

Structure of the 0.767-eV oxygen-carbon luminescence defect in 450 °C thermally annealed Czochralski-grown silicon

W. Kürner, R. Sauer, A. Dörnen, and K. Thonke

*Physikalisches Institut, Universität Stuttgart, Pfaffenwaldring 57, Postfach 80 11 40,
D-7000 Stuttgart 80, Federal Republic of Germany*

(Received 28 November 1988)

The oxygen-carbon luminescence defects with no-phonon emission at 0.767 eV ("P line") and 0.79 eV ("C line") created in pulled silicon after 450 °C thermal annealing or electron irradiation, respectively, are investigated in a comparative study. This includes investigation of all major local modes in samples ^{13}C or ^{18}O enriched to practically 100% abundances. Many new isotopic line shifts are observed on both spectra, and those already reported in the literature are confirmed. Striking similarities in the two vibronic sideband spectra, the sensitivity of the individual local modes to carbon or oxygen isotopic substitution, and the nearly identical electronic properties of the two defects lead us to conclude that the defects possess an identical "core." The core structure is identified as the isolated interstitial carbon C_i (a bonded carbon-silicon pair along $\langle 001 \rangle$ sharing a substitutional site) as adopted from the recently published model of the 0.79-eV center. The defects are distinguished by their oxygen structure (which for the 0.79-eV defect was identified as an interstitial oxygen atom O_i). We argue that in the 0.767-eV center a di-oxygen molecule or a more complex oxygen aggregate deriving from the molecule is bonded to C_i . Evidence for this is taken from literature data on di-oxygen formation kinetics and from our observation of the C line in heated silicon proving the presence of interstitial carbon as a result of self-interstitial generation in the process of oxygen pairing.

I. INTRODUCTION

When high-oxygen-content Czochralski-grown silicon is thermally heated at around 450 °C for 1 h to several hundred hours, many sharp photoluminescence (PL) lines emerge in the range from near-band-edge energies around 1.1 down to ≈ 0.77 eV.¹ In the early stages of the anneals, up to some 10 h, there are mostly two prominent lines, at photon energies of 0.767 and 0.926 eV, usually labeled the P line and H line, respectively.¹ After the original report of the lines by Minaev and Mudryi,¹ the P line, in particular, was intensely studied. Doping investigations on pulled (i.e., oxygen-rich), high- and low-carbon-content silicon seemed to indicate that carbon is unfavorable for the P-line center suppressing or slowing down its formation.²⁻⁴ In contrast, PL measurements on ^{13}C isotopically enriched silicon showed a broadening and high-energy shift of the 0.767-eV transition which was interpreted as being due to an isotope effect indicative of the incorporation of carbon in the optical center.^{5,6} Other work focused on the electronic properties of the 0.767-eV defect. It was found in uniaxial-stress measurements that the defect belongs to the monoclinic I (C_{1h}) symmetry point group⁷ and possesses an effective-mass (EM)-like electron-excitation spectrum in its luminescent state, classifying the defect as a deep-hole trap at $E_v + 368$ meV.^{8,9} Two strong local modes were identified in the PL spectrum and could also be detected as anti-Stokes lines in photoluminescence excitation (PLE) spectroscopy.^{8,9} All these data, though potentially important for a microscopic identification of the center, were not

strong enough to deduce a specific structure. Much of the interest in the 0.767-eV center apparently originates in its formation conditions¹⁻⁴ being identical to those of the 450-°C thermal donors¹⁰ in the initial annealing process of virgin oxygen-rich silicon: The defect grows in at around 400 °C, peaks in luminescence intensity at 450–500 °C, and disappears at slightly higher temperatures of 550–600 °C. Involvement of oxygen in the formation of the defect is obvious as the 0.767-eV line is not observed in oxygen-lean float-zone silicon. However, direct proof that oxygen is incorporated in the center (as, for example, by an oxygen isotope shift) has not yet been given.

It was noted in previous publications^{8,9} that the electronic properties of the 0.767-eV defect are very similar to those of the 0.79-eV ("C line") optical center. This center is dominant in oxygen- and carbon-rich silicon after damage by electron irradiation in the 2-MeV range and partial annealing between room temperature and 400 °C. Isotope effects on the 0.79-eV no-phonon (NP) transition and on associated local-mode satellites in the PL spectrum showed that oxygen and one carbon atom are part of the defect and gave also evidence for the particular role of a silicon atom in the structure.^{5,6,11,12} Absorption studies¹³ demonstrated the identity of the optical 0.79-eV defect and the infrared C(3) defect associated previously with a C_i-O_i center, with oxygen not directly bonded to carbon.^{14,15} This suggestion was essentially confirmed in recent work which advanced a detailed model: Trombetta and Watkins¹⁶ used stress-induced alignment measurements to show that the 0.79-eV line, as

observed by PL, and the Si-G15 defect spectrum, as observed by electron paramagnetic resonance (EPR), do arise from the same defect. The G15 center was, in turn, identified by EPR as an interstitial carbon atom trapped near an interstitial oxygen atom. (This model is shown in Fig. 9.) With this microscopic model and a tremendous amount of available optical data, the 0.79-eV defect is— together with the 0.97-eV $C_s-S_i-C_s$ defect¹⁷—the best understood structural luminescence defect in undoped silicon.

The present paper is a comparative study, with the discussion of the microscopic structure of the *P* line defect based on the model of the 0.79-eV defect. Experimentally, we study the 0.767- and 0.79-eV defect lines and their associated sidebands down to low energies with large sensitivity. In particular, oxygen and carbon isotope effects are investigated showing that the dominant lines in the two electronic-vibronic bands are equivalent with respect to carbon but inequivalent with respect to oxygen. This leads us to identify the split interstitial (C-Si) pair as the core of the 0.767-eV center as well. An oxygen structure is suggested using literature data on di-oxygen formation at 450-°C heating. Enhanced production of the 0.767-eV spectrum in silicon irradiated at increased temperatures in the range 200–300°C and the observation of the 0.79-eV line in 450-°C-annealed silicon without damage are critically discussed in view of the new model and found to be consistent with it.

The paper is organized in six sections describing experimental details (Sec. II), luminescence spectra extended to low photon energies (Sec. III), isotope effects (Sec. IV), the defect model along with a discussion (Sec. V), and a summary (Sec. VI).

II. EXPERIMENT

The PL measurements were carried out in a standard luminescence setup. The samples were strain-free mounted in an optical cryostat equipped with fused silica windows, and kept at a controlled low temperature. The excitation was performed using the 647-nm Kr-ion or 514-nm Ar-ion laser lines at maximum powers of 1.5 W. The luminescence light was dispersed by a Spex Industries 1-m grating monochromator or a Jobin-Yvon 0.6-m grating monochromator. Small isotope shifts on NP transitions were recorded with high spectral resettability as described previously:¹⁸ The monochromator is set fixed to a wavelength close to the peak of the line under investigation, and the spectrum is scanned by rotating an electrically driven quartz plate in the optical beam inside the monochromator. The achieved resettability accuracy is estimated to be ± 0.001 nm. All isotope effects were obtained by comparing ¹³C- or ¹⁸O-enriched samples with ordinary silicon under identical experimental conditions. The monochromator and, partially, the optical path outside the instrument were purged to diminish perturbing atmospheric absorption in the spectral regions investigated. Cooled Ge, InAs, or PbS detectors were employed for light detection, and the signals were processed by conventional lock-in techniques.

