

New model of the irradiation-induced 0.97-eV (*G*) line in silicon: A C_S -Si* complex

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We report on a high-resolution photoluminescence and absorption study with the application of external stress and magnetic fields on the 0.97-eV (*G*) line. We determine the symmetry of the related center to be monoclinic *I*. It is shown that satellite lines *E*, *E'*, and *E**, which are observed in luminescence or absorption, are local modes of the *G*-line center. The low-energy local modes *E* and *E'* both exhibit isotope effects upon ^{13}C implantation of the Si samples. The doublet structure due to ^{12}C and ^{13}C gives evidence that one substitutional carbon atom is incorporated in the complex. We observe a nonthermalizing and stress-independent triplet structure of the *G* line in luminescence as well as in absorption with intensities almost identical to the natural abundances of ^{28}Si , ^{29}Si , and ^{30}Si . This establishes our basic model of substitutional carbon atom interacting with a single silicon atom, Si*, in a prominent position. Relaxation of the complex leads to a symmetry lowering from a trigonal $\langle 111 \rangle$ defect configuration to a monoclinic $I(C_{1h})$ symmetry with a (110) mirror plane. Two particular models are discussed in detail, one being a C_S -Si_{*l*} dumbbell having relaxed off a bond-centered $\langle 111 \rangle$ position, the other being a carbon-vacancy complex similar to the electron-paramagnetic-resonance Si-*E* center.

I. INTRODUCTION

The 0.97-eV emission line, frequently labeled *G* line, is one of the most prominent and most widely studied luminescence lines which arises in silicon crystals after irradiation damage by high-energy electrons, neutrons, ions, and gamma rays and subsequent annealing of the samples between room temperature and 200 °C (maximum intensity); beyond this temperature the line anneals out. Early reports on the line were, e.g., given by Yuhnevich,¹ Yuhnevich and Tkachev,² Spry and Compton,³ and Bortnik *et al.*⁴ The appearance of the *G* line was found to be independent of whether the starting material was *n*- or *p*-type, and no dependence on the donor or acceptor species could be established.⁵ There are divergent observations on a possible correlation of this line with oxygen or carbon as persistent, unintentional impurities in silicon: Johnson *et al.*⁶ reported similar luminescence intensities from Czochralski (C and O rich) as well as from float zone (C and O poor) material. Mudryi *et al.*⁷ did not find a correlation with oxygen contents, whereas Konoplev *et al.*⁸ observed lower intensities in oxygen-rich samples. No dependence on carbon concentrations was reported in these studies. Kirkpatrick *et al.*,⁹ however, found that high carbon doping is favorable for the *G*-line luminescence. The *G* line was also observed in ab-

sorption after sample annealing at $T_A > 250$ K, and was particularly strong in oxygen-poor crystals with high carbon concentrations.¹⁰⁻¹²

In view of these divergent experimental findings, a correlation of the *G* center with specific microscopic models turned out to be difficult. Jones and Compton¹³ tentatively attributed the *G* line to the divacancy as did Jones *et al.*⁵ This interpretation was doubted by Noonan *et al.*^{14,15} Instead, these authors favoured the *G*11-EPR center, a carbon-split interstitial,¹⁶ as responsible for the *G* line. This center was independently proposed by Konoplev *et al.*⁸ Another interpretation in terms of a divacancy-carbon associate center was given by Tkachev and Mudryi.¹⁷

An unambiguous interpretation was impeded by a previous controversy about the symmetry of the *G*-line center. Originally, Jones and Compton¹³ reported that the *G*-line center had trigonal $\langle 111 \rangle$ symmetry, and Jones *et al.*⁵ ascribed the line to a singlet-to-doublet transition at a trigonal $\langle 111 \rangle$ center. Walker¹⁸ contradicted this interpretation showing that a symmetry classification as based on the available experimental data was rather monoclinic than trigonal. A determination of the *G*-center symmetry as monoclinic *I* was actually made by Yuhnevich and Mudryi¹⁹ from their stress-dependent photoluminescence study, and Tkachev and Mudryi¹⁷ also reported the same sym-

metry although experimental data were not shown in this work. Foy *et al.*²⁰ recently confirmed the monoclinic *I* symmetry classification of the *G*-line center.

In this paper, we report on a study of the *G* line in photoluminescence and in absorption under uniaxial stress and in magnetic fields. The stress splittings unambiguously coordinate the *G* line to a π oscillator at a center of monoclinic *I* symmetry. Local modes of the *G* line were identified and isotope effects could be detected in the local modes as well as in the main *G* line. We propose that one silicon atom is the favorite partner of a substitutional carbon atom in the center and discuss two specific models.

The paper is organized in the following way: In Sec. II, experimental details are described, and in Sec. III, experimental results and a discussion of our model are presented. Section III is subdivided into five parts, A–E, on basic photoluminescence, absorption, and temperature effects, on stress data, on isotope effects, on the triplet structure of the *G* line, and on a model discussion, respectively. Most of the results presented in this paper were obtained in the framework of two unpublished diploma works.^{21,22}

II. EXPERIMENTAL

Irradiation damage of the samples which we used in our study was performed in different ways. In the early stage, damage was achieved by thermal neutrons, but the major part of our crystals was electron-irradiated at electron energies in the range from 1.5 to 2 MeV at fluences of 5×10^{16} electrons/cm². Damage was generally performed at sample temperatures below 100 K. The samples were isochronally annealed for 1 h in a long quartz tube under a continuous flow of argon buffer gas. Anneal temperatures which yielded the strongest luminescence were found to be close to 150–200 °C as in prior publications.

