ing on the field. The range of fields in which the slope is $\frac{1}{2}\beta$ is too small to account for the $\frac{1}{2}\beta$ slope observed in the case of field-assisted thermal excitation in amorphous selenium. Neither of these models can account for the low β values obtained at short wavelengths. Since a realistic model is lacking in the case of amorphous selenium, further attempts to account for the discrepancy are purely speculative.

CONCLUSION

The photogeneration of mobile carriers in amorphous selenium has been shown to be electric-field-dependent. A correlation of the generation of holes and electrons to the applied field, incident photon energy, and the temperature has been obtained. The general feature of the relation suggests a field-assisted thermally activated photogeneration process. The empirical expression obtained experimentally is similar to the one derived by Frenkel for this type of process.

ACKNOWLEDGMENT

The authors wish to thank Dr. P. Warter for his helpful and stimulating discussions in the preparation of this manuscript and for his suggestion regarding the possibility of field-assisted photogeneration process in vitreous Se.

PHYSICAL REVIEW VOLUME 173, NUMBER 3 15 SEPTEMBER 1968

Photoconductivity Studies of Defects in Silicon: Divacancy-Associated Energy Levels*†

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(Received 26 February 1968)

A new technique using stress-induced reorientation of defect configuration in single crystals and measurement of the photoconductivity spectra with polarized light is developed and is applied to study defects in electron-irradiated silicon. The annealing behavior and the uniaxial stress response of the 1.5-MeV electron irradiation-induced defects causing the $E_c-(0.39$ eV) and the $E_c-(0.54$ eV) energy levels are studied. The results strongly indicate that these two levels arise from different charge states of the same defect having an atomic symmetry around a $\langle 111\rangle$ direction and a transition dipole along a $\langle 110\rangle$ direction. The activation energy for the annealing of the $E_c-(0.39$ eV) level is about 1.25 eV Correlating these results with those of previous electron-paramagnetic-resonance studies and infrared-absorption studies leads to the conclusion that the defect in question is the divacancy. Further evidence that the 0.32-eV (3.9-μ) photoconductivity band arises from the divacancy in silicon is given. This band is observed in high-resistivity (nominally undoped) p-type silicon, and it anneals in the same temperature region as the divacancy. The results are compared with linear combinations of atomic orbitals (LCAO) calculations. The dominant photoconductivity observed in 45–50-MeV electron-irradiated silicon is found to be an "energy band" that extends from the band edge down to energy of ≈ 0.3 eV, whereas in 1.5-MeV electron-irradiated silicon it is found to be single levels and the energy band is much smaller in both magnitude and extent, extending only down to ≈ 0.8 eV.

I. INTRODUCTION

PHOTOCONDUCTIVITY studies performed during the past several years have concentrated on determining the energy levels of radiation-produced defects.[1–7] No microscopic information concerning the defects has resulted from such measurements. However, Corbett[8] has pointed out that many defects are anisotropic and can be preferentially aligned under a mechanical stress. Photoconductivity spectra measured with polarized light should reflect this alignment and give information about the microscopic configurations

* Research supported by the National Aeronautics and Space Administration under a research grant and a NASA Traineeship to A. H. Kalma.

† This paper is taken from the Ph.D. Thesis of A. H. Kalma submitted to the faculty of the Nuclear Engineering and Science Division at Rensselaer Polytechnic Institute.

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of defects. In this paper, we present the results of a study employing uniaxial stress and polarized light to study the photoconductivity of defects in electron-irradiated n-type silicon. In particular, we shall identify energy levels located at $E_c-(0.39 \text{ eV})$ and $E_c-(0.54 \text{ eV})$ with the divacancy.[9]

The first reported study of this type was made by Cheng,[10,11] using polarized light and uniaxial stress to study the 3.9-μ photoconductivity band in neutron-irradiated p-type silicon. Because of the shape of the band, Cheng concluded that it is not caused by direct ionization from the valence band to the defect level. Rather, the band is an excitation from the ground state to an excited state of the defect followed by the emission of a hole from the empty ground state. This type of transition is more akin to an infrared-absorption transition than a "normal" photoconductivity transition in which the final state is a carrier band. For a defect-state-to-defect-state transition, only one dipole-moment direction is allowed by group theory. However, for a defect-state-to-band transition, all dipole-moment directions are allowed. Since the initial state is a defect state, we would expect that the dominant oscillator strength would still reflect the defect symmetry. The result of this is that anisotropic absorption of polarized light resulting in a "normal" photoconductivity transition should be smaller than, but of the same sense as, that predicted for a defect-state-to-defect-state transition.

A review of previous infrared-absorption (IR)[1,12–20] and electron-paramagnetic-resonance (EPR)[21,22] studies of defects identified with the divacancy has been presented by Cheng *et al.*[23] in their paper correlating the

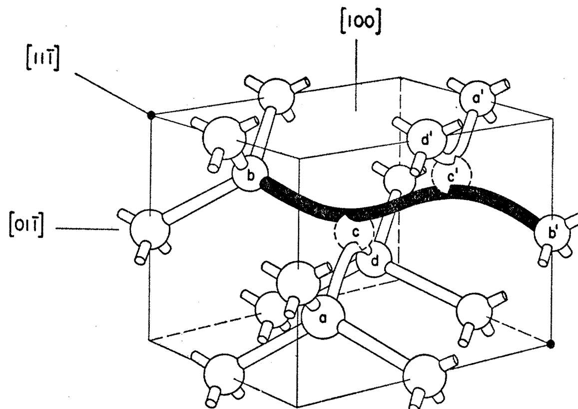

FIG. 1. Model of the divacancy in silicon deduced from EPR studies.

1.8-, 3.3-, and 3.9-μ infrared-absorption bands with the divacancy. Figure 1 presents the model of the divacancy given in the paper by Corbett and Watkins.[21] The vacancy-vacancy axis is along a $\langle 111\rangle$ direction and the transition dipole moment is in an $\{110\}$ plane (an X-Y dipole). The angle of the dipole in this plane is found to be close to the X axis (the [110] direction in Fig. 1). In making the identification of the $E_c-(0.39 \text{ eV})$ and $E_c-(0.54 \text{ eV})$ levels with the divacancy, we shall compare our results with IR and EPR results and also results relating to the 3.9-μ photoconductivity band in p-type silicon which has been identified by Cheng[10,11] as arising from the divacancy. We shall also present some further results on the 3.9-μ band in p-type silicon and on the effect of disorder on photoconductivity spectra. A preliminary report of this study has already been presented.[24]

II. EXPERIMENTAL PROCEDURE

Rectangular-bar samples ($\sim\frac{1}{2}\times\frac{1}{8}\times\frac{1}{8}$ in.) were cut from commercially available floating-zone ($\lesssim 10^{16}$ oxygen/cm^3) silicon ingots. Ohmic contacts were made by heating the sample and pressing arsenic-doped gold into the ends of one of the faces with a hot probe. The sample surfaces which were exposed to infrared light were polished with No. 6 Universal Diamond Abrasive and 0.3-μ alumina abrasive to increase transmission. The crystal orientations were determined from the growth marks[20] or by an optical-reflecting technique[25] if the growth marks were not clearly discernible.