The samples in this study were Czochralski-grown sil-

icon with variable amounts of carbon up to some 10^{17} cm^{-3} . They were annealed at 450°C for several hours to produce the 0.767-eV spectrum or were irradiated either at low temperature (≈ 100 K), room temperature ($< 50^\circ\text{C}$), or higher temperature (200–300°C) by 1.5–2-MeV electrons at doses of $\leq 10^{18}$ cm^{-2} to create the 0.79-eV defect. Isotope effects were studied in two different kinds of samples. (i) ¹³C was introduced into the melt to an amount exceeding the concentration of ¹²C by orders of magnitude. The 100% abundance of ¹³C in the pulled crystals was tested by infrared-absorption measurements on the 607- cm^{-1} (¹²C) and 589- cm^{-1} (¹³C) local modes of substitutional carbon,¹⁴ or by observing in photoluminescence the “*E*” local mode of the 0.97-eV center known to be sensitive^{19–22} to isotopic substitution of ¹²C by ¹³C. (ii) ¹⁸O was introduced in a specifically constructed diffusion apparatus.²³ The starting material was float-zone silicon cut into square-based long rods of typical sizes $3 \times 3 \times 120$ mm^3 . These rods were sealed in a quartz ampoule in an ambient of ¹⁸O gas under a pressure of 160–200 Torr and heated to $\approx 1400^\circ\text{C}$ for up to 2 weeks to diffuse the ¹⁸O. Heating was performed in a “light oven” by light from four halogen lamps carefully focused onto the rod so as to leave the quartz ampoule cool and, hence, to avoid out-diffusion of naturally abundant ¹⁶O from the ampoule. After diffusion the crystals contained $\approx 90\%$ ¹⁸O and $\approx 10\%$ ¹⁶O on the average in the bulk as monitored by the 9- μm infrared-absorption band of interstitial oxygen²⁴ measured at 4.2 K in a Fourier spectrometer. In photoluminescence, which is more sensitive to the surface, no significant contribution of ¹⁶O was observed in any of the emission lines of the ¹⁸O-enriched samples.

III. LUMINESCENCE SPECTRA

Photoluminescence spectra of the 0.767- and 0.79-eV defects are plotted in Fig. 1 down to energies of 0.56 eV. The absolute positions of the lines and their displacement energies from the corresponding NP transitions are listed in Table I.

We discuss the *C* line (0.79 eV) spectrum first. Earlier, the local-mode satellites *L1'*, *L1*, *L2'*, *L2*, (*), (**), (***) , *L3*, and *L4* were reported in the literature.^{5,6,11,12,25} *L1* and *L2* show fine structure on their high-energy side due to ¹⁸O. This was seen in 12% ¹⁸O-enriched samples^{11,12} and, much more clearly, in specimens containing ¹⁶O and ¹⁸O in a ratio of 1:3.^{5,6} In addition, there is a second fine structure superimposed on *L2*, showing that this line is a triplet with relative intensities consistent with the natural abundances of the silicon isotopes ²⁸Si, ²⁹Si, and ³⁰Si. The spacing of the triplet lines corresponds to the full silicon mass effect expected in a harmonic-oscillator model.⁵ Therefore, *L2* and, most probably, also *L1* are primarily due to the vibration of a silicon atom. The Λ line was depicted in various survey spectra but was not discussed; the lines labeled by asterisks and *L3* and *L4* were observed as weak features.²⁵ Our present experiments reveal the following extra findings: (i) The Λ line is always observed in the *C* line spectrum at a constant intensity ratio to the NP transi-

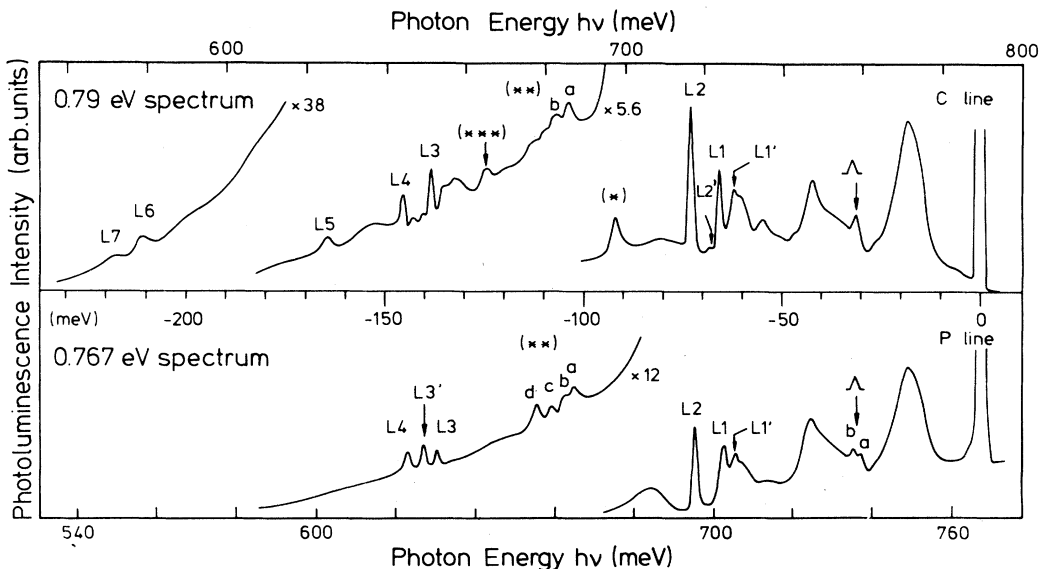


FIG. 1. Low-temperature PL spectra of the oxygen-carbon defects emitting no-phonon lines at 0.79 eV (C line) and 0.767 eV (P line).

tion. Hence, it is part of the sideband spectrum. Carbon and oxygen isotope shifts (see Sec. IV) confirm this conclusion. (ii) The (***) line consists of two major components, labeled a and b. Further weak components may exist at lower energies, but are not certain owing to residual atmospheric absorption lines in this spectral region. (iii) The spectral range around the (***) line is also perturbed by absorption peaks; therefore this line could have additional unresolved structure. (iv) The lines labeled $L5-L7$ are new. The discussion of the local modes is continued in Sec. IV.

Next, we describe the sideband spectrum of the 0.767-eV P line. It was shown previously^{8,9} that the lines labeled 7 and 8 at that time are due to local modes of the defect. The lines (now relabeled as $L1$ and $L2$, respectively) are relatively sharp and are the dominant vibronic lines in the sideband. In addition to these features, there are a number of new lines which we report here: (i) The present data (Fig. 1) strongly suggest that the line 6 previously ascribed to TO lattice phonons is an independent local mode (now relabeled $L1'$) superimposed on the broad TO lattice replica. (ii) At lower displacement energies (≈ 32 meV) from the NP transition, a doublet Λ emerges which is also invariably related to the P line spectrum and is ascribed here to a defect in-band mode. (iii) A fourfold structure [(***) a-d] is detected at lower energies. Again, due to residual atmospheric absorption between the b and c components of this structure it is possible that b and c are only one single line close to an average displacement energy of 106.3 meV. (iv) A triplet $L3$, $L3'$, and $L4$ emerges at about twice the displacement energy of $L1$ and $L2$.