The samples were excited by a cw Kr-ion laser (647-nm wavelength, ≤ 500 -mW power) or by a cw Ar-ion laser (514.5-nm wavelength, ≤ 1.5 -W power). The luminescence light was dispersed by a 0.75-m grating monochromator (Spex 1702), detected by a cooled germanium detector of high detectivity (North Coast E0-817) or by a cooled PbS cell (SBRC), and amplified by conventional lock-in technique (lock-in amplifier Ithaco Dynatrac 3). The light source in the absorption mea-

surements was a tungsten filament lamp used with the same monochromator and detectors as in emission. For the sake of particularly accurate absorption measurements, a two-ray equipment was installed which eliminated background structures not due to the physical effects to be investigated. Time-resolved measurements were performed exciting the radiation by single pulses from a cavity dumped mode locked Ar-ion laser. The photodetector was in this case a cooled photomultiplier with S1-cathode spectral characteristic, and the signal was processed by single-photon counting technique. The time resolution of this setup corresponded at the *G* line wavelength to 10 nsec. For the measurements under uniaxial stress, sample specimens were cut before irradiation and annealing to bars of approximate sizes $2 \times 2 \times 8$ mm³ with the long axis parallel to the $\langle 100 \rangle$, $\langle 110 \rangle$, and $\langle 111 \rangle$ crystallographic directions. The stress equipment is described elsewhere.²³ It allows for application of stress up to about 400 MPa. The temperature dependence of the line was measured in a special cryostat after Gmelin²⁴ which holds a chosen temperature between 1.5 and ≈ 80 K even at relatively high excitation powers of up to 50 mW. The preparation of samples for studying isotope splittings is described in part C, Isotope effects, of Sec. III.

III. RESULTS

A. Basic photoluminescence and absorption data

Figure 1 shows a typical photoluminescence spectrum obtained after sample treatment as

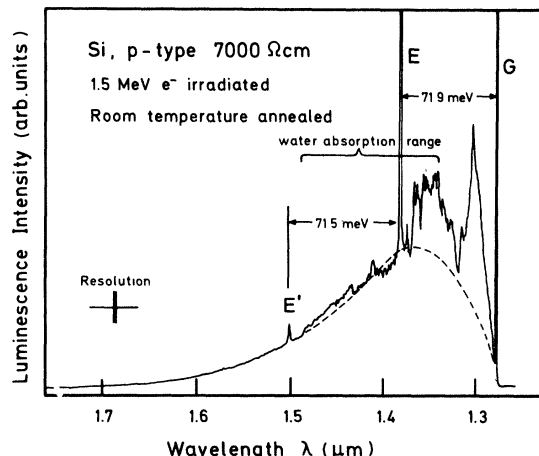


FIG. 1. *G*-line spectrum at $T = 4.2$ K.

TABLE I. Parameters of G line and of associated local-mode transitions. Δ is the half-width of the lines and refers to $T = 4.2$ K.

Line	Wavelength λ (μm)	Energy E (meV)	Line spacings ΔE (meV)	Δ (\AA)	Δ (meV)
G	1.2786	969.4		0.7	0.053 (Lum.)
			71.9		
E	1.3810	897.5 ± 0.1		9.0	0.58
			71.5		
E'	1.5006	826.0 ± 0.2		22.8	1.25
			70.7		
E''	1.6411	755.3 ± 0.5		90.0	4.15
E^*	1.1923	1039.6 ± 0.1	70.2 (from G)	5.5	0.48

described above. The spectrum consists of the dominant G line no-phonon (NP) transition at about $1.28 \mu\text{m}$ along with two low-energy lines labeled E and E' . A very weak single sharp line E'' also belongs to the spectrum but is not contained in Fig. 1 (see Table I). The broad and relative intense structure at $\simeq 1.3 \mu\text{m}$ is displaced from the G line by about 19 meV. It is a familiar feature of G line spectra and is usually ascribed to a transverse acoustic (TA) phonon [the momentum conserving TA phonon energy as deduced from the narrow line recombination radiation of excitons bound to shallow donors or acceptors is 18.7 meV (Ref. 25)]. Another relatively broad band follows, centered at about $1.35 \mu\text{m}$. The entire spectrum of the G line, the TA phonon line, and the band is replicated from the E line on. The fluctuations from 1.35 to $1.48 \mu\text{m}$ are due to water-vapor absorption. This was tested by working in a dry atmosphere (flushing of monochromator and the optical way by dried nitrogen gas). All these lines are superimposed on a broad unsymmetric band indicated in Fig. 1 by a dashed line. No luminescent features other than those in Fig. 1 were observed from the samples which we used for the experiments to be described in the following parts of this paper. Neither do we observe near band-gap free or bound exciton radiation as is typically existent in the low-temperature spectra of undamaged silicon, nor are there any indications of other irradiation-induced lines as are present in most previous publications (e.g., the C line, $0.79 \text{ eV} \triangleq 1.57 \mu\text{m}$). The absence of emission which is not correlated with the G line is absolutely necessary for observing weak structures such as the E'' line near the C emission. Our few-line spectra were obtained

by taking float-zone silicon, p - or n -type, at arbitrarily low ($\leq 10^{15} \text{ cm}^{-3}$) doping concentrations, and annealing the specimens near room temperature. When we annealed the samples at higher temperatures up to $T_A \simeq 200^\circ\text{C}$, we observed the appearance (and later disappearance again) of other irradiation-induced lines; for example, the C line increases up to $T_A \simeq 300^\circ\text{C}$. Other lines are also relatively stronger or even predominant when we start with oxygen-rich Czochralski-grown silicon.

Under the condition of a few-line spectrum as in Fig. 1 we find that the intensity ratios of lines E , E' , and E'' to line G are independent of the particular sample within the experimental error. There is not only a systematic decrease in line intensities of E through E'' to lower energies, but also a systematic increase of linewidths. The line parameters are listed in Table I. These observations show that a close correlation between the G and the E , E' , and E'' lines exists. It is suggestive to interpret these low-energy satellites as due to local modes of the G -line center. This tentative explanation is confirmed later in this paper by the stress splitting of the lines and the isotope effects. We note that in previous publications the E line was ascribed to a NP transition from the same upper state as the G line to an excited electronic state of the center.^{5,13,17,26} Only Kirkpatrick *et al.*²⁷ explained the E lines as due to the excitation of a local mode but without advancing arguments.