The 40–50-MeV electron irradiations were performed on the Rensselaer Polytechnic Institute linear accelerator at room temperature and the sample temperature was maintained $\lesssim 40^\circ$C. The 1.5-MeV electron irradiations were performed on the General Electric Research

[9] Energy-level positions quoted here are taken to be the energy at which ionization begins.
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and Development Center cathode-ray accelerator. The 1.5-MeV-irradiated samples were placed in contact with a plate behind which ice water flowed and the samples were turned over after completion of half of the irradiation so as to ensure more homogeneous production of damage. These samples remained below room temperature during irradiation.

The photoconductivity spectra were measured at liquid-nitrogen temperature. The cryostat used was an Andonian Associates liquid-helium cryostat model MHD-3L-30N including the Andonian Associates option-24 tail piece. The cryostat and sample holder were constructed so that the stress could be applied to the sample while it was in the cryostat. The cryostat and associated stress attachments have been described in detail previously.[26]

A Perkin-Elmer model 98 monochromator which could be purged with clean and dry nitrogen instrumented with a LiF prism was used as a source of monochromatic light during most of the study. Also, a Spex model 1500 evacuable grating monochromator was used. However, because gratings polarize light strongly in certain regions, the prism instrument was used for all polarization studies. A wire-grid polarizer was placed at the entrance slit of the monochromator to polarize the infrared beam. The spectrum of the globar light source remained constant throughout the duration of the study. However, as a precaution, a source spectrum was measured just prior to or after any sample spectrum where the energy level was to be carefully determined. The source spectra were measured with a lead-selenide detector that was placed at the sample position and operated at the same temperature and in the same manner as the sample.

Measurement of the photoconductivity signal was carried out with a Princeton Applied Research model HR8 lock-in amplifier with the type-A high-impedence preamplifier. A Keithley electrometer model 610A was used for impedence matching. The monochromatic light was chopped at 13 cps in order to achieve high sensitivity. The high-temperature stress was applied by a hydraulic press with the sample heated in an oil bath. Annealing was performed in a temperature-controlled furnace with the samples in air, with the samples receiving a careful polish after each heat treatment.

III. EXPERIMENTAL RESULTS AND COMPARISON WITH DIVACANCY

A. Energy-Level Shape

In photoconductivity measurements, one would like to determine as a function of energy the actual amount of photoconductivity resulting from the ionization of a single energy level (the energy-level shape). Since photoconductivity is an additive effect, once there is enough energy to ionize electrons from a defect state, the electrons usually can be ionized at all higher energies. This means that a photoconductivity spectrum is a superposition of several defect energy levels of undetermined shape and the shape of any one level can not be determined unambiguously.

The dichroism measurement itself provides a method of determining energy-level shapes.[27] The difference in the spectra measured with two distinct light polarizations is a result of different numbers of defects absorbing in those orientations. By requiring that this difference and the energy-level shape for each light polarization be the same and requiring, in addition, that the dichroism of the energy level be the same at all energies, the energy-level shape of the state in question is determined. This method is similar to the one used by Cheng *et al.*[20,23] to determine the background and band shape in infrared-absorption studies.

Figure 2 presents an example of this type of analysis performed on the E_c- (0.39 eV) level. The subscripts $\|$ and $\perp$ refer to spectra measured with polarized light whose electric vector is parallel to and perpendicular to the stress direction, respectively. The subscript BKg refers to the photoconductivity of all other levels except the one in question (background). Since $\Delta\sigma/\sigma_0\omega$ is common for all spectra, it will be omitted on subsequent

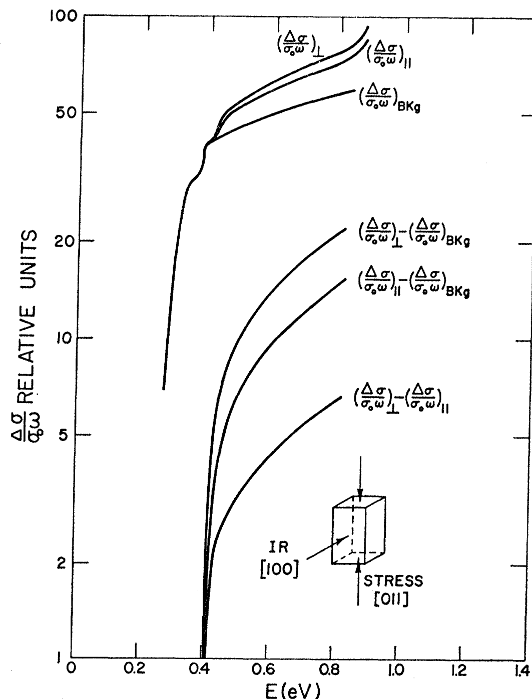

FIG. 2. Energy-level-shape determination of the E_c- (0.39 eV) level using the dichroism exhibited at 78°K as a result of a stress of 1130 kg/cm² applied during the measurement. Sample is 1-Ω cm arsenic-doped.

[26] A. H. Kalma, Ph.D. thesis, Rensselaer Polytechnic Institute, 1968 (unpublished).

[27] By "dichroism" we mean the ratio of the photoconductivity due to the single level in question measured with the infrared light polarized perpendicular to the stress direction to that with the light polarized parallel to the stress direction.

TABLE I. Dichroism[a] results on 1.5-MeV electron-irradiated 1-Ω cm silicon stressed at 78°K.

Sample doping	Stress (kg/cm²)	Stress direction	IR direction	Dichroism E_c- (0.39 eV)	Dichroism E_c- (0.54 eV)	Dichroism theory
P	1230	[100]	[011]	0.75	...	0.63
P	1200	[011]	[100]	1.35	1.35	1.71
P	1230	[100]	[011]	0.72	...	0.63
As	1130	[011]	[100]	1.40	...	1.69
As	1130	[011]	[0$\bar{1}$1]	1.27	...	0.92
As	1390	[011]	[100]	...	1.20	1.80
As[b]	1390	[011]	[100]	1.24	1.20	1.80

[a] Dichroisms are quoted to ±0.05 at worst.
[b] Measured with white light on the sample.

figures and only the subscripts will be used to label the spectra. Spectra labelled with 0 represent the ones measured with no polarizer in the infrared beam.

Figure 3 shows the energy-level-shape determination of the E_c- (0.54 eV) level as well as the E_c- (0.39 eV)[28] level up to the energy where the E_c- (0.54 eV) level begins ionizing. It can be seen that qualitatively the shape of these two levels is similar. There is an initial rapid rise in photoconductivity beginning at the stated energy-level position. At slightly higher energies the slope begins to decrease, although it remains positive as far as the levels are observed. Quantitatively, the initial rapid rise is spread over ~0.2 eV for the E_c- (0.54 eV) level but only over ~0.05 eV for the E_c- (0.39 eV) level.

B. Uniaxial-Stress Studies

1. *Electronic Reorientation*

Measurement of the photoconductivity spectrum with polarized light during the application of uniaxial stress at 78°K results in a measurable dichroism in the E_c- (0.39 eV) and E_c- (0.54 eV) levels. At this temperature, only electronic reorientation takes place for the divacancy defect. Figure 2 shows the spectra resulting from such an experiment. Table I presents the results of a quantitative study for various stress and viewing directions. The theoretical values of the dichroism listed in the table are calculated for electronic reorientation of the divacancy from the formulas developed by Cheng *et al.*[23] using a model arrived at by a linear combination of atomic orbitals (LCAO) approach. The angle of the transition dipole from the X axis, θ, is taken to be $-10°$. This is the angle found to give the best fit to data in previous studies. The values of M, the energy change per unit strain, used in the calculation were the ones that describe the singly negative charge state. This is because we shall identify the two levels that we observe with the doubly and singly negative charge states and because experimental values of M from EPR[22] are only available for the singly negative and positive states. In all cases but one, the sense of the measured dichroism is the same as that predicted by the model. However, for all of the others, the measured dichroism is less than the predicted value. This is what is expected for a "normal" photoconductivity transition from a state to band with no single allowed transition dipole moment.