Comparison of the two spectra in Fig. 1 and in Table I gives intuitive evidence that the 0.767- and 0.79-eV defects possess very similar vibronic sidebands. This applies, in particular, to the dominant local modes $L1$ and $L2$. The most striking difference is in the 90-meV region

where the (*) line of the 0.79-eV spectrum has no counterpart in the 0.767-eV spectrum. Possible differences in the 102–108-meV region are not clear, but an equivalent of the (***) line of the 0.79-eV spectrum definitely does not exist in the 0.767-eV spectrum.

IV. ISOTOPE EFFECTS

The 0.79-eV spectrum will again be treated first. Previous PL work reported a well-resolved doublet structure of the NP transition in silicon isotopically enriched as $[^{13}\text{C}]:[^{12}\text{C}]=0.6:0.4$, indicating one carbon atom per optical center.^{5,11} In our isotopically “pure” samples, we observe the same line shift of 0.089 meV (Fig. 2), confirming the earlier result. In addition, there is also a small oxygen isotope shift of 0.024 meV on this line which was not detected in the previous measurements. Figure 3 depicts the isotope shifts of the $L1$ and $L2$ modes due to the substitution of ^{16}O by ^{18}O . As we are recording single lines in the individual samples, the accuracy is much better than previously reported.^{5,6,12} We have not aimed at also detecting the weak fine structure on $L2$ due to the naturally abundant silicon isotopes of mass 28, 29, and 30.^{5,6,12} $L3$ and $L4$ are sensitive to oxygen isotopic substitution, with shifts of 0.4₈ or 0.5₀ meV, respectively (Fig. 4). Moreover, small carbon isotope shifts are seen on $L3$ and $L4$, amounting to 0.1₈ or 0.3₄ meV, respectively (Fig. 5). The (*) line, with $\hbar\omega=91.5$ meV, is insensitive to carbon isotopic substitution, but exhibits a large oxygen isotope shift of 4.0 meV (Fig. 6). This is the full size expected for a pure oxygenlike vibration in a harmonic-oscillator model, $(\sqrt{18/16}-1)\hbar\omega=5.5$ meV. Finally, a small carbon and an even weaker oxygen isotope shift are detected on the Λ line rather similar to those on the NP line (Fig. 6). In this context it is necessary to note that all shifts are calculated from the NP line in the same material, i.e., the shifts given are net effects.

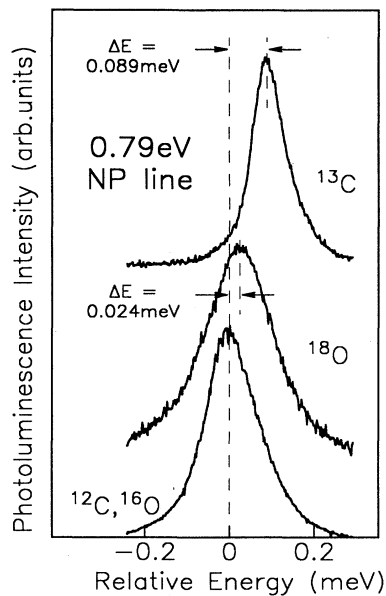


FIG. 2. Carbon and oxygen isotopic shifts on the no-phonon (NP) transition at 0.7894 eV of the C line spectrum.

Combining our results with previous data,^{5,6,11,12} the following picture arises. The dominant modes *L1* and *L2* are mainly due to the vibration of a silicon atom with a small influence of oxygen different for the two modes. Carbon is not involved in these vibrations. The (*) line is mainly due to vibrating oxygen and is not influenced by carbon within experimental accuracy. The modes *L3* and *L4* were originally ascribed²⁵ either to independent modes with $\hbar\omega = 138.4$ and 145.3 meV, respectively, or to combination modes involving $L1+L2$ or $2\times L2$, respectively. The latter interpretation is inconsistent with both the carbon and oxygen isotope effect. As the sensitivity of the modes to these atomic species is weak, far below

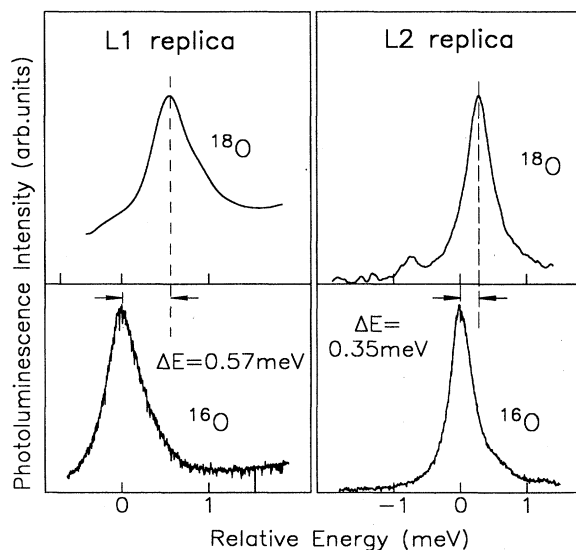


FIG. 3. Oxygen isotope shifts on the *L1* and *L2* local-mode replicas of the 0.79-eV NP line.

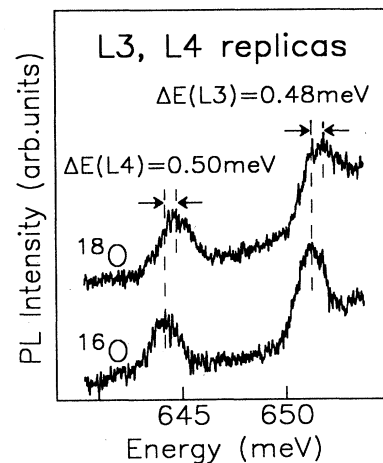


FIG. 4. Oxygen isotope shifts on the *L3* and *L4* local-mode replicas of the 0.79-eV NP line.

full-size isotopic shifts, and their vibration energies are probably too high for any mode involving primarily silicon an interpretation of their nature is not straightforward. It is interesting, however, that Bean *et al.*²⁶ reported several oxygen infrared-absorption modes in the 138-meV region for irradiated silicon containing carbon and oxygen. In these cases, oxygen isotopic line shifts were not measured. Davies *et al.*,¹³ when showing that the optical 0.79-eV spectrum and the infrared C(3) spectrum originate from the same defect, identified the 138.4-meV *L3* mode with the C(3) absorption mode at 1115 cm^{-1} (138.2 meV). Our data demonstrate that this assignment is incorrect, as the 1115-cm^{-1} mode exhibits the full carbon isotope shift (4.61 meV for ^{13}C - ^{12}C substitution),¹⁴ whereas the *L3* mode is influenced to only ≈ 0.2 meV. We emphasize that this result has no bearing on the concluded identity of the 0.79-eV and C(3) defects,¹³ as this was derived from reaction kinetics comparing irradiation-dose, annealing, and carbon-concentration dependences of the two defects. A

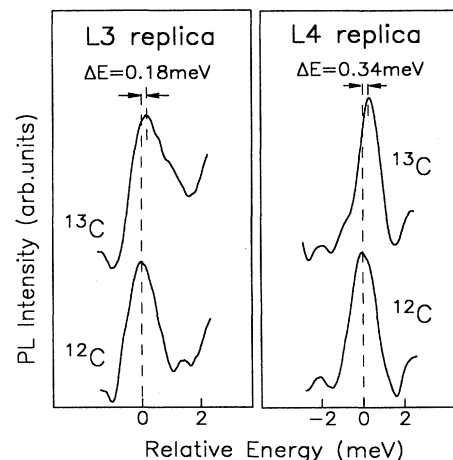


FIG. 5. Carbon isotope shifts on the *L3* and *L4* local-mode replicas of the 0.79-eV NP line.

