

Photoluminescence spectroscopy of an Al-C complex in silicon

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Here we describe the results of an investigation of an Al-C defect complex in silicon. The defect center, with a zero-phonon line energy at ~ 922 meV, is produced by anneals at temperatures in the region 450 – 550 °C for times ranging from 8 h to hundreds of hours. Uniaxial stress measurements have shown that the defect symmetry is monoclinic I (point group C_{1h}), and Zeeman spectroscopy reveals that the transition can be regarded as the recombination of a spinlike electron and hole, with a slight anisotropy evident in the hole g factor due to mixing of orbital character into the hole wave function. Our investigations have led us to agree with previous suggestions that the defect is an Al-C complex. Perhaps most interestingly, we see striking parallels between this defect and a previously reported Al pair defect, displaying almost identical uniaxial stress and Zeeman behavior, with a zero-phonon line energy difference of ~ 37 meV. The relationship between these two defects is discussed in terms of similar behavior shown by other defects in silicon. [S0163-1829(99)00915-7]

I. INTRODUCTION

The behavior of defects in silicon remains a topic of considerable research interest, particularly the complexing of these defects with other impurities or native defects in the material. The electrical behavior and conductivity type of the material can be greatly affected by the formation of such complexes, and the details of their structure and formation conditions are of considerable importance. A great deal of research has been done on the behavior of Al in silicon, as it is commonly used p -type dopant, with concentrations up to 10^{18} atoms/cm³. Al-related complexes, in particular their relationship to thermal donor formation, have been extensively studied using a number of techniques.^{1–3} In addition, the creation, behavior, and complexing of native defects in silicon such as interstitials and vacancies has also been an active research topic for a great many years, and an enormous volume of literature exists on these defects and their complexing behavior, and a good overview of such topics, was given in the review by⁴ Watkins. The work presented here is a continuation of work begun by Drakeford and Lightowers⁵ on a defect with zero-phonon line (ZPL) energy at 922 meV observed in Al-doped, C-rich Czochralski (CZ)-grown silicon. These authors reported the production conditions, ZPL energies, and vibrational band shape, and suggested a possible formation mechanism for the defect. We have extended their investigations to include an examination of the temperature dependence of the photoluminescence (PL) spectrum, its behavior under both uniaxial stress and magnetic-field perturbations, and some preliminary comments about the defect chemical identity and creation process suggested by Drakeford and Lightowers.⁵

II. EXPERIMENTAL DETAILS

We used standard grade CZ silicon with Al concentrations in the range 10^{15} – 10^{17} cm⁻² as a starting material. The intensity of the 922-meV PL signal was not dependent solely

on the Al concentration, indicating that some other impurity in the material has an effect on either the defect formation or luminescence efficiency. The samples were RCA cleaned before all heat treatments, and were annealed in a clean quartz tube for a range of times for temperatures up to 800 °C. The optimum temperature to observe the 922-meV luminescence was found to be ~ 450 °C for periods of >100 h, although reasonable samples could be obtained by annealing at 550 °C for ~ 10 h, in confirmation of the results of Drakeford and Lightowers.⁵ Samples used in uniaxial stress measurements were cut into rectangular parallelepipeds (with approximate dimensions $10 \times 3 \times 1.5$ mm³), with the sample long axis parallel to the crystal axes $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$. Data for the $\langle 110 \rangle$ stress direction were taken with the collection optical axis parallel to the $\langle 001 \rangle$ crystal axis.

The luminescence was excited using either the 514-nm line of an argon-ion laser, or the 800-nm line of an IE Optomech model DM laser diode, and the excitation power was typically ~ 150 mW (unfocused) on the sample face. The data were recorded using a Bomem DA8 Fourier transform infrared spectrometer, coupled to a LN₂ cooled germanium detector (North Coast model EO-817 ED2). A closed-cycle Janis CCS-500 cryostat was used for exploratory work where temperatures of ~ 15 K were sufficient, while an Oxford Instruments CF1204 helium flow cryostat was used for measurements down to 4.2 K. Zeeman measurements were made on an Oxford Instruments SMD6 superconducting magnet, up to a maximum field of 7 T. The Zeeman measurements were made in the Voigt configuration, with a magnetic field perpendicular to the direction of the PL emission. The apparatus used for the uniaxial stress measurements is described elsewhere.⁶

