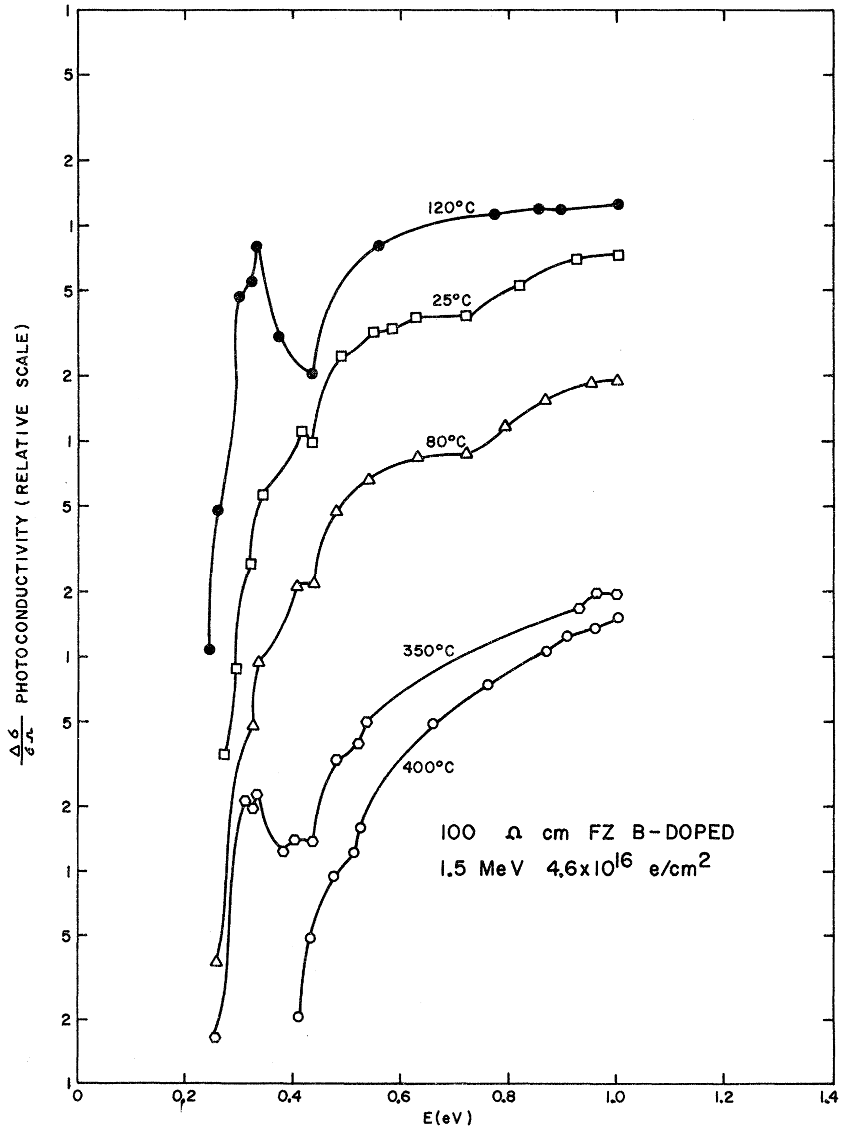

FIG. 6. Isochronal annealing of boron-doped 100-Ω cm FZ silicon irradiated with 4.6×10^{16} e/cm^2 at 1.5 MeV. Experimental error is less than the circle points.