The result showing a discrepancy between measurement and theory deserves further comment. The stress direction is [011] and the infrared beam was incident in the [0$\bar{1}$1] direction. No previous study[10,11,17,19,20,23] of optical properties identified with the divacancy has measured the electronic reorientation for this particular combination of directions. All other measured values listed in Table I agree in sense with dichroisms measured

[28] Fermi levels are measured by monitoring the resistance of the samples as a function of temperature. A rough check on the position was obtained by observing what levels gave rise to photoconductivity and knowing that the Fermi level must be closer to the majority carrier band than the lowest energy level.

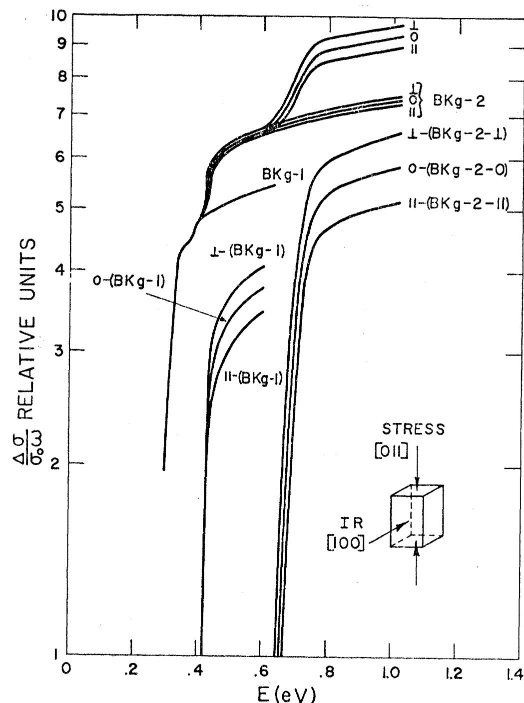

FIG. 3. Energy-level-shape determination of the E_c- (0.54 eV) and E_c- (0.39 eV) levels using the quenched-in dichroism exhibited at 78° as a result of a stress of 1770 kg/cm² applied at 160°C for 15 min. Sample is 1-Ω cm phosphorus-doped.

TABLE II. Dichroism[a] results on 1.5-MeV electron-irradiated 1-Ω cm silicon stressed at ~160°C.

Sample doping	Stress (kg/cm²)	Stress direction	IR direction	Dichroism $E_c-(0.39\text{ eV})$	Dichroism $E_c-(0.54\text{ eV})$	Dichroism theory
As	1540	[011]	[100]	1.25	...	1.26
As	1540	[011]	[0$\bar{1}$1]	1.15	...	1.17
Sb	1450	[011]	[100]	1.20	...	1.25
P	1760	[011]	[100]	1.25	1.30	1.29
P	1600	[100]	[011]	1.00	1.01	1.00

[a] Dichroisms are quoted to ±0.05 at worst.

previously. Also, we shall later identify the $E_c-(0.39\text{ eV})$ energy level with the doubly negative charge state of the divacancy. This is the level for which the discrepancy occurs. The doubly negative charge state cannot be observed in EPR studies, and therefore our results do not disagree with those obtained previously. It is possible that the model itself is not completely correct. For example, in the calculation,[23] only one component, M, of the tensor relating the energy of an elastic dipole to the strain tensor has been used. This is the component along the bonding-atom direction. Other components are assumed to be zero. Since the calculation results in a dichroism only slightly less than 1 for the case in question, it may be that inclusion of the other components would change the calculated sense.

2. *Atomic Reorientation*

At elevated temperatures (~150°C), it is possible for the atomic configuration of the divacancy defect to reorient under stress. Cooling the sample to room temperature while still under stress and the removal of the stress results in the atomic reorientation being frozen in, while the electronic distribution will order itself in its unstressed configuration. Subsequent measurement of the spectra at 78°K with polarized light will give a measure of the frozen-in atomic reorientation. Figure 3 shows the spectra resulting from such an experiment. Table II presents the measured dichroisms for several stress and viewing directions. These high-temperature results agree in all cases with those calculated from the divacancy model and measured in IR, EPR, and photoconductivity experiments on effects associated with the divacancy. In particular, when the stress was applied along the [100] direction, no significant dichroism was measured. This is consistent with a defect whose atomic symmetry is around a ⟨111⟩ axis, since all four ⟨111⟩ axes are at equal angles to the [100] direction and none would be preferred under [100] stress.

Isochronal annealing of the frozen-in dichroism in the $E_c-(0.54\text{ eV})$ and $E_c-(0.39\text{ eV})$ levels are presented in Fig. 4(a). For comparison, the results of similar experiments on the divacancy in EPR[22] and the divacancy-associated 1.8- and 3.3-μ bands in N-type silicon[20,23] are shown in Fig. 4(b). The recovery of the frozen-in dichroism is similar in all of the effects shown in Fig. 4.

C. Annealing Studies and Fermi-Level Dependence of Spectra

Figure 5 shows the results of isochronal annealing on the spectra of a phosphorus-doped, 1-Ω cm sample. The spectra are normalized to the 1.24-eV point. The only energy level present after irradiation and annealing as high as 138°C is located at $E_c-(0.54\text{ eV})$. After annealing to 168°C, levels located at $E_c-(0.39\text{ eV})$, $E_c-(0.36\text{ eV})$, and $E_c-(0.22\text{ eV})$ are observed and the $E_c-(0.54\text{ eV})$ level disappears. These remain until an annealing temperature of 279°C, where they all disappear (see Fig. 5).

The temperature of 168°C, where the $E_c-(0.54\text{ eV})$ level disappears in this sample, is not so meaningful as the Fermi-level position. When the $E_c-(0.54\text{ eV})$ level is observed, the Fermi level is located below $\sim E_c-(0.22\text{ eV})$, and when it is not observed, the Fermi level is

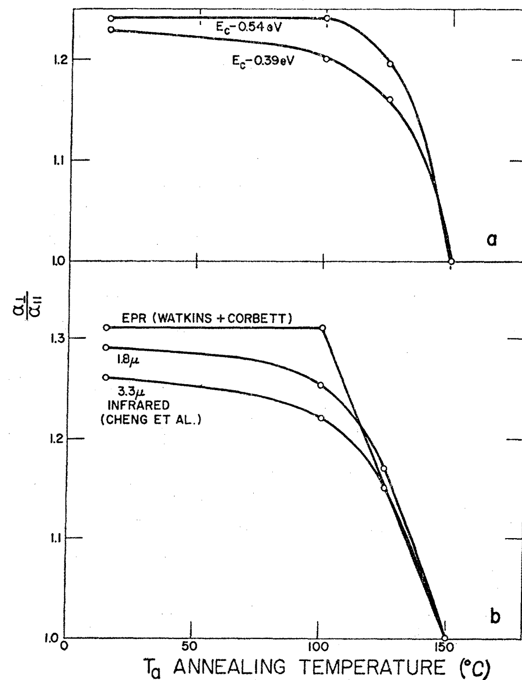

FIG. 4. Isochronal annealing of the frozen-in dichroism resulting from 160°C stress: (a) the $E_c-(0.54\text{ eV})$ and $E_c-(0.39\text{ eV})$ photoconductivity levels compared with (b) the 1.8- and 3.3-μ infrared-absorption bands and the divacancy defect found in EPR.