III. RESULTS AND DISCUSSION

A. PL spectrum

In Fig. 1 below, we show a spectrum at 30 K of a CZ-grown Si:Al sample (with aluminum concentration

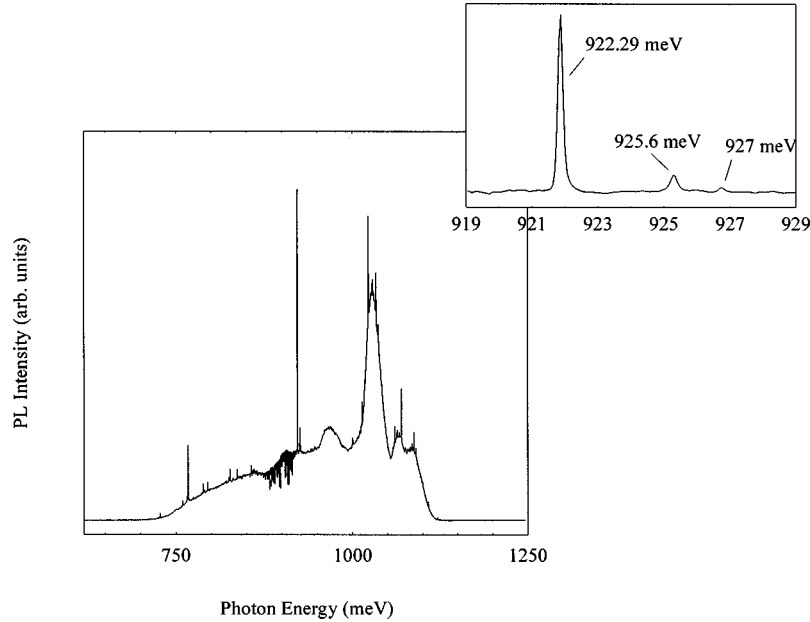


FIG. 1. Si:Al spectrum at 30 K, showing ZPL detail.

$\sim 10^{17} \text{ cm}^{-3}$) annealed at 450°C for 408 h, and in the inset the ZPL region of the 922-meV defect. The ZPL is located at $922.29(5) \text{ meV}$, close to the water vapor absorption band at $\sim 919 \text{ meV}$. The form of the phonon sideband was published by Drakeford and Lightowers,⁵ and we have not studied this sideband further. We have indicated two other lines in the inset of Fig. 1. The line marked 925.6 meV is seen in much of the CZ Si:Al samples we have studied, but it does not thermalize with the 922-meV line, and survives at temperatures where the 922-meV system is completely quenched, and thus we feel that it is unrelated to the 922-meV line. A C-related defect with ZPL at 925.6 meV has been previously reported,^{7,8} and we feel that this is a likely candidate for the 925.6-meV line we see. A weak feature at $\sim 927 \text{ meV}$ is also observed, whose intensity grows with increasing temperature, and we believe this to be a weak transition from an excited state of the 922-meV center. Our thermalization data on this feature, while showing reasonable linearity on an Arrhenius plot with activation energy close to the spectral line separation, are too poor to definitely confirm this assignment. The broad features at higher energies are due to bound exciton luminescence broadened by intercenter interactions. The lines in the region $1100\text{--}1150 \text{ meV}$ are due to luminescence from a range of acceptor-related defects unrelated to the 922-meV system.⁵