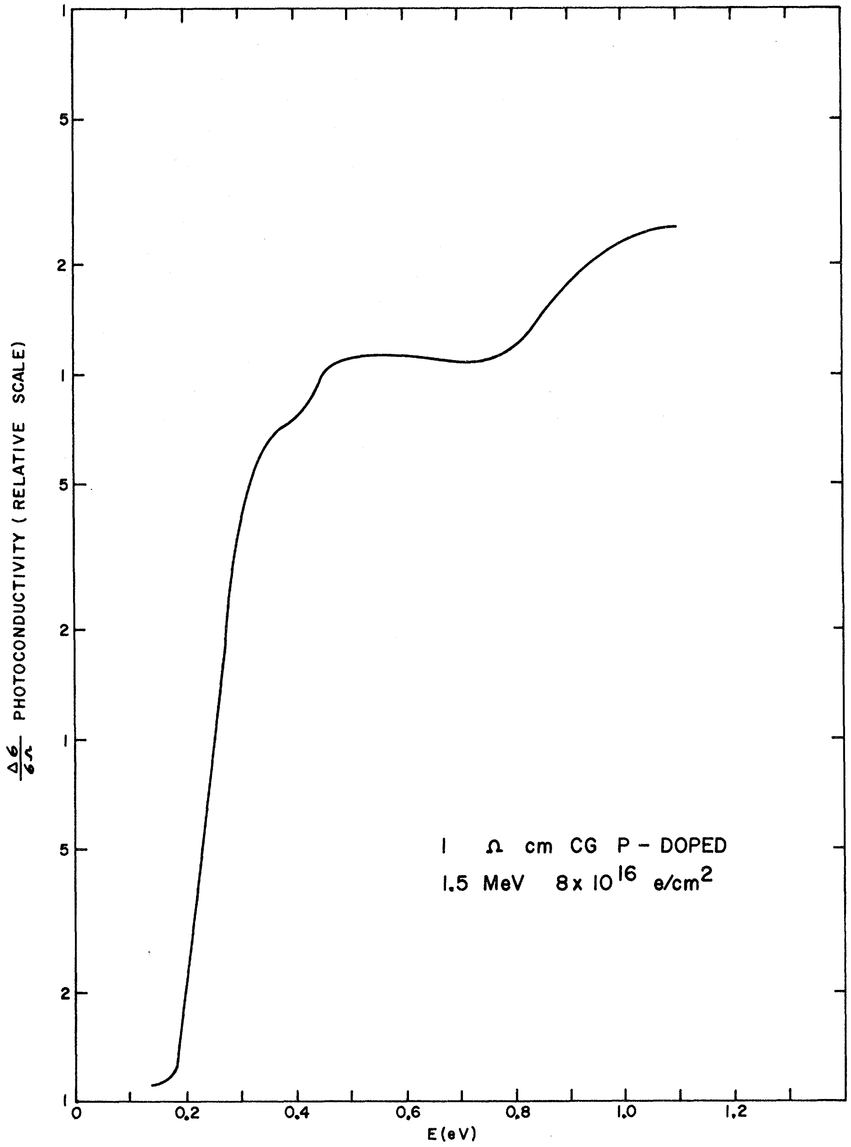

FIG. 7. Photoconductivity spectrum of 1-Ω cm phosphorus-doped CG silicon irradiated with 8×10^{16} e/cm^2 at 1.5 MeV. Experimental error as in Fig. 3.

important. Experimentally, it can be obtained by observing what energy level gave rise to photoconductivity and knowing that the Fermi level must be above that particular energy level in *n*-type material. To avoid the nonequilibrium trapping mechanism which might occur during the measurement, it was suggested[14] that the spectrum be measured from lower to higher energies (i.e., from long wavelengths to short wavelengths). This was done and from Fig. 7, which gives the result, we therefore can be certain that the Fermi level of this sample is somewhere above $E_c - 0.18$ eV, i.e., all the defects in this level are filled with electrons.

Figure 8 gives the annealing spectra up to 400 °C of a 100-Ω cm CG sample irradiated with 10^8 rad of ^{60}Co γ rays. The $E_c - 0.18$-eV level was not clearly seen until after 150 °C annealing. The same phenomenon was found also in electron-irradiated samples and are shown in Fig. 9. The reason for this is that there are many deeper-lying acceptor levels produced by such high radiation doses which take the electrons away from the *A*-center defects. After the 150 °C anneal some deeper levels such as $E_c - 0.54$ eV are annealed out (see Fig. 10). Therefore, there are now additional electrons available to be trapped by the defect remaining, i.e., the *A* center. As we can see from Figs, 4, 8, and 9, the $E_c - 0.18$-eV level starts to anneal out at about 200 °C with subsequent appearance of new levels at $E_c - 0.28$ and $E_c - 0.32$ eV. These latter levels may also be oxygen associated, and similar behavior has been observed in infrared studies on the annealing of the 12-μband (*A* center) with subsequent evolution of other vibrational bands in the 10- to 11.7-μ