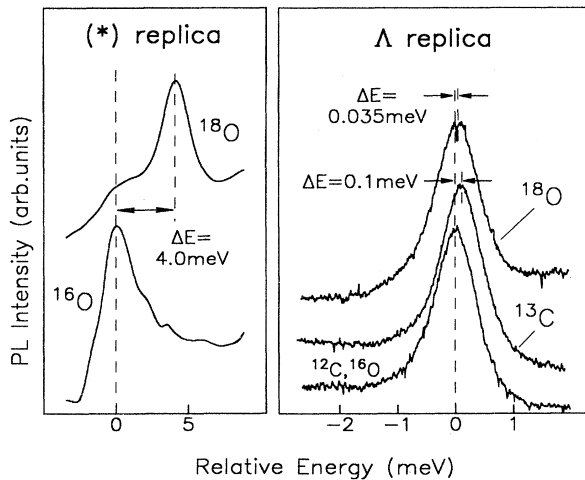


FIG. 6. Oxygen and carbon isotope shifts on the (*) and Λ local-mode replicas of the 0.79-eV NP line.

different possible assignment not mentioned by Davies *et al.*¹³ could be to identify the infrared 742-cm^{-1} (92-meV) mode with the optical 91.5-meV mode; this could be tested by observing an oxygen isotope shift on the former line as we have detected on the latter line. It is consistent with the suggestion that neither line exhibits a carbon isotope shift. The remaining lines in the 0.79-eV spectrum can be assigned to combination modes, $L5=L2+(\ast)$, $L6=L4+L1$, and $L7=L4+L2$; these assignments are consistent with the line energies and their relative strengths compared to the parent one-phonon lines.

Second, we discuss the 0.767-eV spectrum. The NP transition shifts to higher energy by 0.079 meV upon ^{12}C - ^{13}C isotopic substitution (Fig. 7). This is close to the corresponding value for the 0.79-eV *C* line. On the other hand, any oxygen isotope effect would have to be smaller than 0.02 meV. The clear carbon isotope effect unambiguously confirms the participation of carbon in the defect, corroborating the earlier less conclusive result by Davies and co-workers^{5,6} and terminating the existing controversy between isotopic spectroscopy and doping studies.¹⁻⁴ The main local-mode satellites *L1* and *L2* are insensitive to carbon isotopic substitution. The accuracy limits in this measurement, ± 0.5 and ± 1 meV, respectively (Table I), are conservatively calculated. They are rather large as the data were obtained from a sample enriched in the bulk to $[^{13}\text{C}]:[^{12}\text{C}]=0.6:0.4$, which exhibited the *C* line spectrum strongly and, in addition, the *P* line spectrum weakly. Therefore the *L1* and *L2* modes appeared close to the shoulders of the much stronger (*) replica in the 0.79-eV spectrum. Oxygen isotope shifts of the *L1* and *L2* lines were studied in ^{16}O and ^{18}O isotopically pure samples unperturbed by the presence of the *C* line spectrum (Fig. 8). *L2* does not shift, while *L1* exhibits a displacement of 0.3 meV. This behavior is different from the *L1* and *L2* lines in the *C* line spectrum. The shift of *L1* directly demonstrates the incorporation of oxygen in the 0.767-eV defect, which was not shown heretofore. All other replicas in the *P* line spectrum were too

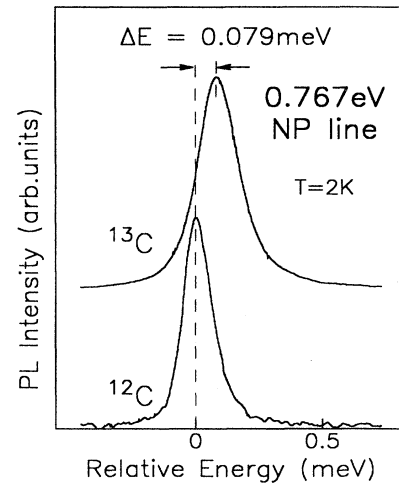


FIG. 7. Carbon isotope shift on the no-phonon (NP) transition at 0.767 eV of the *P* line spectrum.

weak for isotope studies. It appears plausible to extend the interpretation of the *L3* and *L4* lines in the 0.79-eV spectrum as one-phonon modes to the present case. Energetically, assignments $L3=L1+L2$ and $L4=2\times L2$ can be made equally well. In this context, it is noteworthy that Bean and Newman²⁷ in 450-°C-heat-treated, high-carbon-content pulled silicon reported a number of oxygen infrared-absorption modes in the range 130–137 meV, with associated carbon modes in the range 70–85 meV. It was suggested that among the four distinct types of carbon-oxygen complexes observed, two involve a carbon atom with two oxygen atoms, but the atomic structure of these complexes was not specified. In our spectra the nature of the *L3'* band remains unclear at present. The *L5* replica, interpreted as a combination mode of *L2* and (*) in the *C* line spectrum, does not appear in the *P* line spectrum, obviously consistent with the fact that the (*) mode does not exist in the *P* line spectrum.

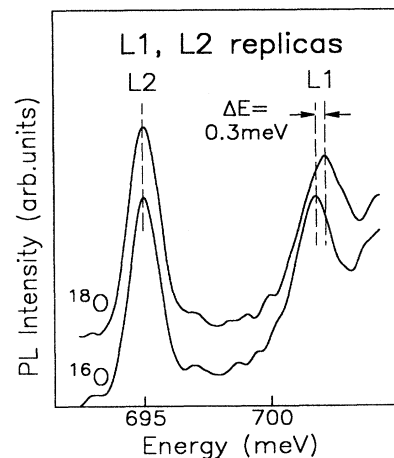


FIG. 8. Oxygen isotope shifts on the *L1* and *L2* local-mode replicas of the 0.767-eV NP line.

V. DEFECT MODEL AND DISCUSSION

First, we recall a number of features common to the 0.767- and 0.79-eV defects as noted previously,^{8,9} demonstrating the close relationship between the two defects. We then use the above data on the PL sidebands and the isotope effects, in conjunction with the 0.79-eV defect model¹⁶ to discuss the structure of the *P* line defect.