The behavior of the PL spectrum in the range $917\text{--}935 \text{ meV}$ is shown in Fig. 2, for a number of temperatures from 4.2 to 50 K . The overall intensity of the 922-meV ZPL grows first, reaching a maximum at $\sim 15 \text{ K}$, and then decreases with increasing temperature, and this temperature-dependent intensity decay is well described by an equation of the form

$$I(T) = \frac{I(0)}{1 + GT^{3/2} \exp\left(-\frac{E_i}{kT}\right)}, \quad (1)$$

with a deactivation energy $E_i = 15.8(\pm 1) \text{ meV}$, where G is the effective band density of states relative to the defect den-

sity. The fit to this equation is shown in the inset of Fig. 2. Behavior of this sort is seen for many defects in silicon,^{9,10} with similar deactivation energies in the range $12\text{--}16 \text{ meV}$, close to the value of the free-exciton binding energy of $\sim 15 \text{ meV}$.⁹ This indicates that the defect-excited state is formed by the capture of a free exciton rather than by capture of free particles. Hence the loss in defect luminescence with increasing temperature is due to a dissociation of the free exciton before it can bind to the defect core.

B. Uniaxial stress and magnetic-field effects on PL spectrum

In Fig. 3 we show the behavior of the 922-meV ZPL under application of uniaxial stress along the three crystal axes $\langle 001 \rangle$, $\langle 111 \rangle$, and $\langle 110 \rangle$. The experiments were performed at 4.2 K to minimize line broadening due to thermal effects. As is commonly the case with PL measurements, we have not obtained particularly good quality polarization data for any stress direction, and it is believed that this is due to

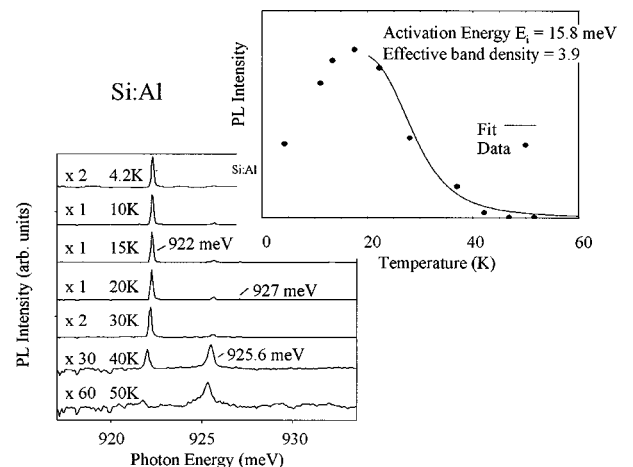


FIG. 2. PL spectra as a function of temperature of the 922-meV PL system, with a fit to Eq. (1).

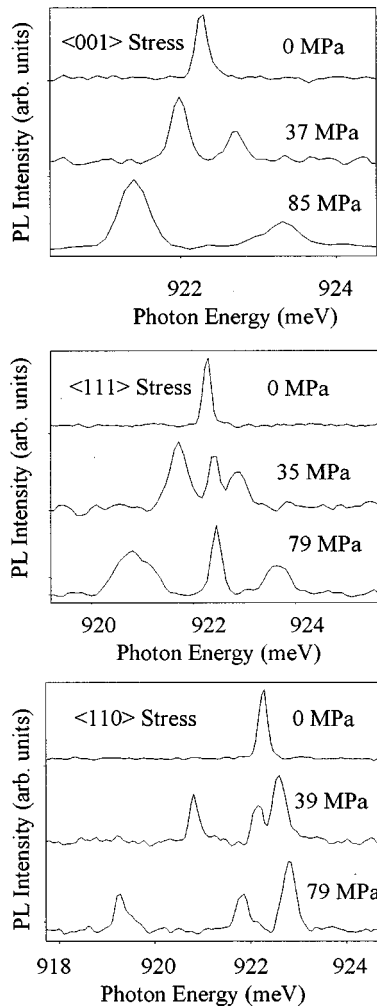


FIG. 3. Behavior of the 922-meV ZPL as a function of uniaxial stress along the principal crystal directions: $\langle 001 \rangle$ (top), $\langle 111 \rangle$ (middle), and $\langle 110 \rangle$ (bottom).