above $\sim E_c-(0.22$ eV). Therefore the temperature at which the $E_c-(0.54$ eV) level disappears depends on when the Fermi level moves above $\sim E_c-(0.22$ eV). This is about the same Fermi-level position that has been found to be the demarcation line for observation of the 1.8- and 3.3-μ infrared-absorption bands.[1,20,23] If the Fermi level is below $E_c-(0.21$ eV), only the 1.8-μ band is observed, and if the Fermi level is above $E_c-(0.21$ eV), only the 3.3-μ bands are observed. However, if white light is shone on the sample during the measurement of the infrared-absorption spectrum and the Fermi level was below $E_c-(0.21$ eV), both the 1.8- and the 3.3-μ bands are observed.[1,20,23] Figure 6 shows the effect of white light on the photoconductivity spectrum when the Fermi level is located below $\sim E_c-(0.22$ eV). As can be seen, the levels located at $E_c-(0.22$ eV), $E_c-(0.36$ eV), and $E_c-(0.39$ eV) are observed as well as the one at $E_c-(0.54$ eV) with the white light on. If the Fermi level is above $\sim E_c-(0.22$ eV), white light has no effect on the shape of the spectrum.

If the Fermi level is near $\sim E_c-(0.22$ eV), both levels can be observed in the sample with no white light. This effect is seen in the spectra shown in Fig. 3, which was used for energy-level-shape determination.

The sample shown in Fig. 5 was irradiated with a total integrated flux of 4×10^{16} e/cm^2 at 1.5 MeV. Figure 7 shows the isochronal-annealing results of a sample irradiated with a total integrated flux of 1.2×10^{18} e/cm^2 at 1.5 MeV. Because of the high flux, the sample resis-

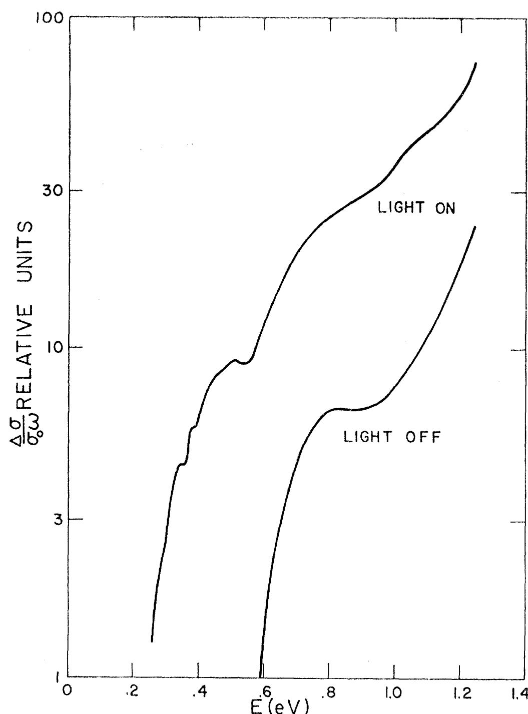

FIG. 6. Effect of white light on arsenic-doped 1-Ω cm, floating-zone silicon irradiated with 1.5-MeV electrons to a condition where the Fermi level was below $E_c-(0.22$ eV).

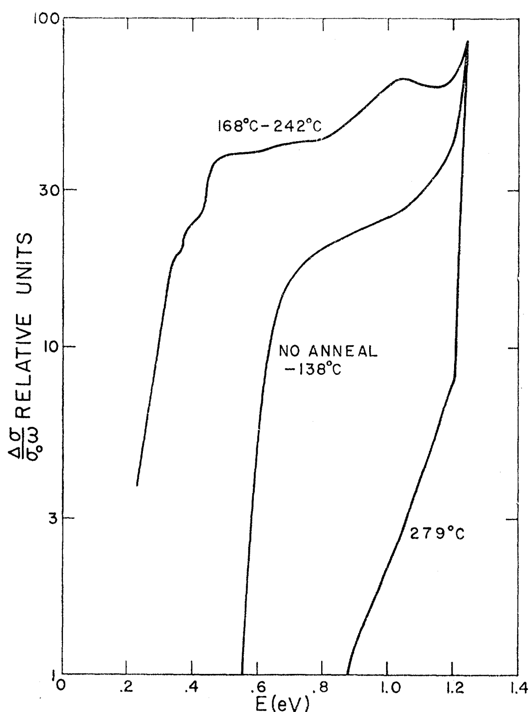

FIG. 5. Isochronal annealing (15 min at each temperature) of phosphorus-doped, 1-Ω cm, floating-zone silicon irradiated with 4×10^{16} e/cm^2 at 1.5 MeV.

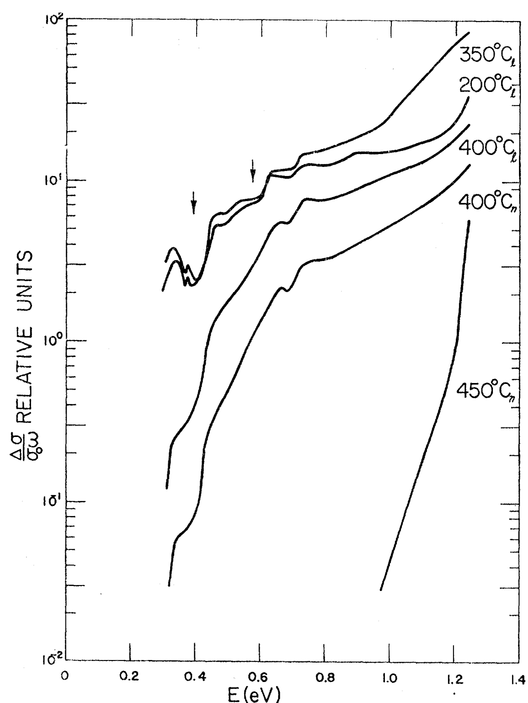

FIG. 7. Isochronal annealing (15 min at each temperature) of phosphorus-doped, 1-Ω cm, floating-zone silicon irradiated with 1.2×10^{18} e/cm^2 at 1.5 MeV. Spectra labeled with temperature subscript l were measured with white light on and those with subscript n were measured with no white light on.

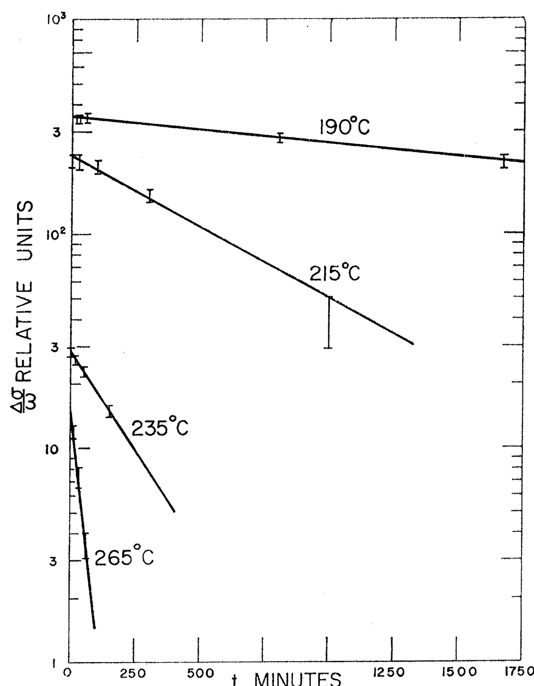

FIG. 8. Isothermal annealing of the $E_c-(0.39\text{ eV})$ level in arsenic-doped, 1-Ω cm, floating-zone silicon.

tance was too high to allow the measurement of the photoconductivity spectrum[29] unless white light is shone on the sample during the measurement. The subscript l on the temperature label indicates that the measurement was made with white light incident on the sample. The subscript n indicates spectra taken with no white light incident on the sample.