Absorption measurements were also performed on the G line. In Fig. 2, we compare emission and transmission intensities with the two diagrams centered at the G -line position. It is striking that both spectra are almost complementary, even in smaller details. We find two sharp and pronounced ab-

sorption lines *G* and, at higher energies, E^* , and a structure in the spectral range marked by TA which in transmission is inverse to emission. In Fig. 2, spectra from two different samples are depicted in order to demonstrate our experimental experience that luminescence and absorption spectra from arbitrarily chosen samples fit almost perfectly together. The most interesting feature when comparing both spectra is difficult to see in the energy scale of Fig. 2: An accurate determination of the displacement energies of E or E^* from *G* yields a difference of 1.7 meV (see Table I). The high-energy satellite E^* is not visible in luminescence, and the low-energy local modes E , E' , and E'' do not show up in transmission. We interpret line E^*

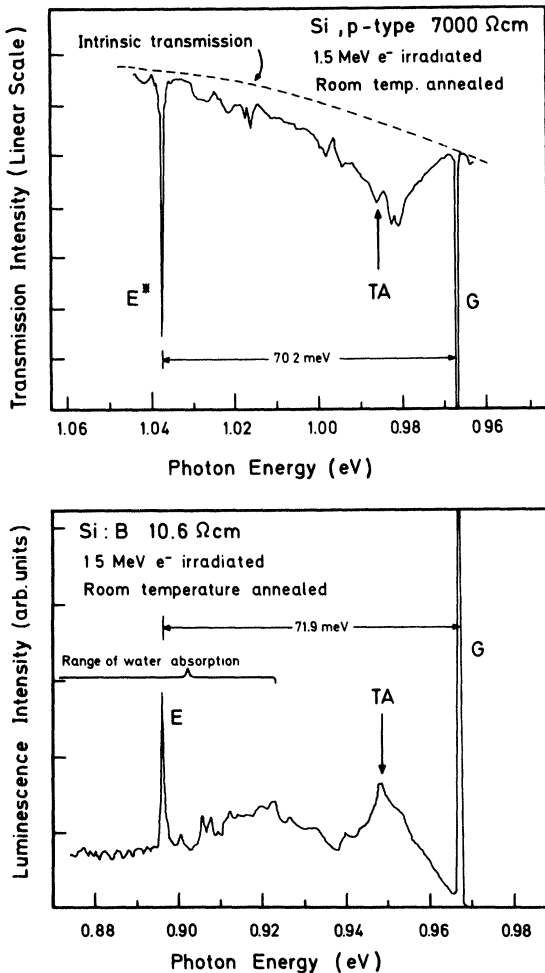


FIG. 2. Emission and transmission spectra centered at the *G*-line transition. Indicated by a dashed line is the transmission curve obtained for undamaged intrinsic silicon in the same experimental setup. The position of the momentum-conserving TA phonon (18.7 meV) replica of the *G* line is marked by an arrow.

as originating from a transition of the *G*-center ground state to an vibronic excited state of the upper (electronic) *G*-line level. This explanation results after removal of a disturbing effect due to an overlapping emission or absorption line of different origin: Line E^* coincides within its half-width with a line I_3 which arises in Czochralski or float-zone silicon after ion implantation or neutron irradiation at $\approx 400^\circ\text{C}$ annealing temperature, and which was tentatively ascribed to multivacancy complexes²⁷ or, alternatively, to the EPR *A8* center.¹⁷

We distinguished E^* from I_3 by sample statistics and by stress measurements. First, it was found that the E^* -line absorption was always high when the *G*-line absorption was high, whereas luminescence due to I_3 at $\hbar\omega \approx 1.039$ eV was seen when samples were treated in such a way that is known to produce high I_3 intensities,²⁷ and in these cases, no correlation with the *G*-line intensities were found. Second, E^* splits under stress like *G*, but I_3 shows a completely different stress dependence.²¹

The properties of the *G* and the various *E* lines as discussed above tend to suggest the simple molecular level scheme in Fig. 3, consisting of vibronic levels in slightly anharmonic potentials (dashed lines) generated by two different electronic configurations. Only the *G* line as an electronic ground-state-to-ground-state transition is observed in luminescence and in absorption, whereas the E^* transition is merely visible in absorption since its upper state is at liquid-helium temperatures and at a vibronic excitation energy of 70.2 meV practically not populated. In absorption, a transition E^{**} from the center ground state to the second vibronic state of the upper scheme should, in principle, be observable. This transition, however, was not observed in our experiments.

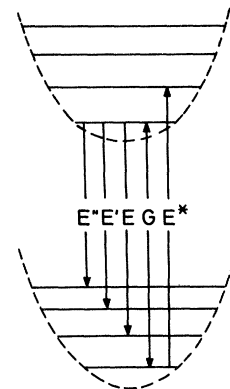


FIG. 3. Molecular level scheme of the transitions associated with the *G* line.

The G line was further studied in temperature-dependent and time-resolved measurements. The temperature-dependent data are threefold: We observe a line broadening and a line shift and determined a thermal activation energy of the G -line upper state. The half-width (Δ) of the G line can be fitted by an experimental law from 4.2 up to 65 K,

$$\Delta = 0.043 \text{ meV} \times \exp(4.7 \times 10^{-2} T \text{ K}^{-1}).$$

From 65 K on, the experimental half-width is to an increasing degree smaller than described by the law. These Δ values are within experimental uncertainty the same as were reported by Jones and Compton¹³ and by Jones *et al.*⁵ who give an expression for the temperature variation of half-width broadening proportional to $T^{4.0 \pm 0.7}$. Hare and co-workers²⁶ in their study of the G line and vibronic spectra in irradiated silicon found agreement of their data with the results of Jones and Compton. The G -line shift with temperature is shown and compared with the band shift in Fig. 4. In the temperature interval from about 35 to 80 K we find a power-law dependence with an exponent of 3.6 ± 0.5 . Below 35 K, there are no significant deviations from the band shift. The band shift $\Delta\lambda(T)$ as plotted in Fig. 4 for comparison was calculated from the experimental relation²⁸ ($T < 150$ K) $\Delta E_g(T) = E_g(T) - E_g(0)$ with

$$E_g(T) = (1.059 \times 10^{-5})T \text{ eV/K} \\ - (6.05 \times 10^{-7})T^2 \text{ eV/K}^2$$

and $E_g(0) = 1.170$ eV. It is evident that the G line at increased temperatures does not follow the band

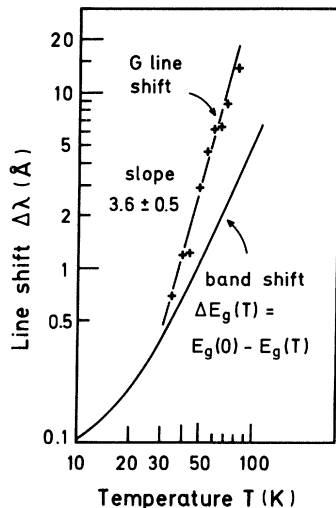


FIG. 4. G -line shift with temperature.

as is typical for deep centers. Our results are not consistent with the measurements of Jones *et al.*⁵ who found a power law in T with an exponent of -2.35 ± 0.25 . This is within the indicated error approximately parallel with the band, since from 40 to 80 K the quadratic term in $\Delta E_g(T)$ is leading.