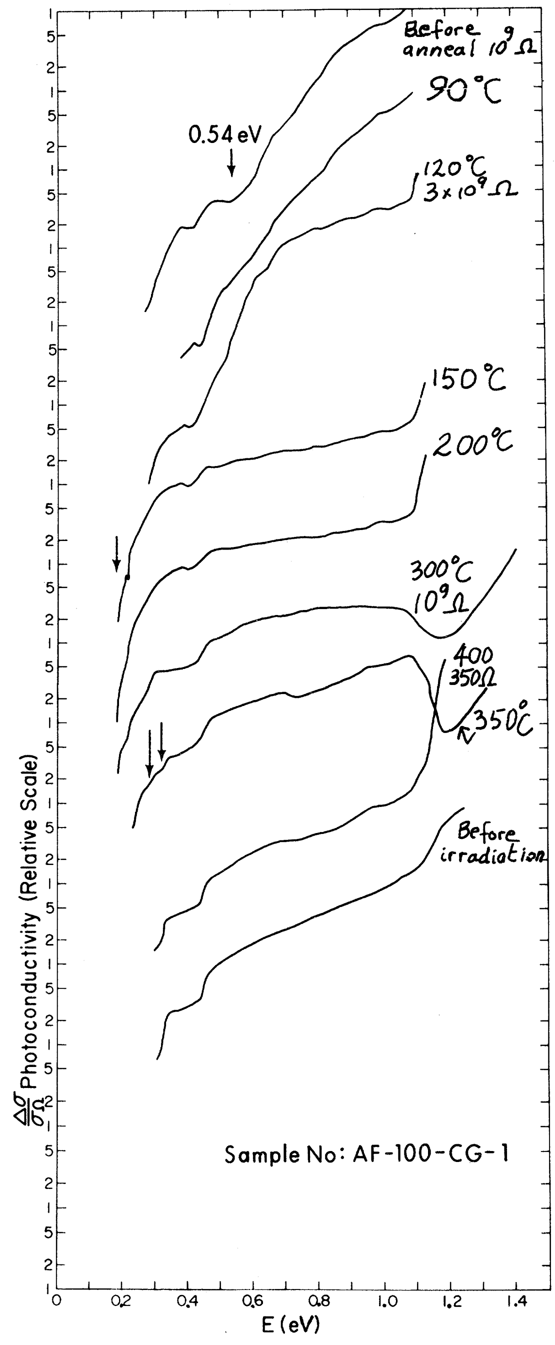

FIG. 8. Isochronal annealing of phosphorus-doped 100-Ω cm CG silicon irradiated with 10^8 rad of ^{60}Co γ rays. Experimental error as in Fig. 3. Measuring temperature: 78 °K; initial resistivity: 100 Ω cm; initial resistance: 380 Ω (78 °K).

TABLE II. Dichroism results on $E_c - 0.18$-eV level for 1-Ω cm phosphorus-doped CG silicon stressed at 300 °K.

Stress (kg/cm^2)	Stress direction	Infrared direction	D (measured)	D (theory)
2050	[011]	[0$\bar{1}$1]	0.70	0.63
2050	[011]	[100]	0.65	0.52
2050	[1$\bar{1}$0]	[1$\bar{1}$0]	0.98	0.94
2050	[100]	[011]	0.80	0.85

wavelength range.[15–17] The $E_c - 0.18$ eV was completely annealed out after 350 °C, which agrees with both the infrared and the EPR results on the annealing temperature of the A center.

Samples of four different orientations have been stressed at liquid-nitrogen temperature. We found no dichroism (i.e., $D=1$) on all the samples in the energy region of 0.18 to 0.40 eV.

Uniaxial stress at room temperature can realign the atomic configuration of the A-center defect. Oriented samples were stressed at room temperature for $1\frac{1}{2}$ h and then cooled down to liquid-nitrogen temperature with stress on so that the preferential defect orientation was frozen in. The stress was released at 78 °K and the photoconductivity spectrum then measured with polarized light. Typical spectra resulting from such a treatment on a 1-Ωcm phosphorus-doped CG sample irradiated with 8×10^{16} e/cm^2 are shown in Fig. 11. The stress direction on this sample was [011] and the stress magnitude was 2050 kg/cm^2. The infrared beam was incident in the [0$\bar{1}$1] direction. The magnitude of the dichroism was 0.70 for this particular orientation. Table II presents results on various samples with different orientations. The theoretical calculation of the dichroic ratio for atomic redistribution for the A-center defect is given in Table III. The a, b, c, d, are four silicon atoms surrounding an oxygen atom (refer to Fig. 12). The experimental error in the determination of the magnitude of the dichroism for this defect level is smaller than the deeper level because there is no shallower level than $E_c - 0.18$ eV present in the sample. Therefore, the error from the indefiniteness in the positioning of the background

TABLE III. Dichroic ratio for the atomic reorientation of the A-center defect.