the multiple reflections suffered by PL as it exits the sample. Attempts to remedy this by the use of suitable masking of the sample edges has proved unsuccessful, and further work is needed to address this issue. Any polarization data obtained were used only as a final check on the consistency of the conclusions drawn from shift rate equations and absolute intensity ratios. The ZPL splits into two components under $\langle 001 \rangle$ stress, into three under $\langle 111 \rangle$ stress, and into three under $\langle 110 \rangle$ stress. Line splittings of 2 for the $\langle 001 \rangle$ axis, and three for the $\langle 111 \rangle$ axis in silicon can be accounted for either by a center with monoclinic I symmetry (point group C_{1h}), or by an $A-E$ transition at a state with trigonal symmetry (point group C_{3v}), both of which require four parameters to fully describe the line splittings.¹¹

The basic equations describing the shift rates of energy levels in a cubic crystal under uniaxial stress were derived by Kaplyanskii,¹² and the symmetry-reduced parameter sets needed to fit the observed splittings are listed there. Attempting a self-consistent fit of the shift rates of the five lines seen under $\langle 001 \rangle$ and $\langle 111 \rangle$ stresses using these parameters, it was observed that only a monoclinic I symmetry gave a consistent fit to these directions *and* continued to give a consistent fit when extended to the $\langle 110 \rangle$ line splittings.

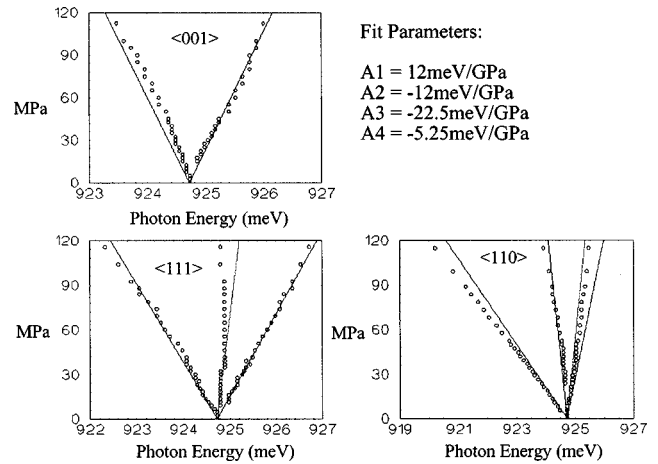


FIG. 4. Monoclinic I fit to 922-meV stress data; fits are shown by solid lines, experimental data are represented by circles.

No strong evidence of interaction effects was seen for any stress direction, but the range of the stress apparatus used ($< \sim 120$ MPa) did not permit a more detailed analysis. In particular, up to 120 MPa, there was no evidence of an interaction between the 922- and 927-meV ZPL's. The best-fit lines to a monoclinic I model are shown in Fig. 4, superimposed on the data points, and the fit is seen to be quite good in all directions. The fit parameters and measured and predicted energy shift rates are listed in Table I. If we assume that the observed spectral lines are due to electric dipole transitions, as is the case for the vast majority of defects in silicon,¹³ the relative intensity ratios of the stress-split components can be easily calculated.^{11,12} For defects with low symmetry in silicon such as triclinic and monoclinic I , however, the dipole orientation is not fully established by the symmetry of the defect.^{11,12} In particular, for the case of an $A-A$ transition at a monoclinic $I(C_{1h})$ center, the dipole can be oriented in any direction in the reflection plane, which Kaplyanskii referred to as a plane oscillator.^{12,14} If we compare the measured line intensities with those predicted for an $A-A$ transition (dipole along the $\langle 112 \rangle$ axis) for a monoclinic center¹⁴ listed in Table I, we can see that good agreement is found between theory and experiment for all stress directions. Thus we feel that the 922-meV center involves an $A-A$ transition at a site of monoclinic I symmetry, with dipole orientation along the $\langle 112 \rangle$ axis.

One rather unusual point is that under $\langle 110 \rangle$ stress, only three components are seen. It is sometimes the case for $\langle 110 \rangle$ stress that certain orientations of the center should be invisible when viewed along the $\langle 001 \rangle$ axis (for example, a monoclinic I center with the dipole parallel to the $\langle 110 \rangle$ axis¹⁴), but we think that this is not the case for the 922-meV defect. The two highest energy predicted components are close (~ 0.3 -meV separation at 60 MPa) compared to the linewidths of the other components (> 0.3 meV at 60 MPa), and we believe that the single highest-energy component we see is actually composed of two overlapping components. Finally we note that our tentative polarization data are in agreement with these conclusions.