The G -line intensities as a function of temperature were measured from 4.2 up to 80 K. Line intensities were determined from the area under the luminescence line because the linewidths strongly vary with temperature. The experimental values could very satisfactorily be fitted by the expression

$$I_G(T) = I_0 [1 + C \exp(-E_A/kT)]^{-1},$$

where

$$C = (2-8) \times 10^4, \quad E_A = 55 \pm 3 \text{ meV}.$$

This expression refers to a two-level model where the lower level is the G -line transition upper state, which can thermally be depopulated into the higher level split by E_A . C is the ratio of degeneracy of these two levels. Our value of E_A is significantly different from $E_A = 35 \pm 5$ meV of Jones *et al.*⁵ The reason for this discrepancy is unclear. From our result, considering the large value of C we conclude that depopulation of the G line with temperature occurs into a band. This defines the G -line upper state to be 55 meV below the band. The excited vibronic state correlated with line E^* is then energetically degenerate with the band. This situation does not necessarily bring about a conflict to E^* as an in-band sharp state since, different from shallow donors or acceptors, the wave function of the present deep center is not made up of low-lying single-band functions close to the band extremum in k space.

We note further that for various samples of different origin we find a linear G -line dependence on excitation level; more accurately, the slope in a double logarithmic plot of the G -line intensity versus excitation power is 0.94 ± 0.06 . Such linear intensity-to-pump power dependence is known from the radiative recombination of bound excitons (for further references, see Ref. 25) and results when both electrons and holes are bound to free excitons which are captured at the impurities. A similar situation can arise when one charge-carrier species is rapidly trapped and recombines nonradiatively as the dominant process and the other species is captured on a defect giving rise to longer-lived radiative recombination.

Finally, luminescence decay times were deter-

mined. An upper bound to the decay time of 4 μsec is heretofore known, given by the response time of the detector (see the Comment section in Ref. 13). We have measured the *G* line with highly improved time resolution and found a new upper bound of 10 nsec which in our case is also determined by the experimental setup. On the basis of the experimental decay time, $\tau_{\text{expt}} < 10$ nsec, we compare absolute line intensities of *G* and of excitons bound to common shallow donors or acceptors. For the latter impurities, exciton radiative quantum efficiencies η are well known from radiative lifetimes (absorption measurements, Dean *et al.*²⁹) and from luminescence decay times (Schmid³⁰). They range from $\eta = 0.2 \times 10^{-4}$ (In) to $\eta = 22 \times 10^{-4}$ (B) with donors P and As in between ($\eta \approx 1.3 \times 10^{-4}$). Taking phosphorus bound excitons as a typical example, our largest intensities obtained from samples of $(10^{15} - 10^{16}) \text{ cm}^{-3}$ doping concentrations are absolutely by at least 10^3 lower than the best *G*-line intensities. Assuming that the *G*-center concentrations are not essentially higher than 10^{16} cm^{-3} , this comparison yields high *G*-line quantum efficiencies $\eta \gtrsim 10^{-1}$. This value is consistent with an estimate of the radiative *G*-line lifetime on applying to the present problem Dexter's theory,³¹ which relates transition oscillator strengths with trap concentrations and the integral absorption of the center. We come to an estimated value of $\tau_{\text{rad}} \lesssim 2$ nsec for the following set of parameters: assumed *G*-trap density 10^{16} cm^{-3} , ratio of degeneracies of transition initial and final states $g_i/g_f = 1$ as suggested by the magnetic field experiments (see later), ratio of no-phonon to vibrational mode absorption correlated with the *G*-center 0.4, and integral absorption $\alpha\Gamma$ of the *G* zero-phonon line with an absorption coefficient $\alpha = (2 - 4) \text{ cm}^{-1}$ at a half-width $\Gamma = 0.12 \text{ meV}$ as extracted from the absorption measurements in this particular highly luminescent sample.

B. Stress data

Stress along the main crystal directions $\langle 100 \rangle$, $\langle 110 \rangle$, $\langle 111 \rangle$ up to 100 MPa was applied to samples of high *G*-line intensities. The *G* and *E* lines in luminescence and the *G* and *E** lines in absorption were investigated. At high stress magnitudes, it was also possible to record resolved components of the *E'* luminescence when the splitting energy exceeded the width ($\approx 1.25 \text{ meV}$) of the *E'* line.

The first aim was to determine the symmetry of the *G*-line center. We found that the *G* line corre-

sponds to a π oscillator of monoclinic *I* symmetry.²¹ This is an independent confirmation of the identical results which were previously obtained by Yuhnevich and Mudryi¹⁹ and very recently by Foy *et al.*²⁰ Therefore, we can be brief in this paragraph.

Figure 5 (left-hand part) is a comprehensive plot of the *G*-line splitting under stress. The splitting pattern for each stress direction was the same in luminescence as in absorption. For the particular stress direction $\bar{X} \parallel [100]$ this is illustrated in the right-hand part of Fig. 5. There is an unexplained difference between emission and absorption in the higher energy *G*-line component. The number of components we observe and the splitting energy is within experimental error for each *G*-line component identical with the data of Foy *et al.* (Fig. 1 of Ref. 20). There are minor differences with respect to the polarization of the lines. Except for $\bar{X} \parallel [110]$, where two inequivalent direction of σ -polarized light exist, Foy *et al.* find purely π - or σ -polarized lines whereas we find, for each stress direction, line components of mixed polarization. We classified our splitting patterns according to Kaplyanskii.³² The following values for the components of the piezospectroscopic tensor \vec{A} were obtained (units in 10^{-6} eV/MPa , uncertainty $\pm 0.2 \times 10^{-6} \text{ eV/MPa}$):