Stress direction	Infrared direction	$\frac{E_\perp}{E_\parallel}$	Dichroic ratio
[100]	[0$\bar{1}$1]	$\frac{[110]}{[100]}$	$\frac{n_{ad}+n_{ab}}{2n_{ab}}$
[110]	[0$\bar{1}$1]	$\frac{[001]}{[110]}$	$\frac{2n_{ab}}{n_{ab}+n_{bc}}$
[110]	[100]	$\frac{[1\bar{1}0]}{[110]}$	$\frac{n_{ab}+n_{bc}}{n_{ab}+n_{ad}}$
[111]	[1$\bar{1}$0]	$\frac{[\bar{1}\bar{1}2]}{[111]}$	$\frac{5n_{ac}+7n_{ab}}{4n_{ac}+8n_{ab}}$

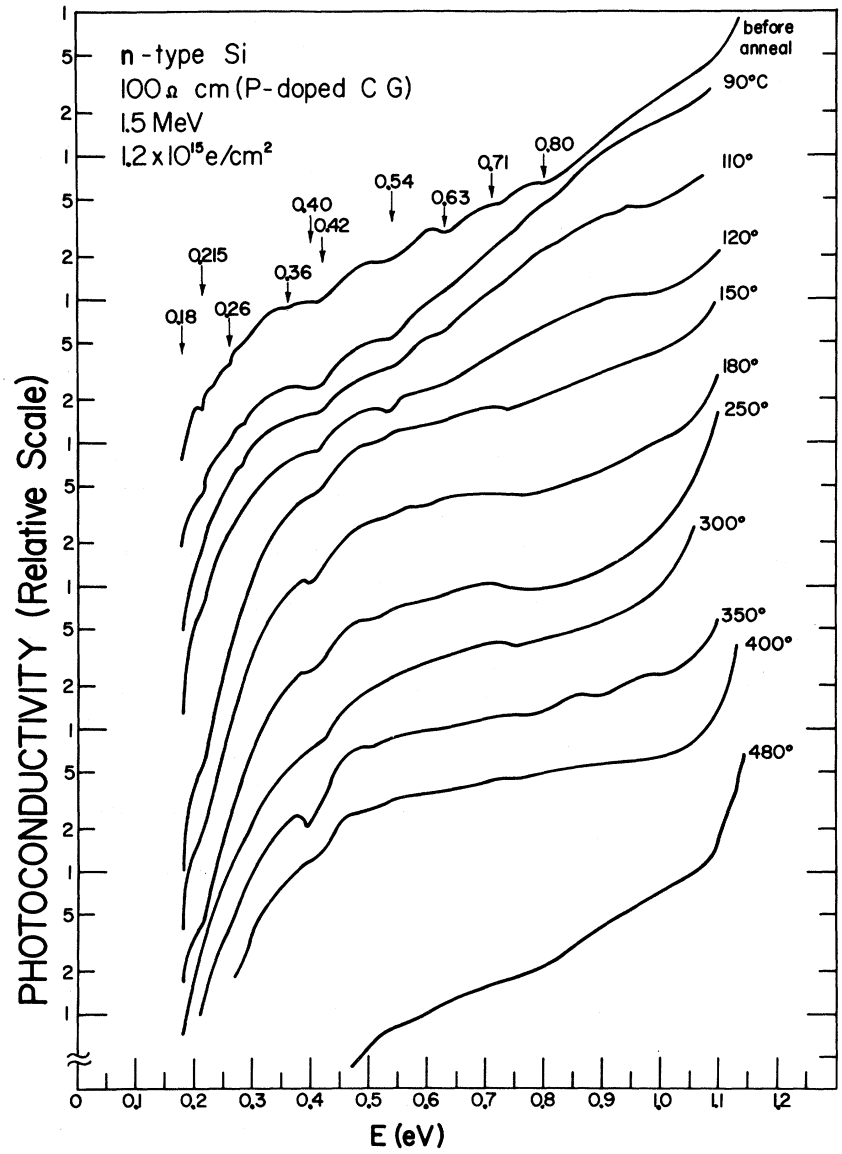

FIG. 9. Isochronal annealing of phosphorus-doped 100-Ω cm CG silicon irradiated with 1.2×10^{15} e/cm^2 at 1.5 MeV. Experimental error as in Fig. 3.

can be eliminated for this particular case. But the errors from other factors such as inhomogeneity of the polarizer, the orientation of the samples after cutting from the ingot (which might be off ±2°), and the leakage of the hydraulic pressure of the jack during the measurement, etc., can cause an error of about ±10% in the magnitude of the dichroism. The results shown in Table II are consistent and in good agreement with the model which was proposed by Watkins and Corbett[9] from EPR studies.