The white light has the effect of causing both the $E_c-(0.39\text{ eV})$ and $E_c-(0.54\text{ eV})$ levels (initial ionization of both levels is indicated by the arrows in Fig. 7) to be observed as well as several other levels. In particular, a peak located at 0.32 eV is observed. This is the peak that has been identified with the divacancy in p-type silicon.[10,11] In some cases, particularly the 0.32-eV peak and the $E_c-(0.54\text{ eV})$ level, energy levels appear to be shifted to slightly higher energies. This energy shift is due to the ionization of other levels in the same energy region which obscures the actual position of the level in question. The low-energy ends of the spectra shown in Fig. 7 are not fully drawn. The lowest-energy-level ionizing is located at $E_c-(0.22\text{ eV})$. Since only the peak at 0.32 eV and the levels indicated by the arrows are of interest here, spectra were only measured down to $\sim$0.3 eV. Other levels are present in the spectra, but they do not concern us in this study. All three levels of interest are present through the 350°C anneal but disappear at 400°C. This annealing temperature is higher than the 279°C found for the $E_c-(0.39\text{ eV})$ level shown in Fig. 5. The difference is due to the larger number of defects in the more highly irradiated sample. This means that either a higher temperature or a longer time at the same temperature is necessary to anneal out the defects.

In Fig. 8 are plotted the results of isothermal anneals run at four temperatures on the $E_c-(0.39\text{ eV})$ level. The level anneals out exponentially with temperature, which means that the recovery follows first-order kinetics. The time necessary for the disappearance of one-half of the level is plotted against $1000/T$ in Fig. 9. From the slope of the line the activation energy is found to be 1.25 ± 0.10 eV. This activation energy and the annealing-temperature region are the same as found for the divacancy.[22]

It was not possible to perform an isothermal-annealing experiment on the $E_c-(0.54\text{ eV})$ level because of the indefiniteness in determining the concentration of this level. This is due to high sample resistances resulting from the depth of the Fermi level necessary to observe the defect energy level. In the region where meaningful measurements could be made while the level is still observed, the Fermi level is close to $E_c-(0.22\text{ eV})$ and the change in the Fermi level upon annealing affects the spectrum as well as the change in concentration of the level. In addition, this level appears to be the deepest one trapping a significant number of electrons. Thus a larger concentration of defects giving rise to the $E_c-(0.54\text{ eV})$ level than total number of donor electrons available to trap is probably present when the level is observed. With a sample in this condition, some

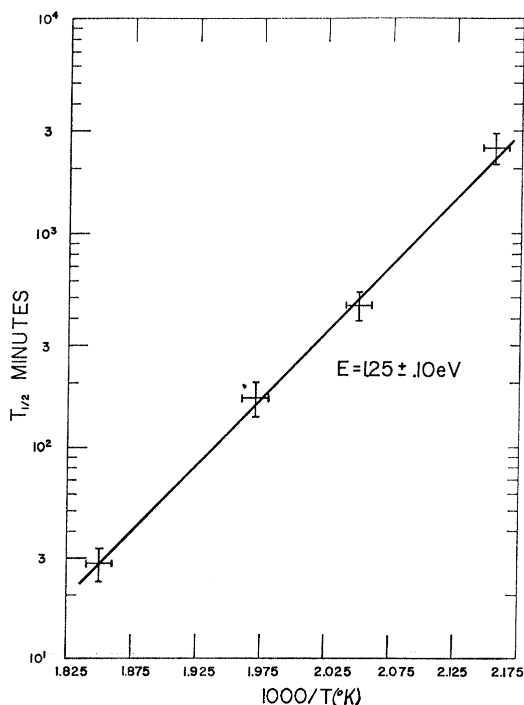

FIG. 9. Time for 50% anneal versus $1000/T$ of the $E_c-(0.39\text{ eV})$ level for the sample shown in Fig. 8.

[29] The capacitance of the input of the measuring circuit was 30 $\mu\mu$F, and RC loss amounted to 99% of the signal for resistances of the order of 10^{11} Ω.

of the defect level would anneal out, but the annealing would not be measured, because all of the electrons could still be trapped on the levels remaining in the sample. For these reasons, the measured photoconductivity is not proportional to the total concentration of defects responsible for the $E_c-(0.54\text{ eV})$ level.

D. Results in *p*-Type Silicon

In Cheng's[10,11] identification of the 3.9-μ (0.32-eV) photoconductivity band (PC band) as arising from the divacancy in *p*-type silicon, he used neutron-irradiated, boron-doped silicon. We have found the PC band in indium-doped as well as boron-doped silicon irradiated with 1.5-MeV electrons. In addition, we have studied 1.5-MeV electron-irradiated high-resistivity (nominally undoped) *p*-type silicon. The results of an isochronal-annealing study on this undoped material are shown in Fig. 10. Immediately after irradiation and before annealing, a level at $E_v+(0.26\text{ eV})$ (curve not fully drawn) and a monotonic rise in photoconductivity for energies above $\sim$0.50 eV are observed. The slight break in the spectrum suggests another level at $\sim E_v+(0.37\text{ eV})$. After annealing to 150°C, a level at $\sim E_v+(0.37\text{ eV})$ is present as well. Upon annealing to 165°C, the peak at 0.32 eV appears and remains through anneals up to 280°C. After annealing to 330°C, the peak disappears, as do the level at $\sim E_v+(0.37\text{ eV})$ and the small dip at 0.36 eV (which appeared at the same temperature as the peak). This annealing temperature of the PC band is in the region where the divacancy anneals.

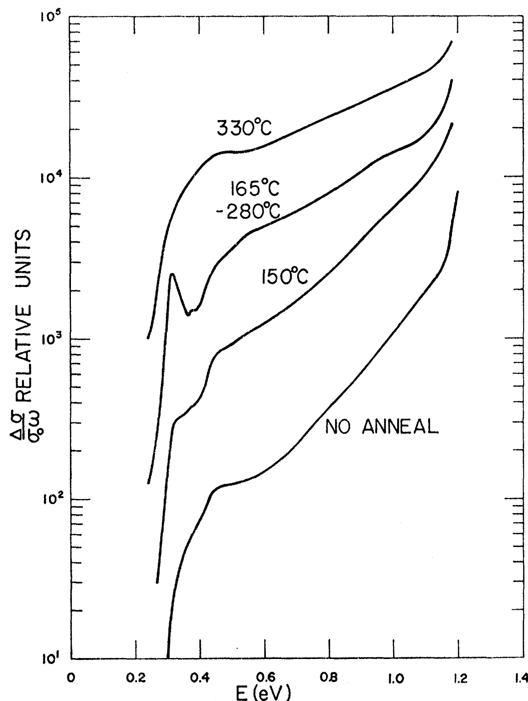

Fig. 10. Isochronal annealing (15 min at each temperature) of high-resistivity, 7100-Ω cm, floating-zone silicon irradiated with 10^{16} e/cm^2 at 1.5 MeV.