(i) Both defects belong to the monoclinic $I (C_{1h})$ point-symmetry group as deduced from uniaxial-stress measurements (Ref. 7 for the *P* line; Refs. 28 and 29 for the *C* line), but are very close to tetragonal symmetry. The NP lines do not split in a magnetic field up to 5.3 T and are therefore singlet-to-singlet transitions. (ii) Both defects exhibit effective-mass-like excited-electron spectra, with electron-ionization energies of $E_e = 34.3$ meV (*P* line) (Refs. 8 and 9) or $E_e = 38.8$ meV (*C* line).^{25,29} As the NP recombination lines are far below the band-gap energy and differ only by 22.4 meV, it follows that both defects are deep hole traps with very similar hole binding energies amounting to $E_h = 368.2$ meV (*P* line) or $E_h = 341.2$ meV (*C* line). (iii) In the manifold of EM-like electron state, the $1s$ ground state of the *C* line defect is split by a total of 15.6 meV into five substates of symmetry A_1 , T_z , T_x/T_y , E^- , and E^+ due to an internal defect-induced strain field.²⁹ Similarly, the $1s$ -electron state of the *P* line defect is split by a total amount of 12.7 meV into five substates (whose symmetry in the proper monoclinic or tetragonal symmetry point group is not yet identified).^{8,9} Therefore, a significant stress field also exists around the *P* line defect, comparable in magnitude to the *C* line defect.

In Sec. IV it was not shown explicitly that the *L*1 and *L*2 modes of the *P* line are "siliconlike," as for the *C* line. We are now making this assumption, which appears to be extremely likely given the general similarity of the two sideband spectra and, specifically, the characteristic form of the doublet *L*1,*L*2 including almost equal vibration energies and the intensity ratio 2:1 for *L*1 and *L*2 in both spectra. (The doublet could be viewed as a triply degenerate silicon mode split in an axial strain field into a single mode and a perpendicular twofold-degenerate mode.) With this assumption, the NP transitions, and the Λ , *L*1, and *L*2 lines, are equivalent in the two spectra, with corresponding sensitivity to carbon isotopic substitution (where measurable), but inequivalent with respect to oxygen isotopic substitution. Most striking is this inequivalence for the (\ast) mode, which is completely missing in the *P* line spectrum. All these observations combine to suggest that the two defects possess an identical silicon-carbon "core" at which the deeply bound hole is preferentially localized, with different oxygen structures. Trombetta and Watkins¹⁶ recently identified the core of the 0.79-eV defect (or the Si-G15 defect) as being essentially the Si EPR-G12 center,³⁰ a bonded carbon-silicon $\langle 001 \rangle$ pair sharing a substitutional lattice site often labeled the "isolated interstitial carbon." In the 0.79-eV defect, the C_i is trapped near an interstitial oxygen atom O_i as shown in Fig. 9(a). We identify in this paper the *P* line defect as a (C_i-Si_i) pair near a di-oxygen molecule or a more complex oxygen aggregate forming from a mole-

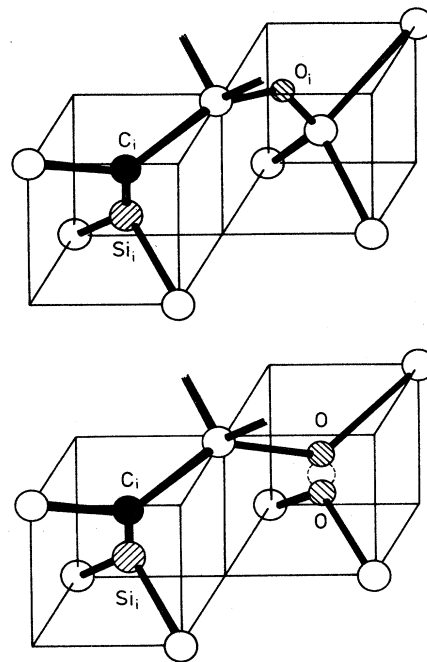
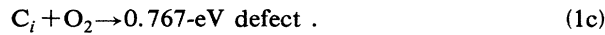
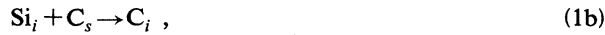


FIG. 9. Upper part: ball-and-spokes model of the 0.79-eV defect after Trombetta and Watkins (Ref. 16). The interstitial oxygen atom O_i lies in the $\langle 110 \rangle$ mirror plane of the defect through the $\langle 001 \rangle$ axis of the (C_i, Si_i) pair. The point symmetry of the defect is monoclinic $I (C_{1h})$. Lower part: Modell's suggestion for the 0.767-eV defect, with O_i of the upper part replaced by a vacancy-di-oxygen (VO_2) structure. More extended oxygen structures deriving from VO_2 are discussed in the text.

cule. For definiteness, we describe the di-oxygen complex as the vacancy-di-oxygen (VO_2) structure as shown in Fig. 9(b) and postpone certain discrepancies in literature data relating to such complexes to a later discussion.

The di-oxygen structure of the 0.767-meV defect is concluded from the production of the center at 450-°C thermal annealing. We use, essentially, the results of Newman *et al.*³¹⁻³³ obtained in studies on thermal donor formation under the same experimental heating conditions of Czochralski-grown silicon as necessary for the *P* line formation. These works were concerned with the fate of dissolved interstitial oxygen present in the starting material when the silicon is heated up. In high-oxygen-content and high-carbon-content silicon it was found that two oxygen atoms are lost from solution for one carbon atom at 450-°C annealing.^{32,33} (This result is confirmed by unpublished data of Weman *et al.*³⁴) Here carbon plays the role of a marker to monitor the following process which was proposed:³¹⁻³³ Pairs of oxygen atoms that are initially close together in the as-grown crystal due to their statistical distribution, diffuse (at their normal equilibrium rate) and form di-oxygen complexes. In this process, self-interstitials are produced to accommodate the volume change. They diffuse through the crystal and are selectively trapped by carbon atoms, which are themselves ejected into interstitial sites.³⁵ This explained the simultaneous losses of oxygen (O_i) and carbon (C_s) in

a 2:1 ratio. We now suggest that it is this process that gives rise to the formation of the *P* line defect: The interstitial carbon C_i which is mobile at $T \gtrsim 300$ K is trapped near a di-oxygen complex, so that the whole formation process is described by the sequence of reactions



In the following we give independent evidence for the production of C_i in the heating process, thus confirming the Newman model, which is crucial for our model of the *P* line. Whereas the infrared measurements^{31–34} detected the simultaneous *loss* of oxygen, O_i , and carbon, C_s , we monitor—in the next stage of reaction kinetics—the *generation* of C_i with the high sensitivity of photoluminescence through the accepted reaction¹³