Zeeman measurements in magnetic fields up to 7 T on a $\langle 001 \rangle$ -oriented sample (rotated in the $\langle 110 \rangle$ plane) have not revealed any shift or splitting of the 922-meV ZPL to a first-order approximation. Specifically, no splittings correspond-

TABLE I. Shift rates and line intensity ratios for the monoclinic $I A-A$ transition model for the 922-meV center ZPL.

Expression for shift rate	Best-fit shift rate (meV/GPa)	Measured shift rate (meV/GPa)	Predicted intensity ratios	Measured intensity ratios
$\langle 001 \rangle$ stress direction				
A_1	12	12.6	1	1
A_2	-12	-11.1	3	2.6
$\langle 111 \rangle$ stress direction				
$\frac{1}{3}(A_1 + 2A_2 - 2A_3 - 4A_4)$	4	0.78	5	3.2
$\frac{1}{3}(A_1 + 2A_2 - 2A_3 + 4A_4)$	18	17.5	5	4.8
$\frac{1}{3}(A_1 + 2A_2 + 2A_3)$	-19	-19.1	6	6
$\langle 110 \rangle$ stress direction (dipole along $\langle 112 \rangle$)				
$\frac{3}{2}(A_1 + A_2 - 2A_4)$	-5.25	-3.47	2	1.8
$\frac{1}{2}(A_1 + A_2 + 2A_4)$	10.5	6.66	2	2
$(A_2 - A_3)$	5.25	6.66	2	2
$(A_2 + A_3)$	-34.5	-39.4	2	2

ing to standard half-integer or integer angular momentum have been observed. Singlet behavior of this nature is common in many defects in silicon, and has been observed for a number of low-symmetry defects (monoclinic I and rhombic I) involving Cd, Zn, and Be,^{10,15,16} in addition to common defects such as the 969-meV “ G ” line.⁵ Such behavior can in many cases be well described by an independent-particle model for an isoelectronic bound exciton complex, where the hole is the tightly bound particle, and consequently has its orbital momentum strongly quenched to leave a predominantly spinlike state. The ZPL then corresponds to electron-hole recombination as shown in Fig. 5. Upon application of a magnetic field, the electron and hole spin doublets split, but only transitions with $\Delta S = 0$ are allowed (transitions a and b in Fig. 5). Hence the ZPL remains unaffected by the magnetic field in this model.

A higher resolution study of the behavior of the 922-meV ZPL, however, reveals fine structure in the ZPL, and that this structure is strongly dependent on the orientation of the sample in the field (as the $\langle 001 \rangle$ sample is rotated in a $\langle 110 \rangle$ -type plane, the magnetic-field direction with respect to the sample changes from $\langle 001 \rangle$ through $\langle 111 \rangle$ directions, and finally to a $\langle 110 \rangle$ direction). This behavior is shown in Fig. 6 for a field of ~ 7 T. Such a structure, and especially its an-

gular dependence, is strongly indicative that the orbital angular momentum of the hole is not fully quenched, introducing anisotropy into the magnetic-field behavior of the defect.¹⁷ The signals from the 922-meV defect during the Zeeman experiment were quite poor, and it was not possible to obtain data of sufficient quality to determine the details of the magnetic behavior. In particular, it was not possible to use the anisotropic magnetic behavior as an independent check of the center symmetry.

From our uniaxial stress and Zeeman results, we feel confident that the center exhibits a pseudodonor behavior, with a tightly bound hole and effective-mass-like electron, at a site of monoclinic I symmetry in the crystal. The anisotropic magnetic-field behavior of the ZPL suggests that the angular momentum of the hole is not completely quenched, with some orbital character admixed into the wave function by the spin-orbit interaction.