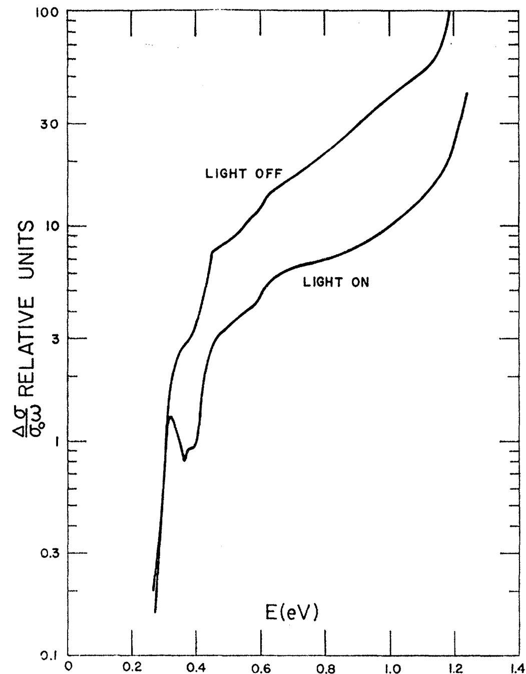

Fig. 11. Effect of white light on *p*-type, indium-doped, 100-Ω cm, floating-zone silicon irradiated with 1.5-MeV electrons to a condition where the Fermi level was too high to observe the 0.32-eV peak.

Vavilov and co-workers[2] have observed that the PC band disappears if the Fermi level is above $E_v+(0.32\text{ eV})$. With this in mind, an explanation of the fact that the PC band is not observed immediately after irradiation is apparent. For this high-resistivity material, an irradiation of 10^{16} e/cm^2 of 1.5-MeV electrons, such as this sample received, drove the Fermi level too high above the valence band to observe the PC band and only subsequent annealing brought it down into the necessary range. Since a level at $E_v+(0.26\text{ eV})$ is observed prior to the 165°C anneal, it would appear that the Fermi level at which the PC band disappears is closer to $E_v+(0.26\text{ eV})$ than $E_v+(0.32\text{ eV})$. This value is more in agreement with the energy level of $E_v+(0.25\text{ eV})$ that divides the neutral and singly positive charge states of the divacancy as found in EPR studies.[22]

White light affects the spectra in *p*-type samples in a manner similar to what was found in *n*-type samples. If the Fermi level is too high to observe the PC band, shining white light on the sample during measurement of the spectrum causes the PC band to be observed. This effect is shown in Fig. 11. It appears to be possible that the *p*-type samples can be irradiated too heavily (Fermi level placed too high) to see the peak even with white light, since some samples did not show this effect if they were of too high resistivity. This is somewhat strange in view of the fact that the PC band was ob-

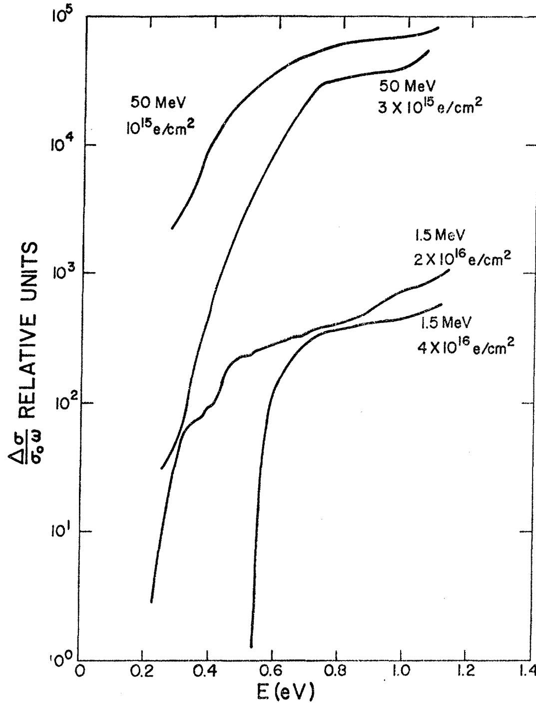

FIG. 12. Contrast between 50- and 1.5-MeV-irradiated phosphorus-doped, 1-Ω cm, floating-zone silicon.

served using white light on heavily irradiated, n-type material (see Fig. 7). The closest that the Fermi level could have been to the valence band was near the middle of the forbidden band. One possible explanation is that the extremely large irradiation caused inhomogeneities in the sample and the further nonequilibrium conditions brought about by the white light allowed the PC band to be observed.[30] White light shone on samples in which the PC band was observed does not affect the shape of the spectrum.

E. 45–50-MeV versus 1.5-MeV Electron Irradiations

The preceding discussion has been concerned entirely with samples that have been irradiated with 1.5-MeV electrons. The predominant irradiation-produced photoconductivity arises from single, well-defined energy levels. In higher-energy, 45–50-MeV electron-irradiated samples, the dominant irradiation-produced photoconductivity is produced not by single levels, but by an "energy band." This contrast is shown in the spectra presented in Fig. 12. The different spectra are positioned for clarity and no meaning is attached to relative photoconductivity values. As can be seen, the higher-energy results are characterized by a gradual decrease of photoconductivity with decreasing energy (the aforementioned "energy band"), with no easily observable breaks in slope signifying energy levels. This energy band extends from ~1.1 down to ~0.3 eV for the 50-MeV-irradiated samples.

The isochronal annealing of the energy band extends from 100 to above 340°C. A typical annealing result is presented in the spectra shown in Fig. 13. The decrease in the spectra at higher energies is because the spectra were measured with a silicon filter in the infrared beam which absorbed light of energy greater than the band gap. The annealing of this energy band resembles what has been observed in IR for 45-MeV electron-irradiated silicon. This has been referred to as "near-edge absorption" in IR measurements.

It can be seen in Figs. 5 and 7 that 1.5-MeV electron-irradiated samples have some of the energy band, but it only extends down to ~0.8 eV and does not give rise to anywhere near the magnitude of the photoconductivity when compared with the single-level photoconductivity that the 45–50-MeV electron energy band does. It is possible to see hints of single levels on the spectra of the high-energy irradiated silicon, but they are all but washed out by the dominant energy band. These single levels are difficult to position and impossible to study using the stress-induced dichroism technique, since the overriding energy band would make any small differences due to the dichroism of the single levels unobservable.

In searching for divacancies, high-temperature (~160°C) stress studies were performed on some of

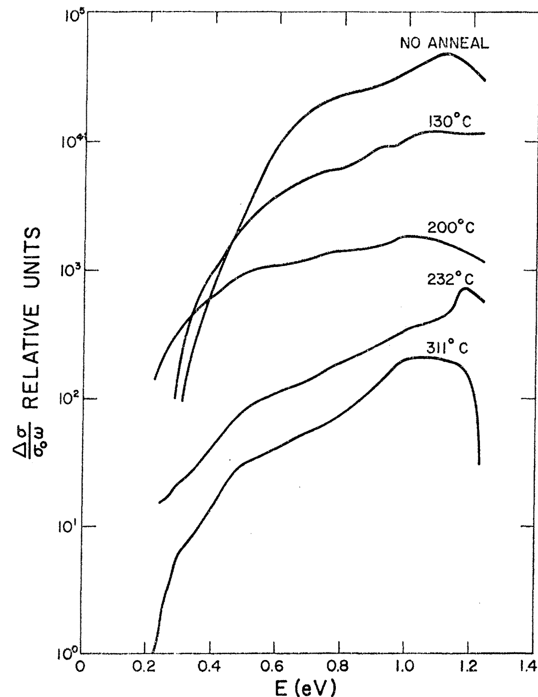

FIG. 13. Isochronal annealing (15 min at each temperature) of antimony-doped, 1-Ω cm, floating-zone silicon irradiated with 5.3×10^{15} e/cm² at 48 MeV.