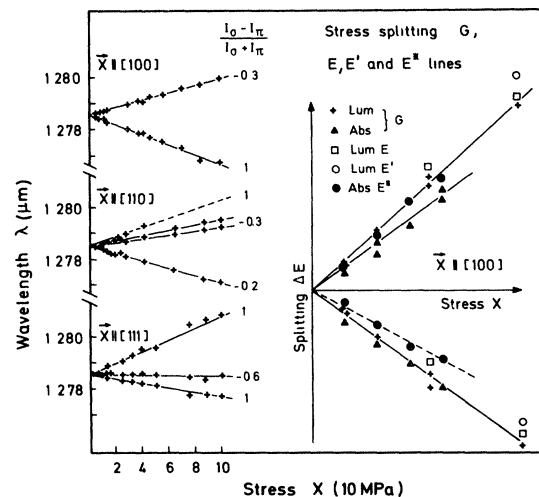


FIG. 5. Left-hand side: Splitting of the *G* line for stress along the main crystallographic directions with experimental polarization degrees indicated. Right-hand side: Relative comparison of *G*-line associated transitions for stress along [100] in luminescence and absorption.

$$A_1 = 14.0, \quad A_3 = 4.0,$$

$$A_2 = -10.0, \quad A_4 = \pm 8.5,$$

with

$$\vec{\mathbf{A}} = \begin{pmatrix} A_2 & A_3 & -A_4 \\ A_3 & A_2 & A_4 \\ -A_4 & A_4 & A_1 \end{pmatrix}.$$

This set of tensor components A_i is close to the values of Foy *et al.*, who found 13.4, -10.7 , 4.84, and ± 9.51 , respectively, in the above indicated order and in the same units.

The tensor $\vec{\mathbf{A}}$ with our values of the components is diagonalized by a rotation of the $[111]$ axis around the perpendicular $[\bar{1}\bar{1}0]$ axis by 15° . The position of the rotated $[111]$ axis corresponds to the symmetry axis of the G -line center.

In Fig. 5 (right-hand part) we show a relative comparison for $\vec{\mathbf{X}}||[100]$ of those G -correlated lines which were detectable either in luminescence or absorption. E splits like G , and E^* splits similar to G with a slight but clear deviation in the low-energy component. Other irradiation-induced lines which we observed in silicon samples of different origin and after lower or higher annealing temperatures showed absolutely different splitting patterns. Therefore, we take the present results as a confirmation that E , E' , E^* , and by analogy E'' , belong to the same electronic transition as G .

C. Isotope effects

As mentioned above, several authors in previous investigations reported on a correlation of the G -line intensities with carbon concentration. It was, therefore, tempting to look for an influence of ^{13}C doping on the G line and on the local modes. Actually it turned out that ^{13}C induces new vibration modes. The new spectral features conclusively demonstrate that a carbon atom on a substitutional site is one of the G -line center's constituents.

Two silicon samples were implanted with ^{13}C at a dose of $7.5 \times 10^{14} \text{ cm}^{-2}$ and an energy of 350 keV. Before implantation, characteristic sample data were

Sample 1	Sample 2
Si:Al, 2.5 $\Omega \text{ cm}$	Si:P, 240 $\Omega \text{ cm}$
$[\text{O}] < 5 \times 10^{15} \text{ cm}^{-3}$	$[\text{O}] < 10^{15} \text{ cm}^{-3}$
$[\text{C}] \approx 3.6 \times 10^{16} \text{ cm}^{-3}$	$[\text{C}] < 10^{15} \text{ cm}^{-3}$
	e^- irradiated,
	room-temperature annealed.

Both samples were isochronally annealed at different temperatures up to $T_A = 450 \text{ K}$. At this stage, sample 1 exhibited weakly the G -line spectra, whereas the luminescence as seen from sample 2 was much more intense. No alteration in the spectra was observed. The ^{13}C -implanted layer of about $1 \mu\text{m}$ depth was then diffused for 6 h at 1100°C under argon buffer gas. We estimate that after this procedure the ^{13}C containing layer was about $5 \mu\text{m}$ deep.

In the next step, both samples were electron irradiated at a temperature below 100 K. Directly after irradiation, no luminescence at all was found in the spectral region of 0.97 eV. Upon room temperature anneal for one to two hours, the familiar spectra were again observed (G, E); no alteration of G was visible but a new line close to E had appeared with a displacement of 1.95 meV from E to higher energies. After renewed annealing for 3 days at room temperature, both lines had largely increased in intensity, and it was also possible to detect E' along with a second new satellite displaced from E' by $+3.9 \text{ meV}$. Figure 6 shows spectra in the range of the E and E' lines at this stage of the experiment. For the sake of control, we recorded the luminescence from the unimplanted side of the samples. This side did not exhibit the displaced extra satellites. Finally, most of this extra luminescence had vanished after room-temperature storage of the two samples for several weeks.

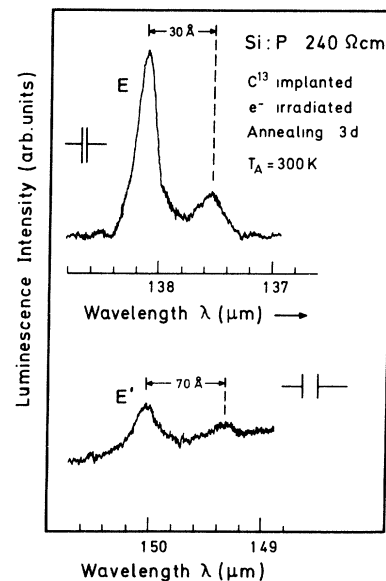


FIG. 6. Spectra in the range of the local modes E and E' with the extra isotopic lines induced by ^{13}C implantation.