Here, the C_i interacts with oxygen in solution which has not undergone pairing. In fact, we detect in all heated pulled silicon samples the *C* line spectrum in addition to the dominant *P* line spectrum. The *C* line is weak probably as the defect is essentially annealed out at 450°C (the usual annealing temperature is around 400°C after defect production by irradiation^{36,37}), and we are observing a small surviving portion of the original, much higher, defect concentration. There are indications in the literature that in all work on the *P* line the *C* line was also present, but this fact has not been explicitly stated before: Minaev and Mudryi,¹ in their original paper on the luminescence from thermally annealed pulled silicon, show *P* line spectra which in all cases are accompanied by a weak peak at the position of the *C* line at 0.7894 meV. This was also the case in later work,² where this weak extra line was labeled line 1. Dörnen *et al.*⁷ resolved a closely spaced triplet at this position with relative intensities varying from sample to sample, thus indicating that these lines are due to independent optical centers. The photon energies of the lines are⁷ 0.7883 eV (line $1'$), 0.7894 eV (line $1''$), and 0.790 eV (line $1'''$). A weak peak close to 0.79 eV is also seen in *P* line spectra shown by Weman *et al.*³⁴ After these findings, we reviewed many spectra recorded previously from a great variety of Czochralski-grown silicon samples heated at 450°C . In all cases the lines around 0.79 eV were present. We demonstrate with a particular sample that line $1''$ is, in fact, the NP transition of the *C* line defect (Fig. 10). In this sample, the triplet is seen at low temperatures. At elevated temperatures, line $1'$ decreases relative to line $1''$, and line $1'''$ is finally no longer resolved from line $1''$. At 20 K and higher temperatures, excited lines appear resulting in the 50 -K spectrum plotted in Fig. 10. This is the typical spectral structure of the *C* line as published previously.^{25,29,38} Hence, we have shown that line $1''$ is actually the NP transition of the *C* line spectrum, and it is evident that under 450°C -annealing conditions the *C* line defect always forms. This result, *regardless* of the present discussion on the *P* line defect, lends support to

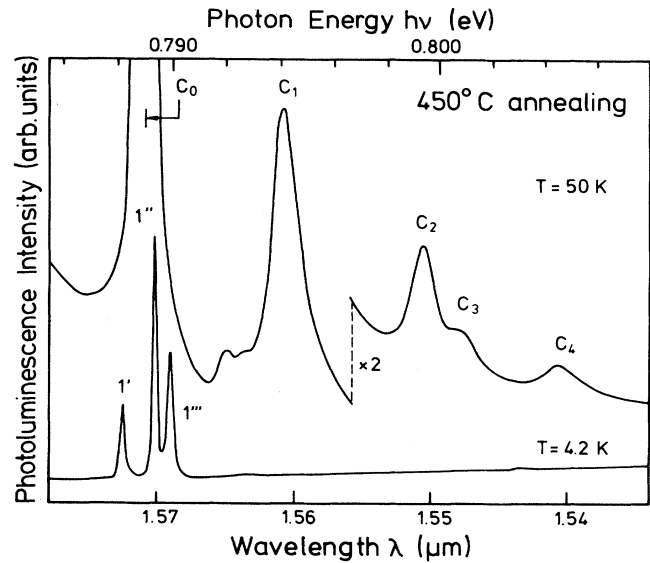


FIG. 10. Lower spectrum: triplet structure of luminescence lines $1'$, $1''$, and $1'''$ in an oxygen-rich silicon sample heated for 10 h at 450°C . Sample temperature is 4.2 K. The *P* line at 0.767 eV ($1.616 \mu\text{m}$) is more than 1 order of magnitude stronger than the triplet. Upper spectrum: the same sample measured at a temperature of 50 K. The shift between line $1'$ and the peak of the line C_0 is due to the temperature-induced band-gap shrinkage. Lines C_0 – C_4 are the characteristic “fingerprints” of the no-phonon *C* line spectrum (Refs. 25, 29, and 38). Photoluminescence intensities in both spectra are not to scale, and resolution is much poorer in the upper spectrum than in the lower one.

reaction (1a) and is thus a new independent confirmation of Newman’s model of di-oxygen formation.

We now consider the usual formation process of the *C* line defect. In this process irradiation initially produces self-interstitials; these, in turn, change sites with substitutional carbon atoms, thus, in turn, creating carbon interstitials [Eq. 1(b)] that are finally trapped at isolated interstitial oxygen atoms [Eq. (2)]. When the irradiation is performed at low temperatures (e.g., at 100 K) and the samples are stored at room temperature, only the *C* line emerges, but there is no indication of the *P* line. However, Pajot and von Bardeleben noted in electronic-vibronic absorption studies³⁹ that electron irradiation at higher temperatures (around 200°C) “simulates a 450°C thermal treatment.” In particular, they could not observe the *P* line in absorption in a sample annealed at 450°C for 10 h, but they did see the line when a second test sample was irradiated for 5 h at a temperature of 200°C . In our experiments we find confirmation of these observations as the *P* line intensities in photoluminescence are definitely much larger than in thermally annealed silicon when the samples are irradiated at higher temperatures estimated to be in the range 200 – 300°C . This agrees with recent findings by Oates *et al.*⁴⁰ on enhanced oxygen migration in Czochralski-grown silicon irradiated at elevated temperatures up to 500°C . The increased rate of oxygen motion for $T < 300^\circ\text{C}$ was ex-

plained and successfully modeled by sequential capture of a vacancy at O_i (forming the VO or A center^{41,42}) and a self-interstitial at VO again liberating interstitial oxygen. For $T > 300^\circ\text{C}$, beyond the range of stability of the intermediate VO , evidence was given for superenhanced oxygen migration by repetitive capture and release of vacancies at O_i . In the present case of the P line center, enhanced oxygen motion under irradiation at higher temperatures accelerates the process of oxygen pairing [Eq. 1(a)] and enhances the rate of formation of the P line defect. In addition, self-interstitials are produced in the primary damage event, subsequently increasing the concentration of C_i and again favoring the formation of the 0.767-eV center. We note an experimental difference between the behaviors of the P line luminescence in samples annealed at 450°C and electron-irradiated samples. When the 0.767-eV spectrum is created by thermal annealing, the PL intensity is relatively low at or near 4.2 K; it increases drastically for elevated temperatures, up to a factor of ≈ 300 for $T=30$ K, before it is quenched upon further temperature increase. This behavior was reported previously² and has been confirmed in our later experiments. On the contrary, when the P line luminescence is created in irradiated samples, the low-temperature PL intensity is constant for temperatures up to ≈ 30 K. An explanation is not straightforward, but could be sought in the production of various deep centers in the damaged crystals strongly binding photoexcited charge carriers, which, in the annealed samples, are loosely bound to shallow impurities and thermal donors, and can be thermally released to be captured at 0.767-eV centers at increasing temperatures.

We return to the models of the 0.79- and 0.767-eV defects in Fig. 9. Trombetta and Watkins¹⁶ emphasized that the local strain field of the isolated carbon is tensile along the $\langle 011 \rangle$ direction, which lies in the C_{1h} mirror plane of the defect, while that of the isolated oxygen in the 0.79-eV defect [Fig. 9(a)] is compressive along its $\langle 111 \rangle$ bonding direction. It was supposed that partial cancellation of the strain fields plays an important role in the binding of the two interstitial atoms in the C line defect. The dominant modes of vibration of the isolated O_i are at 1106 cm^{-1} (137.1 meV) and 515 cm^{-1} (63.8 meV) at room temperature, with the former vibration being an antisymmetric stretching mode along $[11\bar{1}]$. When the strain around O_i is relaxed the vibration energy should be lowered. It is then evident that the optical mode (*), with $\hbar\omega=91.5$ meV exhibiting the full oxygen isotope shift, corresponds to this relaxed stretching motion. This lends further support to the importance of strain reduction in the C_i - O_i center. Conversely, the (*) mode is not observed in the P line center, demonstrating a different oxygen structure of this defect. This touches on a discrepancy in the literature in which we get involved with the model in Fig. 9(b). Newman *et al.*³¹⁻³³ describe the pairing of oxygen mostly in terms of di-oxygen formation without specifying the structure, except in one place, where it is associated with the vacancy-di-oxygen complex VO_2 .³² These authors stated that no strong new infrared modes emerge when pairing occurs confirming similar results by Pajot and von Bardeleben.³⁹ Therefore,