[30] It is possible that the small 110-V light bulb powered by a Variac did not provide enough light in some cases. However, if the effect was observed at all, it was possible to observe it with very little voltage applied to the bulb (~20 V).

these 50-MeV-irradiated samples. No dichroism was found for the dominant energy band. This means that divacancies do not form a significant portion (if any) of the defects causing the energy band. The sample shown in Fig. 13 is a 1-Ω cm, Sb-doped one. This same effect has been observed in 1-, 10-, and 100-Ω cm, Sb-, As-, and P-doped samples.

IV. DISCUSSION

The experimental results which we have presented lead to the conclusion that the $E_c-(0.39\text{ eV})$ and the $E_c-(0.54\text{ eV})$ levels arise from transitions associated with the divacancy. These experimental results are summarized below.

(1) The isochronal annealing temperature of both levels is in the same region as that of the divacancy.

(2) If n-type samples are irradiated heavily enough that the 0.32-eV peak, identified by Cheng[10,11] as being associated with the divacancy, as well as both levels are observed with white light incident on the sample, all three effects anneal at the same temperature.

(3) Isothermal annealing of the $E_c-(0.39\text{ eV})$ level follows the same kinetics and has the same activation energy as the divacancy.

(4) Both levels exhibit a quenched-in dichroism at 78°K as a result of stress at ~160°C, which agrees in sense with that predicted by the LCAO model of the divacancy and with that measured experimentally in EPR and IR studies for atomic reorientation of the divacancy.

(5) The quenched-in dichroism of both levels anneals out isochronally at the same temperature as that of the divacancy.

(6) Both levels also exhibit a stress-induced dichroism at 78°K. In all cases but one, this dichroism agrees in sense with that predicted by the LCAO model for electronic reorientation of the divacancy. The discrepancy occurs on a charge state of the divacancy which cannot be measured in EPR studies and for stress and infrared directions not previously studied in optical experiments. Therefore the dichroism agrees in sense with dichroisms of electronic reorientation of the divacancy measured previously.

In addition to these results, some further evidence that the $E_c-(0.39\text{ eV})$ and $E_c-(0.54\text{ eV})$ levels are associated with the divacancy has been found. Both levels occur in n-type samples regardless of chemical species of dopant (As, Sb, or P) and the conditions under which either or both levels are observed are the same in all samples. In addition, the isochronal annealing temperature is independent of doping and is the same in samples with the same initial defect concentration. The consistency of the results in differently doped materials means that the defects giving rise to the energy levels are independent of chemical species of dopant.

One further observation is that both levels cannot be seen at the same time if the sample is in equilibrium, except in rare cases where the Fermi level is near $\sim E_c-(0.22\text{ eV}$.) This suggests the conclusion that both levels arise from the same defect in different charge states.

All of these results except one discussed previously support the conclusion that the defect responsible for both the $E_c-(0.39\text{ eV})$ and $E_c-(0.54\text{ eV})$ levels is the divacancy.

A few words are now in order concerning other levels observed in n-type silicon. Most of the experimental evidence tying the $E_c-(0.39\text{ eV})$ level with the divacancy could be applied equally well to the $E_c-(0.36\text{ eV})$ and $E_c-(0.22\text{ eV})$ levels. The effect of the $E_c-(0.36\text{ eV})$ level is relatively small and it occurs very close to the energy at which the $E_c-(0.39\text{ eV})$ level ionizes. Because of this, stress-induced dichroism of the $E_c(-0.36\text{ eV})$ level cannot be measured, since the $E_c-(0.39\text{ eV})$ masks it. Therefore no conclusion can be drawn as to whether the $E_c-(0.36\text{ eV})$ level is associated with the divacancy or not. The $E_c-(0.22\text{ eV})$ level is separated from the others enough that dichroism could be observed for it. Dichroisms on this level observed during the course of this study were opposite in sense from those observed on the $E_c-(0.39\text{ eV})$ level in many cases. Thus the $E_c-(0.22\text{ eV})$ level is not associated with divacancy transitions of the type that we are studying in these experiments (X-Y-type electric dipole). It is possible that it arises from another type of divacancy transition (such as the Z-type electric dipole), but no systematic observations have been made and no conclusions can be drawn at the present time.

If we assume that the identification of the $E_c-(0.39\text{ eV})$ and $E_c-(0.54\text{ eV})$ levels with different charge states of the divacancy is correct, the next thing to do is to identify these charge states. Drawing on the rough energy positioning of the various divacancy charge states arrived at in EPR[22] and IR[1,20,23] studies, it is natural to associate the $E_c-(0.39\text{ eV})$ level with the doubly negative charge state and the $E_c-(0.54\text{ eV})$ level with the singly negative charge state. This identification is in good agreement with the positioning of levels in EPR studies.[22] Infrared-absorption studies, on the other hand, place the dividing energy between the singly and doubly negative charge states at $\sim E_c-(0.21\text{ eV})$.[1] Cheng *et al.*[20] have attributed this discrepancy to errors in both measurements due to sample inhomogeneities. However, the photoconductivity measurements made in this study lend support to both of these measurements, but as measures of two separate entities. The change of the divacancy charge state from singly negative to doubly negative occurs when the Fermi level moves up through the position of $\sim E_c-(0.22\text{ eV})$, but the actual energy level of the doubly negative state is $E_c-(0.39\text{ eV})$.

It is possible that energy levels measured by optical and electrical techniques are different because of the Franck-Condon principle.[31] Thermal transitions occur

[31] R. H. Bube, *Photoconductivity of Solids* (John Wiley & Sons, Inc., New York, 1960).

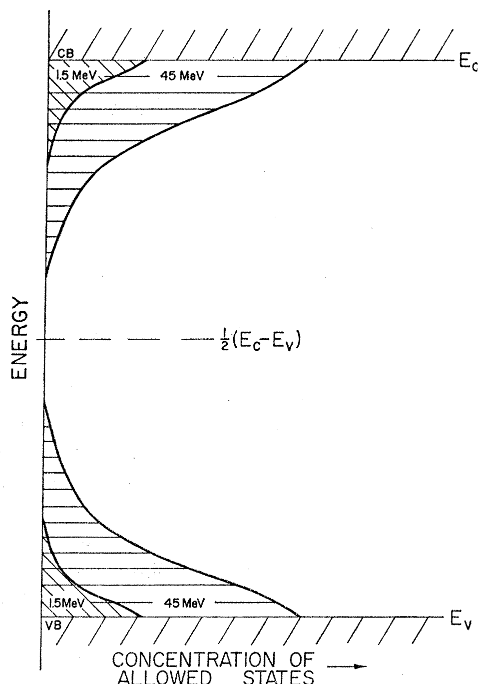

FIG. 14. Schematic of the decrease in the forbidden gap energy resulting from 45- and 1.5-MeV electron irradiations [following Vavilov (Ref. 37)].

predominantly when the local atomic configuration has relaxed so as to provide a minimum ionization energy, whereas optical transitions occur with no atomic relaxation in general and the optical ionization energy is larger than the thermal ionization energy. However, Sonder and Templeton[32] have observed an energy level in electrical studies located at about the same energy position as the E center [$\sim E_c-(0.4\text{ eV})$], but which anneals at temperatures around 300°C, where the divacancy anneals, and not at $\sim$150°C, where the E center anneals. In addition, they[32] also observe E-center levels at about this same energy that anneal at $\sim$150°C. Therefore it is possible that the electrical-energy-level position of the doubly negative charge state of the divacancy may be about the same as the optical position and that the Fermi-level position of $\sim E_c-(0.22\text{ eV})$ is not a measure of the electrical energy level.