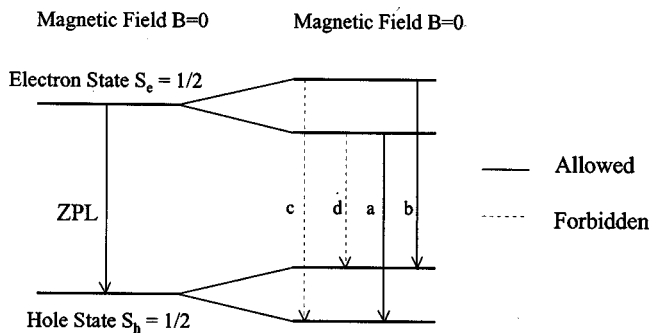


FIG. 5. Independent-particle model for singlet magnetic behavior of the 922-meV ZPL.

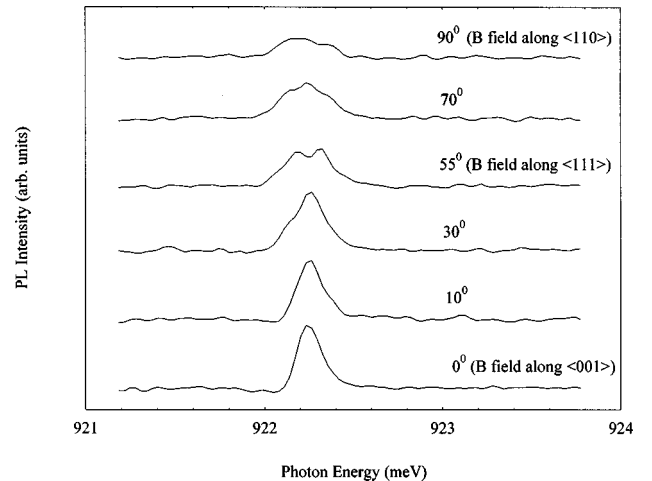


FIG. 6. Fine structure of the 922-meV ZPL as the $\langle 001 \rangle$ sample is rotated through 90° with respect to the magnetic field in the $\langle 110 \rangle$ plane.

TABLE II. Details of stress shift rates of 922- and 885-meV centers.

Stress shift rates (meV/GPa)	Stress shift rates	
	922-meV defect	885-meV defect
(001)	12.6	11.9
	-11.1	-13
(111)	17.5	16
	0.78	0
(110)	-19.1	-17.3
	6.66	7.9
	-3.47	-6
	-39.4	-40

C. Relationship between the 922-meV center and 885-meV center seen in FZ silicon

In a study of bound exciton luminescence at Al-related defects in electron-irradiated floating zone refined (FZ) silicon, Irion *et al.*¹⁸ reported a ZPL at 885 meV which they attributed, on the basis of annealing experiments and electron paramagnetic resonance measurements, to an Al_s-Al_i pair. Uniaxial stress measurements indicate that the defect has a monoclinic I symmetry, and Zeeman measurements indicate that the ZPL is a magnetic singlet, corresponding to the recombination of a spinlike electron with a spinlike hole which has a slight anisotropy in its g factor. The most interesting aspect of this defect from the point of view of this paper is the striking similarity of the behavior of the two ZPL's under both uniaxial and Zeeman perturbations. For stresses <120 MPa, the behaviors of the 922- and 885-meV defects are virtually identical. They show identical fan diagrams, and a fit of the data to a monoclinic I model gives virtually identical stress parameters. Irion *et al.*¹⁸ constrained their fit to have only three lines under the $\langle 110 \rangle$ axis, and so their published parameters differ from ours. However, if their data are used with the same unconstrained fit we used on our data, almost identical best-fit parameters are found. These data are summarized in Table II, where we list the line-shift rates of both centers under uniaxial stress. The shift rates for the centers are seen to be almost identical, and any differences can be related to the difficulties in precisely determining the shift rates of the 885-meV center from the published figure.¹⁸ The only difference between the two is that the dipole of the 885-meV transition is oriented differently from that of the 922-meV line, revealed by the differing line intensities of the stress-split components in the two defect systems. These authors also saw some evidence from temperature dependence data for the presence of an excited state ~ 3 meV above the 885-meV ZPL, and this is also seen in their high stress (>150 MPa) spectra. Finally, the Zeeman behaviors of both defects are virtually identical, showing magnetic singlet behavior and anisotropy in the g factor of the spinlike hole, although the more detailed Zeeman measurements on the 885-meV ZPL reveal evidence of a dynamic Jahn-Teller effect. Our Zeeman data on the 922-meV line has not been sufficiently well resolved to see such an effect (if it exists for this center).