IV. DISCUSSIONS AND CONCLUSIONS

A. Correlation of E_c-0.75-eV Level with the Neutral Charge State of the Divacancy

We have assigned the $E_c-0.75$-eV photoconductivity energy level with the transition to the conduction band from the neutral charge state of the divacancy. This argument was based upon several correlations between the divacancy model as previously studied by EPR[18] and infrared[4,5] work.

(i) From the one-electron molecular-orbital energy levels associated with the divacancy model as shown in Fig. 1, the divacancy has neutral charge state with two electrons in the antibonding $b-b'$ orbital. In the n-type sample, if the Fermi level is above these levels, then we should expect to see the transitions between these levels and conduction-band edge. From detailed infrared studies Chen[5] has concluded that the 0.36- and the 0.34-eV infrared abosrption bands can be correlated with the transition from the neutral charge state, i.e.,

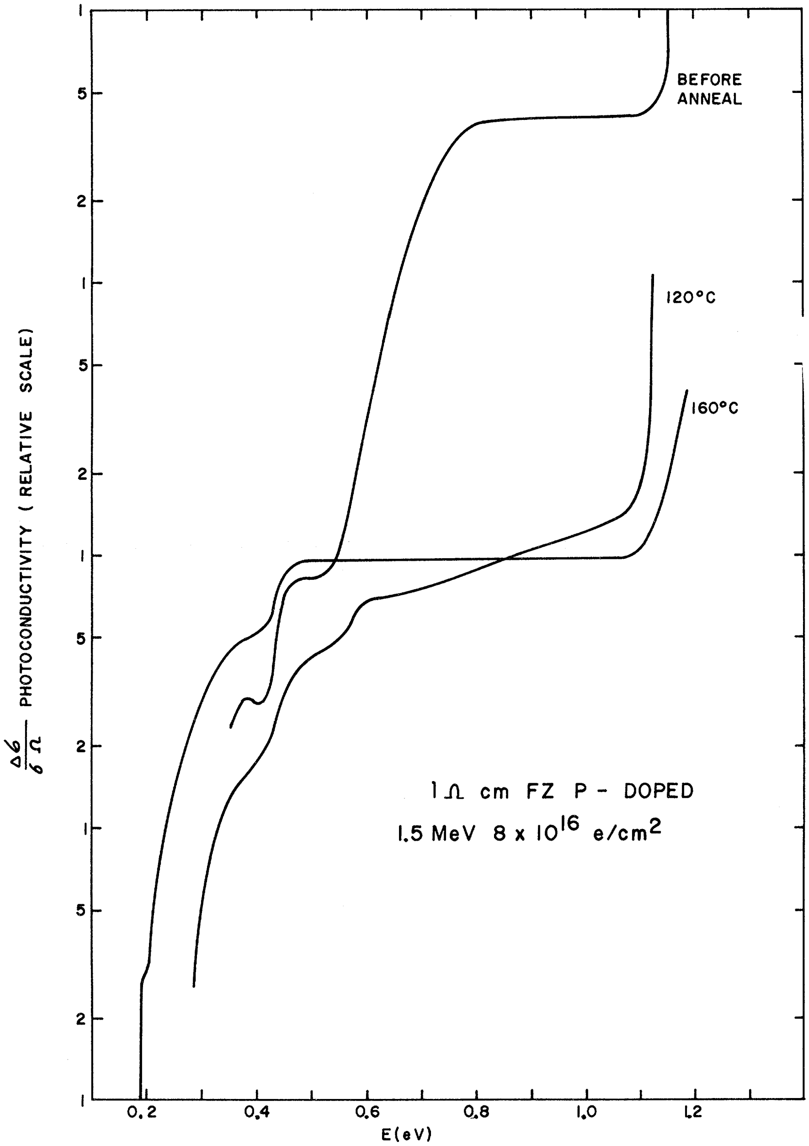

FIG. 10. Isochronal annealing of the $E_c - 0.54$-eV energy level.

the γ transition. The photoconductivity work by Kalma and Corelli[3] correlated the transitions from the $b - b'$ state to the conduction-band edge with the $E_c - 0.39$-eV level. Therefore, it is reasonable to suggest that the $b + b'$ state is located ≈ 0.75 eV from the conduction-band edge.