It is clear from the experimental conditions that we have observed isotope splittings due to ^{13}C atoms. Further evidence to the effect as due to carbon comes from the quantitative isotope splittings. The displacement energies $\Delta h\nu$ of the local modes from the *G* line are for line *E*,

$$\frac{\Delta h\nu(^{12}\text{C})}{\Delta h\nu(^{13}\text{C})} = \frac{71.90 \text{ meV}}{69.95 \text{ meV}} = 1.028$$

and for line *E'*

$$\frac{\Delta h\nu(^{12}\text{C})}{\Delta h\nu(^{13}\text{C})} = \frac{143.4 \text{ meV}}{139.5 \text{ meV}} = 1.028 .$$

These values are almost the same as the ratios of substitutional ^{12}C to ^{13}C vibrational frequencies from infrared studies^{11,34}

$$\frac{\omega(^{12}\text{C})}{\omega(^{13}\text{C})} = \frac{607.5 \text{ cm}^{-1}}{589.1 \text{ cm}^{-1}} = 1.031 .$$

The similarity of these values is particularly striking since the frequency ratio is by no means proportional to the square root of the atomic masses. The same frequency ratios appear to result from carbon vibrating in an interstitial position.^{11,34}

The appearance of the ^{13}C local-mode satellites is the first direct proof that carbon is involved in the *G*-line center. Moreover, our results allow for a number of further conclusions. First, we observed a *doublet* isotope splitting of the local modes *E* and *E'* which corresponds to *single* isotopes ^{12}C or ^{13}C in the complex. If, for example, the complex contained two carbon atoms, we should have seen triplet isotope splittings due to the possible carbon combinations ($^{12}\text{C},^{12}\text{C}$), ($^{13}\text{C},^{13}\text{C}$), and ($^{12}\text{C},^{13}\text{C}$). Therefore, only one carbon atom is incorporated in the complex. Implicitly, we have assumed that all carbon atoms in the defect show up in the luminescent features. An equivalent reasoning was recently used by Canham *et al.*³³ to show that the center responsible for the 1.045-eV irradiation line in silicon contains two Li atoms resulting in the observed triplet isotope splitting. Second, we conclude that the carbon atom in the *G*-line complex is located on a lattice site, C_S . The local mode energy we observe is 71.9 meV (^{12}C) or 69.95 meV (^{13}C). Substitutional carbon is known to produce vibrational bands at frequencies 607.5 cm^{-1} (^{12}C) or 589.1 cm^{-1} (^{13}C) at 77 K corresponding to energies of 75.3 or 73.0 meV, respectively.^{11,34} Our vibrational mode energies are consistent when we assume that the vibrating substitutional carbon atom is slightly disturbed by a partner of larger mass in the center. In the follow-

ing paragraph this partner will be identified as silicon. Calculations by Elliott and Pfeuty³⁵ show that for substitutional-interstitial pairs as well as for substitutional pairs one vibration frequency is expected to be close to the vibration frequency of the isolated substitutional atom and another frequency is close to that of the isolated partner. For the case of boron pairs this could experimentally be verified. It is important to note that no other infrared vibrational absorption bands are known in the energetic range of 70 meV except for those which are correlated with acceptor and donor doping. In particular, interstitial carbon induces bands at largely different energies, visualized at 114.5 meV \triangleq 924.1 cm^{-1} (^{12}C) and at 106.4 meV \triangleq 858.7 cm^{-1} (^{13}C) (Ref. 11).

D. Fine structure of the *G* line

In our high resolution measurements we found that the *G* line is not a single line but consists of three components of largely different intensities (Fig. 7). The *G* line described up to now is the low-energy line of this triplet. The two other lines are split off by $1.55 \text{ \AA} \triangleq 0.11 \text{ meV}$ and by $3.10 \text{ \AA} \triangleq 0.22 \text{ meV}$. The triplet structure exists in *all* samples which we investigated provided the luminescence was strong enough to resolve the lines. The triplet does not thermalize as was probed by measurements between 2 and 8 K in our temperature-regulated Dewar. Increasing temperatures cause only broadening of all lines, but do not affect the relative triplet line intensities. Under stress along $\langle 100 \rangle$, the *G*-emission splits into two components. In each component, the unchanged triplet structure is retained except for worse resolvability, which is probable due to slight stress inhomogeneities (Fig. 7, inset). The triplet was also seen with identical relative intensities in high resolution absorption. All these properties conspire to suggest an explanation in terms of an isotope effect. The identical line spacings in the triplet of 0.11 meV hint to a very simple situation which may, e.g., be encountered in successive isotope masses. From simple inspection we obtain estimated intensity ratios of the triplet lines of about 90:6:4. We looked for elements in the Periodic Table with similar ratios of natural isotope abundancies. There is only one, Si, which fits the condition. The natural isotope abundancies are³⁶ [^{28}Si]:[^{29}Si]:[^{30}Si] as 92.21:4.70:3.09. In order to have more accurate experimental triplet intensities on hand for comparison, we fitted the shape of the

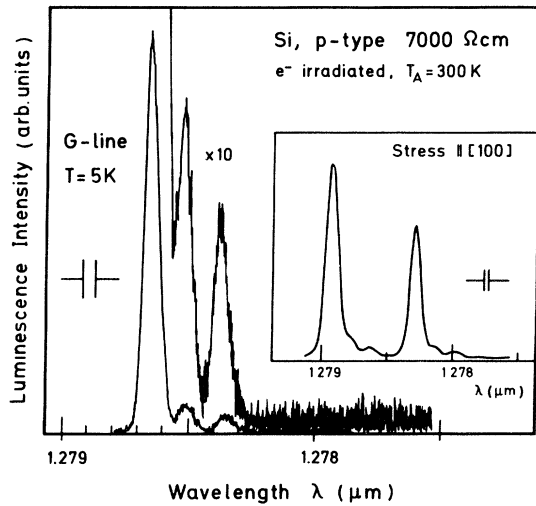


FIG. 7. Fine structure of the G line without external fields (original spectra) and for stress along $[100]$.

G main line by a computer. Since the experimental shape is asymmetric, the fit was composed of two Gaussian halves of adjustable widths. Once a good fit for the main line was obtained, we applied this fixed theoretical line shape to the weak satellites. This procedure yielded an excellent overall fit of the G emission when the intensities were 91.3:5.4:3.3. These ratios are in remarkably good agreement with the above given natural Si isotope abundancies.