The striking similarities in the behavior of the two defects argues strongly for a relationship between them. Such simi-

TABLE III. Details of some C-modified defects observed in Si.

Atomic species	Complex without C	C-modified complex	Change in ZPL	Reference
Be	1076 meV	1117 meV	41 meV	20, 21
Li	1044 meV	1082 meV	38 meV	19
Al	886 meV	922 meV	36 meV	5, 18

larities have been observed before for a number of complexes in silicon [such as Li and Be (Refs. 19–21)], and are interpreted in terms of a modification of the bare complex by the addition of a nearest-neighbor C atom, resulting in an increase in the ZPL energy of the C-modified defect of ~ 40 meV (see Table III). The fractional increase in ZPL energy of the 922-meV defect with respect to the 885-meV defect follows this trend very closely, and thus we feel quite confident that the 922-meV center is a C-modified version of the 885-meV center, composed of an Al_s-Al_i pair with a nearest-neighbor C_s atom, and this is in agreement with the original prediction of Drakeford and Lightowlers,⁵ which is discussed more fully in Sec. III D below. A possible atomic model for such a system, which has the appropriate symmetry, is shown in Fig. 7.

The addition of a C atom to all the above centers is seen to have the effect of increasing the ZPL line energy. Both the 922- and 885-meV centers display a pseudodonor type of structure, but in the absence of data on the excited-state structure of both systems we are unable to comment on the detailed effects of the carbon modification on the electron and hole electronic structures. We can, however, say that the effects on the ZPL of the nearest neighbor C are not due simply to the strain effects of the C atom, because the dipole moment of the transition is changed by the C modification (as noted above), which cannot be explained simply in terms of a strain effect on the 885-meV center.

D. Production mechanism of the 922-meV center

A tentative model for the creation of the 922-meV defect was given by Drakeford and Lightowlers,⁵ based on the circumstantial evidence associated with the relatively long annealing times at 450–550 °C. Such annealing times and temperatures are characteristic of the movement and aggregation

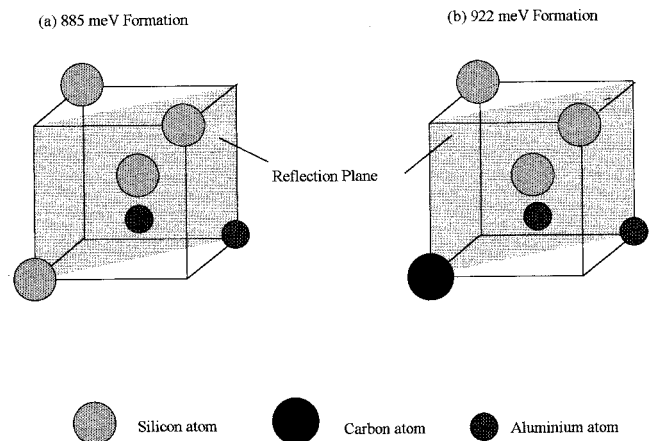


FIG. 7. Possible atomic models for 922- and 885-meV defects.

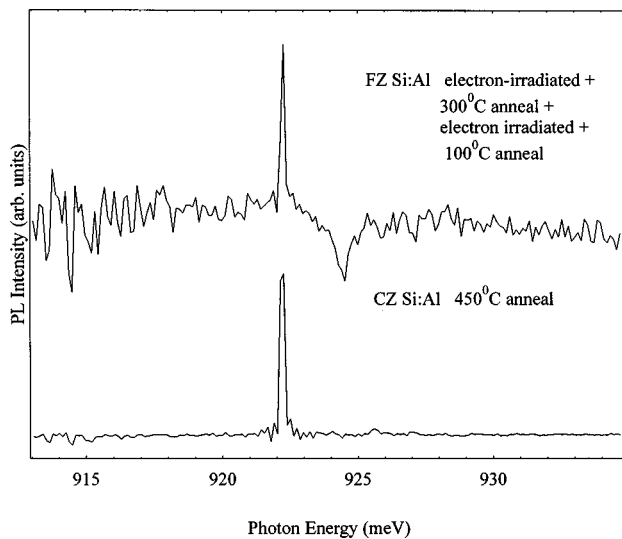


FIG. 8. Comparison of double-electron-irradiated FZ Si:Al with CZ Si:Al.