(ii) The isochronal annealing experiment shows that the level disappears after 350 °C, which is the same temperature that the 0.32-eV photoconductivity band anneals out.

(iii) The level occurs in n-type samples regardless of chemical species of dopant (P, As, or Sb) in both FZ and CG crystals.

(iv) The level occurs in heavily electron-irradiated p-type silicon when the Fermi level is too high to observe the 0.32-eV photoconductivity band. This level disappears as the 0.32-eV photoconductivity band comes in during the annealing, which indicates that these two levels arise from the same defect with electrons filling up the same orbital of different charge state.

(v) The measured dichroisms at liquid-nitrogen temperature are of the same sense as those calculated from the neutral charge state of the divacancy.

The theoretical calculation of the neutral charge state of the divacancy has been worked out by Callaway and Hughes.[19,20] Two localized states of different symmetry, which belong to the A_{1g} and A_{2u} representations of the D_{3d} point group, are found to be possible. The energies of these two bound states

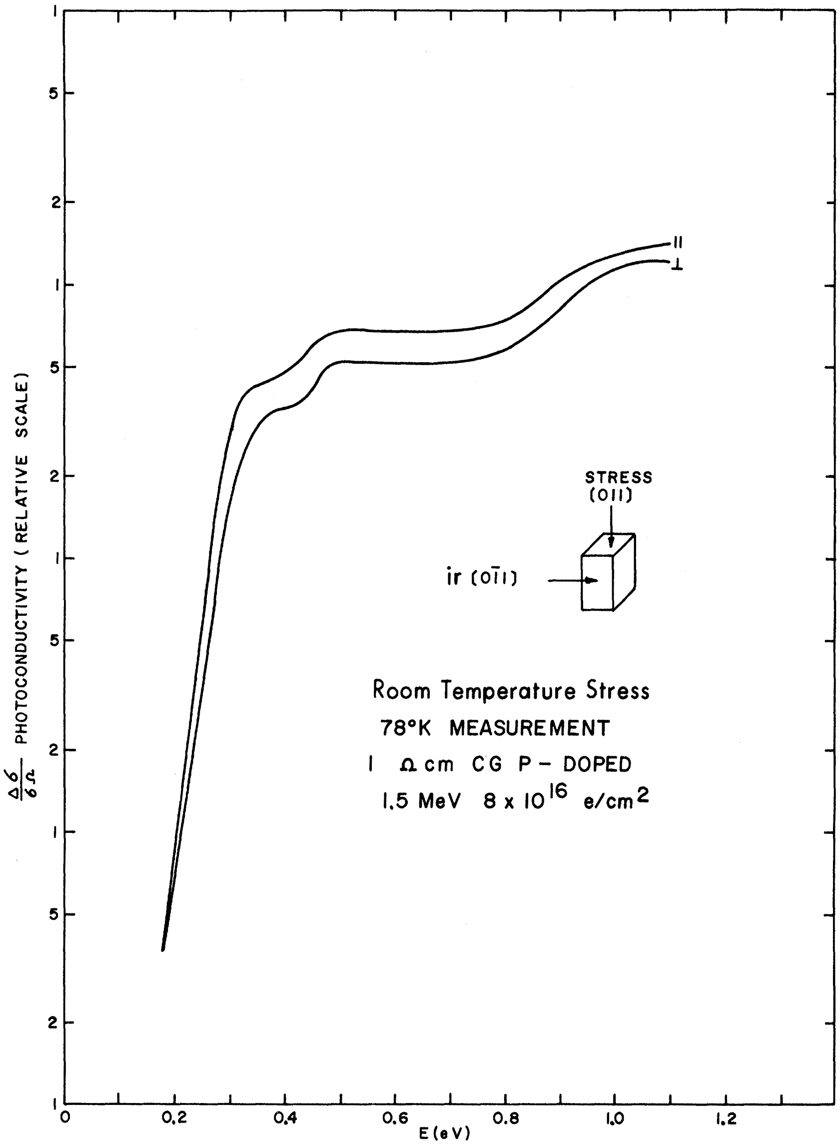

FIG. 11. Dichroism after stress of 2050 kg/cm^2 at room temperature exhibited by 1-Ω cm phosphorus-doped CG silicon irradiated with 8×10^{16} e/cm^2 at 1.5 MeV. Experimental error given in text.