Our conclusion is that one silicon atom is the partner of carbon in the G -line complex. The possibility of two or more equivalent silicon atoms is excluded since we do not observe more than three G -line components, as would be necessary for compatibility with the various possible isotope combinations in such a complex. This conclusion implies that there are no silicon atoms which are "optical inactive." The minimum intensity we would experimentally observe is by a factor of at least 20 below the intensity of the weakest triplet line (Fig. 7, original spectrum at enlarged amplification). If, for example, the G -line center contained two equivalent silicon atoms, five components should exist with relative intensities 85:8.7:5.9:0.3:0.1. These values are entirely different from our empirical values; moreover, with the experimental sensitivity of our setup, we should have detected four isotope components instead of only three. We emphasize in particular that the observed intensity ratios of the triplet are not consistent with a carbon isotope effect. Assuming that the triplet resulted from the three possible combinations of two equivalent carbon atoms, ^{12}C and ^{13}C , which could

be involved as the most abundant isotopes of this ever-persisting defect we would obtain intensity ratios of 97.81:2.18:0.01, in clear disagreement with the experimental values.

E. Model and discussion

In the past years, the G line has frequently been ascribed to the so-called $G11$ center, a carbon-split interstitialcy which is very well known from EPR.^{16,37} This interpretation is conflicted with our results. First, it cannot explain the appearance of only one displaced local-mode line after ^{13}C implantation but would require two displaced lines from the different vibrational frequencies of pairs ($^{12}\text{C}, ^{12}\text{C}$), ($^{12}\text{C}, ^{13}\text{C}$), and ($^{13}\text{C}, ^{13}\text{C}$). Second, it cannot explain the triplet structure of the no-phonon main G line as was discussed in the preceding paragraph.

From our results, we may directly conclude that one substitutional carbon atom preferentially interacts with one silicon atom. Based on this we discuss in the following two different specific models where the first one seems to be simpler and the second one to be more probable. The first model which we propose for the G -line center is drawn in Fig. 8. It is a carbon atom on or near a substitutional lattice site with a neighboring silicon atom on an interstitial site. An extra silicon atom is chosen to be consistent with the experimentally suggested prominence of one silicon atom. Two configurations are possible: The silicon atom may be located near a high symmetry T_d interstitial site (Fig. 8) or it could be near a bond-centered position. The first configuration seems to be more probably from geometric reasons. The axis of the $\text{C}_5\text{-Si}_I$ dumbbell has relaxed off the $\langle 111 \rangle$ direction by an angle of 15° , thus reducing the sym-

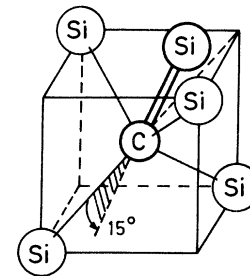


FIG. 8. Model of the silicon 0.97-eV (G) line center. The axis of the carbon-silicon dumbbell is rotated by 15° from the $[111]$ direction in the $(1\bar{1}0)$ plane. Lines interconnecting the atoms are not bonds but are to facilitate the geometric perspective.

metry of the center from trigonal to monoclinic I, C_{1h} , with a $\{110\}$ mirror plane. An additional lattice relaxation around the center probably takes place but is not shown in Fig. 8.

This model is mainly deduced from the symmetry classification of the center, from the isotope effects occurring in the local modes, and from the triplet structure of the *G* line; it is consistent with other luminescence data which are known. It is evident that a center made up from carbon and silicon satisfies the correlation of the *G*-line luminescence with carbon concentrations and its independence of any intentional doping, in particular of shallow donors or acceptors, as was previously reported in literature. Theoretically molecular-orbital cluster calculations exist on a similar system consisting of interstitial carbon in a diamond matrix.³⁸ It was found that $\langle 100 \rangle$ and $\langle 111 \rangle$ interstitial configurations are much more stable than $\langle 110 \rangle$ configurations with a minor preference to the $\langle 100 \rangle$ case. For $\langle 111 \rangle$, a lattice relaxation was expected. Similar results were obtained for boron and nitrogen interstitials in the diamond lattice.³⁹

Relaxation of the present C-Si dumbbell off one particular $[111]$ axis, e.g., by a static Jahn-Teller effect, may occur to three equivalent positions of C_{1h} symmetry with the dumbbell in equivalent $\{110\}$ planes. Under stress, preferential alignment of the center axis occurs to the positions of lowest energy. Foy *et al.*²⁰ in their study of the *G* line reported that the time to reestablish thermal equilibrium after changing the temperature ($T \approx 20$ K) was less than 100 sec. This is much faster than the similar reorientation time observed by Brower¹⁶ for the *G*11 center. Part of this discrepancy may be removed in our model considering that interstitial silicon in *p*-type material is mobile even at temperatures as low as 1 K in contrast to interstitial carbon (*G*11) although no different behavior of the *G* line in *n*- or *p*-type material was found in our work.

There is a possible relation of this model with the so-called *G*12 center investigated by Watkins and Brower⁴⁰ in EPR. The *G*12 center shows up after irradiation damage of silicon and is formed by a carbon and a silicon atom in a $\langle 100 \rangle$ configuration occupying a single substitutional site. The symmetry (C_{2v}) allows for location of the carbon atom anywhere along the line between the interstitial tetrahedral site (T_d) and the substitutional site (Fig. 9). This paramagnetic center has a single positive charge where the unpaired electron resides

in a nonbonding *p* orbital on the carbon atom and a corresponding orbital on the silicon atom is perpendicular to that and empty. The *G*12 center anneals out at 65°C, and simultaneously the formation of the *G*11 center was observed. Two reaction channels may be imagined when the *G*12 center anneals out. One is the migration of the carbon atom with subsequent capture by a substitutional carbon atom and formation of the *G*11 carbon-split interstitialcy, whereas the remaining *G*12 silicon atom is repositioned on a substitutional site. It is unimportant at the moment whether the deliberation of carbon atoms to migrate takes place via the Watkins replacement mechanism⁴¹ or not. The other channel may be the direct conversion of the *G*12 to the 0.97 eV center by the combined effects of charge neutralization and change of configuration from $\langle 100 \rangle$ to near $\langle 111 \rangle$. Once the new center has formed it is stable up to anneal temperatures of 200°C. Stabilization of the new center may be enhanced by two bonding molecular π orbitals along the center axis resulting from the *G*12 nonbonding *p* orbitals after rearrangement in the same plane through the new center axis. The possibility of change of the configuration upon a change of charge state was discussed and experimentally verified by Lee and co-workers⁴² in their EPR study of the $\langle 100 \rangle$ split di-interstitial. The second process described is consistent with the following observations we made. The *G* line does not split in a magnetic field up to field strengths of 5.5 T. This was also found in independent work.⁴³ As the simplest explanation we may conclude that the *G* line is a transition between upper and lower states of one-dimensional representations which is dipole allowed from group theory (relaxation could in this case not be attributed to the Jahn-Teller effect which requires degenerate levels to be split by spontaneous internal strain). The states are made up from two electrons coupled at the center to a