It is difficult for us to reconcile the location of an energy level at $E_c-(0.39\text{ eV})$ that does not become populated until the Fermi level moves higher than $E_c-(0.22\text{ eV})$ with the fact that all levels positioned below the Fermi level should be populated. There does not appear to be any easy answer to this paradox and further study is necessary to shed some light on the matter. It is possible that sample inhomogeneity is the answer and that the measured Fermi level is determined by defects other than the divacancy, but it is not in the same position in the vicinity of divacancy defects.

[32] E. Sonder and L. C. Templeton, J. Appl. Phys. **34**, 3295 (1963).

The photoconductivity band in p-type silicon centered at 0.32 eV has been identified with the singly positive charge state of the divacancy.[10,11] We give further proof of this conclusion by the observation of the band in high-resistivity, undoped p-type silicon. For the transition giving rise to the band to be observed, the Fermi level must be closer to the valence band than $\sim E_v-(0.26\text{ eV})$. It is tempting to put the energy position of the state at $\sim E_v+(0.26\text{ eV})$, but from the different Fermi-level and energy-level positions for the doubly negative charge state in n-type material, this reasoning could easily be incorrect. The explanation of the band as a transition from the ground state to an excited state of the defect followed by decay of a hole from the empty ground state to the valence band[10,11] means that the position of either the ground state or the excited state from the photoconductivity results cannot be determined.

Thus far, we have confined our comparisons with theory to the model developed by an LCAO treatment. Callaway and Hughes[33,34] have done a calculation on the divacancy, using an energy-band-type calculation. However, comparison of our results with the calculations of Callaway and Hughes[33,34] is difficult and the comparison can only be made in a speculative fashion. This fact is especially true when one considers that the calculations[33,34] are not applicable to energy states of the defect having more than one charge, as is true for the divacancy defect which can exist in one of four change states. Consequently, in view of the fact that more applicable calculations do not exist, we shall not dwell further on comparison of theory and experiment in this paper.

We shall now turn our attention to the experimentally observed "energy band" in the photoconductivity measurements. The difference in the effect of 45- and 1.5-MeV irradiations observed in this study means that the two different energies produce different degrees of defect complexities. It is not merely a production of more of the defects causing the energy band at the higher energy that makes it more dominant at 45 MeV. If this were true, sufficient 1.5-MeV irradiation would eventually produce the same effect as 45-MeV irradiation does. It was determined in the course of our experiments that 1.5-MeV irradiation of $\gtrsim 10^{18}$ e/cm^2 does not produce anywhere near the effect that 10^{14} e/cm^2 of 45-MeV electrons does. A reasonable explanation of this difference is that the greater damaging power of 45-MeV electrons causes disordered regions and 1.5-MeV electrons do not. We have previously observed that 50-MeV electrons produce disorder in germanium, whereas 15-MeV electrons do not,[35] and the same qualitative effect should hold in silicon. The 1.5-MeV electrons are simply

[33] Joseph Callaway and A. James Hughes, in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968).

[34] Joseph Callaway and A. James Hughes (private communication).

[35] A. H. Kalma, J. C. Corelli, and J. W. Cleland, J. Appl. Phys. **37**, 3913 (1966).

not energetic enough to produce disorder. The maximum recoil energy that can be imparted to a silicon atom by a 1.5-MeV electron is 110 eV, while it is ~150 000 eV by a 45–50-MeV electron.[36]

The effect of disordered regions would be destruction of a good deal of the periodicity of the lattice. Since the energy bands are a result of the lattice periodicity, destruction of some of the periodicity would have the effect of destroying the sharp division between forbidden and allowed energies at the band edges. This would put a continuous spectrum of allowed energies in the forbidden gap extending from the band edges into the gap. The shape of the resulting photoconductivity spectrum would depend on the amount of disorder.

Vavilov[37] has schematically drawn a possible representation of this energy band, where a continuous spectrum of levels extending from both band edges into the gap is produced upon irradiation. Following Vavilov, we have drawn a similar schematic to represent the measured decrease in forbidden gap energy resulting from 45- and 1.5-MeV electron irradiations. This is given in Fig. 14.

Simple defects introduced by 1.5-MeV electrons are also a form of disorder and would cause some narrowing of the forbidden band, but to a much lesser degree than 45-MeV electron-induced disordered regions. Thus the disordered-region explanation is reasonable and accounts for the gross observed effects in the photoconductivity spectra.

V. SUMMARY

This study has led to the conclusion that in 1.5-MeV electron-irradiated *n*-type silicon, the $E_c-(0.39\text{ eV})$ energy level is associated with the doubly negative charge state of the divacancy and the $E_c-(0.54\text{ eV})$ energy level is associated with the singly negative charge state of the divacancy. These conclusions were reached by examining the atomic and electronic configurations of the defect giving rise to the levels by employing uniaxial stress and polarized light, by studying the annealing of the levels, annealing of the atomic reorientation, by observing the lack of dependence on dopant of the levels, and by observing the Fermi-level dependence of the levels. These results were correlated with previous EPR and IR studies of the divacancy[20–23] to aid in the defect identification.

Further proof that the photoconductivity band centered at 0.32 eV in irradiated *p*-type silicon is associated with the singly positive charge state of the divacancy has been given. This is the observation of the band in nominally undoped silicon as well as silicon doped with both indium and boron impurities. The maximum distance of the Fermi level from the valence band for the observation of the 0.32-eV band has been determined to be $E_v+(0.26\text{ eV})$.

The predominant defect photoconductivity in 45-MeV electron-irradiated *n*-type silicon arises from an energy band which is most likely caused by disordered regions. This energy-band effect is present also in 1.5-MeV electron-irradiated *n*-type silicon, but it is nowhere near as large in either magnitude or wavelength extent as it is in 45-MeV-irradiated samples.

We shall apply the methods developed in this investigation to a study of impurity associated defects (e.g., *E* center and *A* center) in order to make additional definitive identifications of energy states and transitions with specific defect configurations.

ACKNOWLEDGMENTS

The authors acknowledge the helpful assistance primarily of J. W. Westhead, and also of W. H. Bohlke, A. R. Frederickson, and R. Chiang during the performance of these experiments. We also thank Dr. J. W. Corbett and Dr. G. D. Watkins of the General Electric Research and Development Center and Dr. L. J. Cheng of the Atomic Energy of Canada Ltd., Chalk River Laboratory, for informative discussions regarding this study. Special thanks are given to Dr. James W. Corbett for his critical reading of the doctoral thesis of one of us (A. H. K.) from which this paper was taken. Finally, we thank T. Haber of the General Electric Company for his help in the 1.5-MeV electron irradiations and the Rensselaer Polytechnic Institute Linac Personnel for their aid in the 45–50-MeV electron irradiations.

[36] F. Seitz and J. S. Koehler, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. II, p. 305.

[37] V. S. Vavilov, in *Proceedings of the Seventh International Conference on the Physics of Semiconductors: Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), p. 115.