they assumed that the di-oxygen complex has a very small dipole moment. On the other hand, Corbett *et al.*⁴³ discussed the formation of VO_2 defects in irradiated silicon by trapping of VO (or A) centers^{41,42} at interstitial oxygen O_i at temperatures in excess of 300°C . This was tentatively suggested from the observation of an infrared-absorption line at 887 cm^{-1} (109.9 meV) which emerges when the absorption line of the A center at 829 cm^{-1} (102.8 meV) anneals out. The identification was challenged by Bosomworth *et al.*⁴⁴ from an analysis of stress splitting of the 887-cm^{-1} line, but it is fully consistent with theoretical calculations on the substitutional oxygen-oxygen pair by DeLeo *et al.*⁴⁵ The discrepancy remains unresolved in the literature. Corbett *et al.*⁴³ expected the two oxygen atoms in the vacancy to pull the silicon neighbors inward, i.e., to create a tensile strain. From the high vibration energy of 887 cm^{-1} along $\langle 111 \rangle$ associated with this complex, we would rather expect that there is remaining compression, although smaller than that for isolated O_i . In fact, the model in Fig. 9(b) implies that strain cancellation between the C_i - Si_i pair and the di-oxygen structure is as important for the stability of the P line complex as it is for the C line. However, no local mode exists in the vibronic sideband of the P line up to ≈ 100 meV, which could be related to oxygenlike vibrations. The splitting of the Λ mode in the P line spectrum could be an indication of a more complex oxygen structure compared to the interstitial oxygen O_i in the C line defect. The absence of the $L3'$ mode in the C line spectrum could be similarly explained.

The di-oxygen structure assumed in the 0.767-eV center is the easiest model consistent with all available data. However, more complex oxygen aggregates forming from the oxygen molecule would also be conceivable. After prolonged heating, formation of larger aggregates would be even more probable. The strength of the P line in 450°C annealed silicon containing amounts of $\approx 10^{18}\text{-cm}^{-3}$ oxygen and some $10^{16}\text{-}10^{17}\text{-cm}^{-3}$ carbon content is significantly smaller than that of the C line in similar material after irradiations at doses in the 10^{17}-cm^{-2} range. Davies *et al.*¹³ estimated the concentration of the 0.79-eV defect in such material to be of order 10^{16} cm^{-3} . Earlier luminescence measurements showed^{8,9,29} that the C and P line defects are neutral in their ground states, and that they bind an electron-hole pair in their luminescent states. This makes an internal radiative quantum efficiency close to unity for both defects plausible and, hence, the difference in PL strength could indicate a relatively low concentration of the P line center, in the range of 10^{14} cm^{-3} or below. Whereas such a conclusion is somewhat uncertain in PL owing to the branching problem of photoexcited electron-hole pairs, this concentration value is consistent with absorption data on the P line.^{39,46} Using second-order reaction kinetics [Eq. 1(a)] with Newman's data,³²

$$d/dt [O_i] = -k [O_i]^2 = +k [O_2] ,$$

where $k \approx 0.5 \times 10^{-24}\text{ cm}^3$, we obtain an upper bound of the P -center concentration for 10-h annealing,

$[P] \leq 2 \times 10^{16} \text{ cm}^{-3}$, provided all carbon interstitials created are efficiently captured at the di-oxygen complex with a reaction constant much larger than k . The value for $[P]$ is too large under the assumptions made and could be reduced to the experimentally estimated value assuming a higher-order oxygen complex to be important in the formation of the 0.767-eV center. When in both PL spectra the $L3$ and $L4$ lines are due to one-phonon, oxygenlike modes, as discussed earlier, this would suggest that part of the oxygen structure in the P defect is equivalent to that in the C defect, tentatively hinting at O_i plus O_2 (or VO_3); the latter complex was suggested to form from VO_2 under prolonged annealing at 450°C .^{43,47} However, a mode corresponding to the (*) line would then be expected in the sideband spectrum of the 0.767-eV defect, which is not detected. In addition, such a complex would be even more extended in space than the defects in Fig. 9 with associated problems of stability. Evidently, there are many more speculations possible, and further well-founded arguments as to an oxygen structure in the P line defect more complex than VO_2 have to await future experimental data.

VI. SUMMARY

In this photoluminescence study we have measured the vibronic sidebands of the 0.767- and 0.79-eV lines down to photon energies around 0.56 eV and have found new local-mode transitions. Isotope effects due to carbon and oxygen atoms were detected on many of the lines in the two spectra in addition to those which were reported previously. A comparison shows that the two optical defects are identical with respect to their carbon and silicon constituents, but different with respect to oxygen. We use the recently proposed model of the 0.79-eV defect¹⁶ to conclude that an interstitial carbon atom is part of the 0.767-eV defect. An approach to the oxygen structure of the defect is derived from literature data on oxygen reac-

tion kinetics studied in conjunction with the formation of the 450°C thermal donors. It is suggested that this part is a di-oxygen molecule VO_2 in a lattice tetrahedron next to that housing the C_i . Like the 0.79-eV defect, the center could be stabilized through the effect of internal stress, with compensation of overpressure in the di-oxygen unit and underpressure in the carbon unit. It was discussed that the very similar electronic properties of the C and P defects are well explained by this model. The reaction paths suggested for the formation of the P line defect required simultaneous production of the C line in 450°C thermally annealed pulled silicon, which was experimentally verified. Conversely, the formation of the P line defect in silicon irradiated at higher temperatures up to 450°C , and the absence of this defect after low-temperature irradiation, are also understood.

ACKNOWLEDGMENTS

We thank W. Zulehner (Wacker Chemitronic, Burghausen) for the gift of float-zone and Czochralski-grown silicon exclusively containing ^{13}C . The loan of a ^{16}O -diffused sample enriched in the bulk to $[^{13}\text{C}]:[^{12}\text{C}]=0.6:0.4$ by G. D. Watkins and J. Trombetta (Lehigh University, Bethlehem, PA) is also gratefully acknowledged. F. Dworschak (Kernforschungsanlage Jülich) supported this study by irradiating several samples at higher temperatures. Low-temperature irradiations were performed with the expertise of L. Raschke and G. Steudle (Universität Stuttgart). One of the authors (R.S.) thanks his colleagues at AT&T Bell Laboratories, Murray Hill, NJ, for their hospitality during his stay and, in particular, T. D. Harris and L. C. Kimerling for the loan of equipment. The financial support of the Deutsche Forschungsgemeinschaft (Contract No. Sa-311/4-3), Bonn, Germany, is gratefully appreciated. Work partially performed at AT&T Bell Laboratories, Murray Hill, NJ 07974-2070.