are functions of a continuous parameter λ. The lowest level of the neutral divacancy has A_{1g} symmetry and requires a λ of about 1.4. This assignment has a good feature in that the symmetry of the ground state is the same as that found by the linear-combination-of-atomic-orbitals (LCAO) technique. For $\lambda = 1.4$, no solution of A_{2u} symmetry exists. Their calculations indicate the transition would be from the A_{1g} level to the conduction band with an energy about 0.72 eV, which agrees with our photoconductivity result.

B. Correlation of the E_c-0.18-eV Level with the A-Center Defect

As we stated previously, the photoconductivity energy level located at $E_c - 0.18$ eV arises from transitions of the A-center defect. The experimental results leading to this identification will now be discussed.

(a) Energy-level position agrees with those found from EPR work and electrical measurements in which they report the level is located at $E_c - 0.17$ eV.[6–9]

(b) The isochronal annealing temperature of this level is about the same as that of A center which anneals out about 350 °C.[15–17]

(c) Uniaxial stress applied at low temperature (78 °K) shows no dichroism if the Fermi level is above the $E_c - 0.18$ eV, i.e., all the A-center-defect levels are filled with electrons. This agrees with the A-center model and the EPR result.[9] From the one-electron LCAO–molecular-orbital treatment of the A center, the ground state of A-

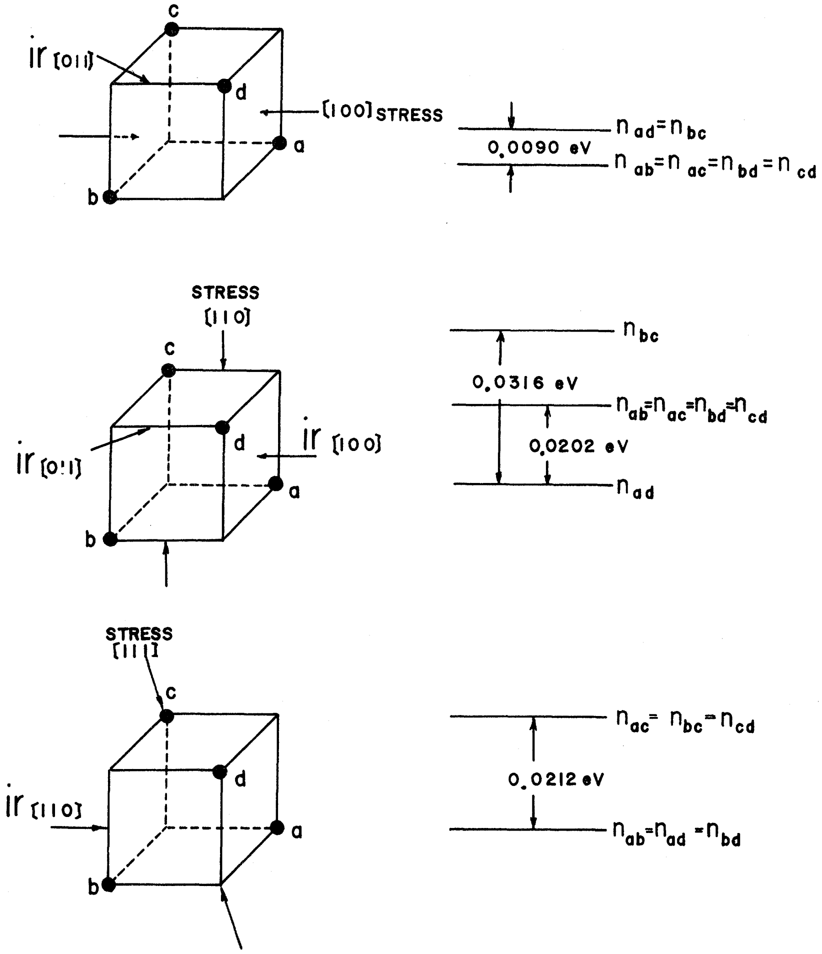

FIG. 12. Nonequivalent-defect-reorientation result by room-temperature stress along three principal crystal axes for the A-center defect.

center defect is a singlet state having no Jahn-Teller distortion. Therefore, when all the centers are filled with electrons, the electronic configuration cannot reorient upon application of uniaxial stress and no dichroism should be observed, which was the case in our experiments.