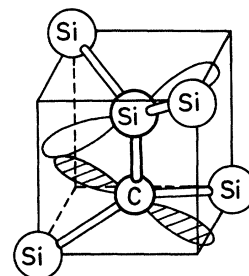


FIG. 9. Model of the Si-*G*12 center after Watkins and Brower (Ref. 40) with bonds indicated by double lines.

singlet level with total zero spin. Actually, the G -line center did not show up in paramagnetic resonance experiments performed in conjunction with the present photoluminescence study. EPR measurements were performed on several samples exhibiting strong G luminescence. The samples were n - or p -type and were investigated in the dark as well as under white-light illumination. In no case was a signal observed other than from familiar paramagnetic centers which were not correlated with $G12$ or $G11$.

Among the deficiencies of the model discussed up to this point we note two as follows. Experimentally, the G -line luminescence is not influenced by the amount of donor or acceptor doping and by the doping species. From EPR data, however, it is believed that silicon self-interstitials produced in the original damage event are mobile at low temperatures and are trapped by the group-III dopant ejecting it into an interstitial site.⁴¹ This process should lead to a detectable difference of G -line intensities between n - and p -type material. A second deficiency is the fact that the interstitial silicon atom of the model provides four negative charges. It is difficult to see how these charges form bonding orbitals since all electronic charges of the surrounding atoms are already neutralized. In the following, we therefore discuss a second model which is consistent with the empirical data and avoids the crucial points of nonsaturated extra charges and n - or p -type dependencies.

The second model is depicted in Fig. 10. A vacancy is trapped near a substitutional carbon atom. The four broken bonds around the vacancy form two new bonds. Two of the remaining silicon atoms pull together to form an electron pair bond, and a similar pair bond is made up between the remaining carbon-silicon pair. There is no charge left behind, thus the center is diamagnetic and would not be observable in EPR as is actually found. This configuration is very similar to the Si- E center⁴⁴ except for the extra charge of the phosphorus atom in the E center replacing the carbon atom in our case. The model is consistent with a previous speculative assignment of the 1.28- μm absorption line to a C- V complex by Bean *et al.*¹⁰ Relaxation due to the Si-Si pair bond and the C-Si pair bond reduces the symmetry to C_{1h} because only one mirror plane of (100) type remains. The arrows in Fig. 10 indicate that part of the relaxation which is responsible for the experimentally determined 15° deviation from the $\langle 111 \rangle$ trigonal symmetry axis without relaxation. The

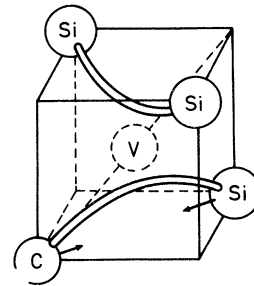


FIG. 10. Model of the silicon 0.97-eV (G) line center. Double lines are bonds. The arrows indicate relaxation leading to the observed symmetry lowering of the atomic configuration from the $\langle 111 \rangle$ trigonal C_{3v} symmetry to monoclinic I , C_{1h} .

carbon atom particularly “feels” the single silicon partner to which it has opened relations by the new pair bond irrespective of the usual bonds to the remaining three nearest-neighbor silicon atoms in $\langle 111 \rangle$ -type directions on undisturbed lattice sites (not shown in the figure). This explains the observed silicon isotope finestructure of the G line. It is obvious that this center may easily form after irradiation of carbon-doped crystals when there is a sufficiently high concentration of vacancies after damage. Considering our model, we find some interesting details of the G -line luminescence in the work of Tkachev and Mudryi.¹⁷ These authors note that owing to the frozen-in dichroism which they observe the atomic axis of the center can preferentially be aligned by an uniaxial stress at elevated temperatures. In particular, they did not observe quenched-in dichroism when stress was applied along a $\langle 100 \rangle$ direction, and they therefore concluded that the center has an *atomic* symmetry along a $\langle 111 \rangle$ direction as is compatible with the present model. Tkachev and Mudryi further note that isothermal annealing of the quenched-in alignment gives activation energies of (1.25 ± 0.01) eV. This is exactly the same value as was found in their work for the activation energy correlated with annealing out of the luminescence. A similar value of the activation energy for annealing, 1.34 eV, was independently published by Wong and Streetman.⁴⁵ Once again, this may easily be understood in the present model: Atomic reorientation of a given carbon-vacancy pair to a different, equivalent $\langle 111 \rangle$ axis is only possible when the vacancy migrates via one of the nearest-neighbor lattice sites. This intermediate step, however, destroyed the whole center leading to the equal values for realignment and for annealing.

Finally, we report an experiment giving evidence

that the *G*-line center can be formed without radiation damage. We chose a *p*-type sample of 10^{17}-cm^{-3} carbon concentration which absolutely exhibited no *G*-line luminescence. The sample was heated up to 1200°C for 7 h and was then rapidly quenched in silicon oil at room temperature. After this procedure, we observed the *G* line unambiguously although at moderately weak intensities. An explanation may be found in terms of both models discussed. With regard to the first model, in thermal equilibrium at higher temperatures, a small amount of interstitial silicon atoms is expected to coexist with substitutional silicon atoms in unirradiated samples. Rapid cooling of a heated sample should result in a concentration of the interstitial silicon atoms in excess of the associated thermal equilibrium density and in the formation of *G*-line centers. With regard to the second model, vacancies are produced complementarily to self-interstitials and will be frozen in by rapid quenching to cooperate with the carbon dopants.

In conclusion, we have demonstrated by a number of new experimental results that the 0.97-eV luminescence band induced by irradiation damage of silicon is not due to the carbon-split interstitialcy as was often assumed in recent times. We discuss two new models of the center, both consisting of a substitutional carbon atom with a silicon atom in a prominent position. The second model

is analogous to the familiar EPR Si-*E* center replacing phosphorus by carbon and seems to be favorable.

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