of oxygen in CZ silicon. The model put forward by these workers is as follows. As oxygen aggregates are formed in the silicon during the anneal, the associated strain is relieved by the release of silicon self-interstitials. These self-interstitials are then captured to release both substitutional C and Al into mobile interstitial sites, which are free to form complexes.

We have attempted to investigate the production mechanism of Drakeford and Lightowlers⁵ outlined in the paragraph above, and to establish more definitely the link with the 885-meV center. Specifically, it appears that there is no reason why the 922-meV defect cannot be created in oxygen-free FZ material, although it has never been observed in this material, as the role of the oxygen in CZ material is simply to provide a source of self-interstitials during the anneal. We have electron irradiated various samples of FZ-grown material with Al concentrations in the region of 10^{16} cm^{-3} , and C concentrations in the range $(0.7-2.3) \times 10^{16} \text{ cm}^{-3}$ in order to produce self-interstitials in the material, and to continue the production of the 922-meV defect from that point. In all cases the irradiation energy was 2 MeV, at a dose of $2 \times 10^{17} \text{ e/cm}^{-2}$.

Our first attempts to create the 922-meV defect in FZ material by means of a single electron irradiation and various anneals proved unsuccessful. We observed only the 885 defect, and saw no evidence of the 922-meV line. We have performed experiments using an initial electron irradiation and anneal at $\sim 300^\circ \text{C}$ for 3 h (Ref. 18) to create the 885-meV defect, followed by a second irradiation (and subsequent anneal) to create self-interstitials which are subse-

quently captured to release C interstitials. These C interstitials may then be captured by the 885-meV defect to form the 922-meV system. Figure 8 shows a spectrum of both CZ Si:Al annealed at 450°C for 400 h, and a FZ sample which has received this double irradiation treatment followed by an anneal at 100°C for 30 min. A weak line at 922.2(1) meV is seen in this sample, coincident with the Al-C 922-meV defect. This line is not seen in any samples which have not received the double-electron irradiation treatment. The signal levels associated with this line are too weak to allow us to identify it with complete certainty as the 922-meV Al-C defect, but we are nonetheless quite confident in this identification. Our future experiments will utilize samples with higher electron irradiation doses to enhance this signal, which will hopefully allow us to observe the 927-meV line, which we believe is due to an excited-state transition of the 922-meV Al-C system, and hence to identify this feature conclusively. Nonetheless, this result provides strong evidence in favor of the production mechanism proposed by Drakeford and Lightowlers.⁵

IV. SUMMARY

We have presented temperature dependence, uniaxial stress, and Zeeman data on the 922-meV defect observed in CZ Si:Al by Drakeford and Lightowlers.⁵ These measurements have enabled us to observe a thermalizing excited state $\sim 5 \text{ meV}$ above the main ZPL, and also to show that the 922-meV transition is due to the recombination of a pseudo-donor-type bound exciton at a site of monoclinic I symmetry in the crystal. Furthermore, we observe that the orbital angular momentum of the hole is incompletely quenched, resulting in an anisotropic fine structure in the Zeeman spectra. Comparison of these data with data on an Al pair defect with a ZPL at $\sim 885 \text{ meV}$ observed by Irion *et al.* reveals striking similarities between the two systems, leading us to assign the 922-meV defect as a C-modified version of the 885-meV system. Finally we have shown the possibility of producing the 922-meV system in FZ material by electron irradiation and annealing treatments, and this provides strong positive evidence for the production mechanism proposed by Drakeford and Lightowlers.⁵

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