(d) Uniaxial stress applied at room temperature reorients the atomic configuration of the A center. There are six different ways that the oxygen atom can be placed between two of the four silicon atoms surrounding a vacancy. The activation energy for the defect reorientation was ≈0.4 eV. Therefore, the defects can reorient thermally at room temperature. The dichroism we found in photoconductivity measurements after room-temperature stress agrees with the model quite well.

All these experimental phenomena support the conclusions that the $E_c - 0.18$-eV energy level in the photoconductivity spectra is due to the electron transition from the A-center defect to the conduction band.

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$$D=\left[\left(\frac{\Delta\sigma}{\sigma\Omega}\right)_{\perp}-\left(\frac{\Delta\sigma}{\sigma\Omega}\right)\mathrm{Bkg}_{\perp}\right]\bigg/\left[\left(\frac{\Delta\sigma}{\sigma\Omega}\right)_{\parallel}-\left(\frac{\Delta\sigma}{\sigma\Omega}\right)\mathrm{Bkg}_{\parallel}\right].$$

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Fluorescence of Graded-Band-Gap $CdS_x Se_{1-x}$ Crystals Produced by Diffusion

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The fluorescence of CdS_xSe_{1-x} mixed crystals with band-gap gradients as large as 1200 eV/cm has been investigated at 77 °K. The graded samples were produced by heating CdSe or CdS_xSe_{1-x} platelets in a sulfur-selenium atmosphere. Some of the diffused crystals were post-treated in a cadmium atmosphere. Removal of surface material shifted the fluorescence spectra of the diffused crystals to longer wavelengths. The spectral position of fluorescence peaks was determined as a function of the thickness of the removed surface layer. Composition profiles were deduced from these data by correlating fluorescence wavelength with crystal composition. Error-function curves gave a good fit to experimentally determined profiles. Diffusion constants of 7.0×10^{-13} and 1.6×10^{-12} cm^2/sec were determined for diffusion temperatures of 600 and 650 °C, respectively.

I. INTRODUCTION

The optical band gap is strongly dependent on composition in most II-VI compound mixed-crystal systems. Optical methods have been used to study composition variations in graded-band-gap mixed crystals of these compounds grown from the vapor phase. Measurements of the spatial dependence of absorption in $CdS_x Se_{1-x}$, $Zn_x Cd_{1-x} S$, and $Zn_x Cd_{1-x} S_y Se_{1-y}$ graded mixed crystals have been made by Reimers,[1] and in $Zn_x Cd_{1-x} S$ by Indradev *et al.*[2] A positional variation in the band-edge fluorescence peak wavelength of $Zn_x Cd_{1-x} S$ crystals has been observed by Van Ruyven and Dev.[3] Bille *et al.*[4] have measured the dependence of stimulated emission wavelength on position in $CdS_x Se_{1-x}$ graded crystals.

Band-gap gradients of 2 eV/cm or less were reported for crystals grown from the vapor phase. Gradients of up to 100 eV/cm have recently been obtained by Biter and Williams[5] by epitaxial growth of CdS onto ZnS substrates and interdiffusion. Photoluminescence observed in the graded region of these crystals was attributed to electron-hole recombination at deep-lying acceptor states.

Graded $CdS_x Se_{1-x}$ crystals have been produced by diffusion from Se vapor into CdS host crystals by Handelman and Kaiser.[6] No measured profiles of band gap vs position were reported, but a diffusion rate was estimated by visual observation of the depth of change of crystal color as a function of diffusion time. In related work, radioactive-tracer techniques have been used by Woodbury and Hall[7] to study impurity diffusion of Se into CdS and CdTe, and by Kato *et al.*[8] to study diffusion of Se into CdTe.

Fluorescence studies on $CdS_x Se_{1-x}$ single crystals with band-gap gradients as high as 1200 eV/cm are reported in this paper. The crystals were prepared by a diffusion process which consists of heating platelets in an atmosphere of sulfur and selenium. Some of the diffused crystals were post treated in a cadmium atmosphere. Photolumines-