- ¹N. S. Minaev and A. V. Mudryi, *Phys. Status Solidi A* **68**, 561 (1981). The P line was also mentioned in earlier work: V. D. Tkachev and A. V. Mudryi, in *Proceedings of the International Conference on Radiation Effects in Semiconductors, Dubrovnik, 1976*, edited by N. B. Utli and J. W. Corbett, Inst. Phys. Conf. Ser. No. **31**, (IOP, Bristol, 1977), p. 231.
- ²J. Weber and R. Sauer, in *Defects in Semiconductors*, edited by J. W. Corbett and S. Mahajan, Proceedings of the Materials Research Society Symposium (MRS, Pittsburgh, PA, 1983), Vol. 14, p. 165.
- ³M. Tajima, P. Stallhofer, and D. Huber, *Jpn. J. Appl. Phys.* **22**, L586 (1983).
- ⁴N. Magnea, A. Lazrak, and J. L. Pautrat, *Appl. Phys. Lett.* **45**, 60 (1984).
- ⁵G. Davies, E. C. Lightowlers, R. Woolley, R. C. Newman, and A. S. Oates, *J. Phys. C* **17**, L499 (1984).
- ⁶G. Davies, E. C. Lightowlers, R. Woolley, R. C. Newman, and A. S. Oates, *J. Electron. Mater.* **14a**, 725 (1985).
- ⁷A. Dörnen, R. Sauer, and J. Weber, *J. Electron. Mater.* **14a**,

653 (1985).

- ⁸J. Wagner, A. Dörnen, and R. Sauer, *Phys. Rev. B* **31**, 5561 (1985).
- ⁹J. Wagner, A. Dörnen, and R. Sauer, in *Microscopic Identification of Electronic Defects in Semiconductors*, Proceedings of the Materials Research Society Symposium, edited by N. M. Johnson, S. G. Bishop, and G. D. Watkins (MRS, Pittsburgh, PA, 1985), Vol. 46, p. 453.
- ¹⁰See, for example, the review by G. D. Watkins, in *Defects in Semiconductors*, Proceedings of the Materials Science Forum, edited by H. J. von Bardeleben (Trans Tech, Switzerland, 1986), Vols. 10–12, p. 953.
- ¹¹K. Thonke, G. D. Watkins, and R. Sauer, *Solid State Commun.* **51**, 127 (1984).
- ¹²K. Thonke, N. Bürger, G. D. Watkins, and R. Sauer, *J. Electron. Mater.* **14a**, 823 (1985).
- ¹³G. Davies, A. S. Oates, R. C. Newman, R. Woolley, E. C. Lightowlers, M. J. Binns, and J. G. Wilkes, *J. Phys. C* **19**, 841 (1986).

- ¹⁴R. C. Newman, *Infrared Studies of Crystal Defects* (Taylor and Francis, London, 1973).
- ¹⁵M. R. Brozel, R. C. Newman, and D. H. J. Totterdell, *J. Phys. C* **8**, 243 (1975).
- ¹⁶J. M. Trombetta and G. D. Watkins, *Appl. Phys. Lett.* **51**, 1103 (1987).
- ¹⁷K. P. O'Donnell, K. M. Lee, and G. D. Watkins, *Physica B+C* **116B**, 258 (1983).
- ¹⁸A. Dörnen, G. Pensl, and R. Sauer, *Phys. Rev. B* **35**, 9318 (1987), and references therein.
- ¹⁹G. Davies and M. C. do Carmo, *J. Phys. C* **14**, L687 (1981).
- ²⁰K. Thonke, H. Klemisch, J. Weber, and R. Sauer, *Phys. Rev. B* **24**, 5874 (1981).
- ²¹G. Davies, E. C. Lightowers, and M. C. do Carmo, *J. Phys. C* **16**, 5503 (1983).
- ²²R. Sauer, in Ref. 9, p. 507.
- ²³W. Kürner, Diploma thesis, Library of the University of Stuttgart, 1988.
- ²⁴H. J. Hrostowski and R. H. Kaiser, *Phys. Rev.* **107**, 966 (1957); H. J. Hrostowski and B. J. Alder, *J. Chem. Phys.* **33**, 980 (1960).
- ²⁵J. Wagner, K. Thonke, and R. Sauer, *Phys. Rev. B* **29**, 7051 (1984).
- ²⁶A. R. Bean, R. C. Newman, and R. S. Smith, *J. Phys. Chem. Solids* **31**, 739 (1970).
- ²⁷A. R. Bean and R. C. Newman, *J. Phys. Chem. Solids* **33**, 255 (1972).
- ²⁸C. P. Foy, *J. Phys. C* **15**, 2059 (1982).
- ²⁹K. Thonke, A. Hangleiter, J. Wagner, and R. Sauer, *J. Phys. C* **18**, L795 (1985).
- ³⁰G. D. Watkins and K. L. Brower, *Phys. Rev. Lett.* **36**, 1329 (1976).
- ³¹R. C. Newman, A. S. Oates, and F. M. Livingston, *J. Phys. C* **16**, L667 (1983).
- ³²R. C. Newman, *J. Phys. C* **18**, L967 (1985).
- ³³R. C. Newman, in *Oxygen, Carbon, Hydrogen and Nitrogen in Crystalline Silicon*, Proceedings of the Materials Research Society Symposium, edited by J. C. Mikkelsen, S. J. Pearton, J. W. Corbett, and S. J. Pennycook (MRS, Pittsburgh, PA, 1986), Vol. 59, p. 205.
- ³⁴H. Weman, B. Monemar, and P. A. Holtz, *Appl. Phys. Lett.* **47**, 1110 (1985).
- ³⁵R. C. Newman and A. R. Bean, *Radiat. Effects* **8**, 189 (1971).
- ³⁶A. V. Yukhnevich, V. D. Tkachev, and M. V. Bortnik, *Fiz. Tverd. Tela (Leningrad)* **8**, 3213 (1966) [*Sov. Phys.—Solid State* **8**, 2571 (1967)].
- ³⁷C. E. Jones, E. D. Johnson, and W. D. Compton, *J. Appl. Phys.* **44**, 5402 (1973).
- ³⁸C. P. Foy, *Physica B+C* **116B**, 276 (1983).
- ³⁹B. Pajot and J. von Bardeleben, *J. Electron. Mater.* **14a**, 685 (1985).
- ⁴⁰A. S. Oates, R. C. Newman, J. M. Tucker, G. Davies, and E. C. Lightowers, in Ref. 33, p. 59.
- ⁴¹G. D. Watkins and J. W. Corbett, *Phys. Rev.* **121**, 1001 (1961).
- ⁴²J. W. Corbett, G. D. Watkins, R. M. Chrenko, and R. S. McDonald, *Phys. Rev.* **121**, 1015 (1961).
- ⁴³J. W. Corbett, G. D. Watkins, and R. S. McDonald, *Phys. Rev.* **135**, A1381 (1964).
- ⁴⁴D. R. Bosomworth, W. Hayes, A. R. L. Spray, and G. D. Watkins, *Proc. R. Soc. London, Ser. A* **317**, 133 (1970).
- ⁴⁵G. G. DeLeo, C. S. Milsted, and J. C. Kralik, *Phys. Rev. B* **31**, 3588 (1985).
- ⁴⁶W. Kürner and A. Dörnen (unpublished).
- ⁴⁷J. Lindström and B. G. Svensson, in Ref. 33, p. 45.