Positron-annihilation investigation of vacancy agglomeration in electron-irradiated float-zone silicon

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Positron-annihilation experiments which combine lifetime and Doppler broadening measurements have been done on 10-MeV electron-irradiated float-zone silicon. After irradiation, a lifetime of 305 ps is observed at 300 K, decreasing to 290 ps at 30 K, and the positron trapping rate decreases strongly with increasing temperature. The Doppler measurements yield, when coupled with lifetime data, a defect S value 6.7% larger than that for the bulk which is nearly twice the value hitherto claimed for divacancies. Isochronal annealing of the 1.8-μm infrared absorption band is accompanied by a significant change in the defect S value to 3.8% larger than for the bulk. Surprisingly, the trapping rate at 50 K decreases only by 20% during the annealing out of the 1.8-μm infrared absorption, and the positron lifetime stays essentially constant. Loose vacancy complexes (a ''sponge'' defect) consisting of discernible monovacancies are suggested to be formed upon annealing as an intermediate step in the clustering of vacancies. [S0163-1829(96)04427-X]

INTRODUCTION

The purpose of this work is twofold. First we wish to establish the characteristic Doppler broadening line-shape parameter S for divacancies in silicon. Second, and perhaps more importantly, we wish to correlate the positron response with that of the 1.8-μm infrared-absorption band which is linked to the presence of divacancies. This turns out to be a complicated matter.

Three estimates have been reported for the divacancy Doppler broadening S parameter, all based on slow positron beam investigations. Mäkinen *et al.*[1] found saturation of the line-shape parameter corresponding to a 3.8% increase relative to the bulk value for an ion dose above 10^{15} Si/cm^2, while Nielsen *et al.*,[2] in a similar experiment, found a value of 4.6%. The first authors ascribe this increase to divacancies. More recently, Goldberg, Schultz, and Simpson[3] estimated 3.3% based on a proton irradiation experiment. Although the three sets of data agree fairly well, none of the experiments does, in fact, prove that the response originates from divacancies.

Here we have combined Doppler broadening and lifetime measurements to investigate 10-MeV electron-irradiated Fz-Si, creating defect concentrations much less than that necessary for saturating the Doppler parameter. Our experimental situation is therefore much different from those in the slow positron experiments.

EXPERIMENT

The samples were float-zone-refined silicon, undoped with a resistivity of 2000 Ω cm, and with an interstitial oxygen concentration below the infrared detection limit of a few times 10^{15}/cm^3. Irradiation was done using a 10-MeV pulsed electron beam (3-μs pulses and 240 pulses/s) to a total dose of 1.2×10^{18} e^-/cm^2 accumulated over a 12-h period. The sample block, of size $10\times10\times25$ mm^3, was irradiated along its long axis and cooled by immersion in running water at 8 °C. Samples were cut from the end facing the electron beam, and then etched in CP4, removing 0.2 mm of material.

The positron lifetime spectrometer had a time resolution of 190 ps, and the Doppler system an energy resolution of 1.2 keV. The Doppler S parameter was defined as the number of counts within the energy range 511 ± 0.7 keV divided by the number of counts in the whole of the bell-shaped spectrum within the range of 511 ± 4.8 keV. Background was stripped from the spectra, taking into account its change across the energy spectrum.

The positron source contribution, which is more important for the lifetime spectra, was minimized by the use of a very thin Al foil (0.8 μm) for source encapsulation, as well as by virtue of a source preparation technique which removes the usual ringlike buildup of source material.[4] The strength of the source was 12 μCi. The only source correction necessary was a 2%, 250-ps lifetime component which had a minuscule effect on the decomposition of the spectra. The lifetime spectra were repeated three times, each spectrum containing 3×10^6 counts, and Doppler spectra were repeated five times (each containing 2×10^6 counts in the 511 ± 4.8-keV energy range). Averaged values are given throughout this paper. The lifetime spectra were analyzed using the computer program ''RESOLUTION'' developed by Kirkegaard and Eldrup,[5] with a start-of-analysis point at 1% of the peak value of the lifetime spectra.

RESULTS

Values of S parameters are shown in Fig. 1 for both the unirradiated and the as-irradiated samples as a function of sample temperature. The unirradiated sample shows a weak temperature dependence which contrasts with the strong temperature dependence for the irradiated sample.

Experiments using the slow positron beam (operated at 30 keV) at the University of Western Ontario, Canada, on the same irradiated samples showed the same temperature dependency. This demonstrates that the response from our conventional positron source is the same as that obtained from slow (30-keV) positrons, which only probe a $\sim$3-μm deep

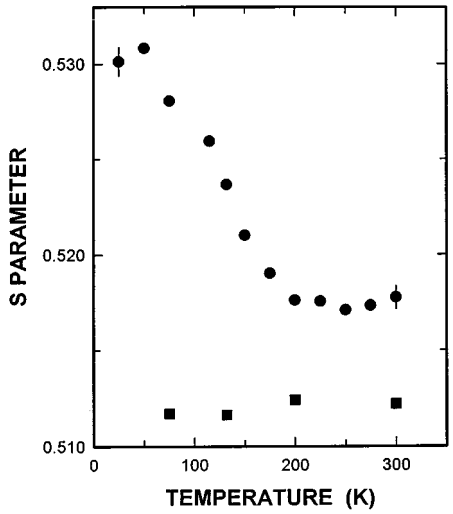

FIG. 1. Doppler S parameter for unirradiated (■) and as-irradiated (●) Fz-Si as a function of sample temperature.

layer as compared to our average 100-μm deep layer.[6]

The lifetime spectra for the same samples as used in the Doppler experiments could be resolved in two lifetime components in the case of the unirradiated sample. These components had values of 220 ps and 1.3 ns at 300 K, with intensities of 99.9% and 0.1%, respectively. The value of the dominating component is close to the bulk lifetime in silicon, albeit slightly larger by 2 ps. This indicates that some small amount of grown-in vacancies is present, but their contribution cannot be resolved. The 1.3-ns lifetime component is rather weak, which makes a physical interpretation difficult. We do mention, however, that its value changes systematically from 1.3 ns at 300 K to 0.65 ns at 30 K. This was found for both the unirradiated as well as for the as-irradiated samples.

For the irradiated sample it was necessary to do three-lifetime decompositions to fit the lifetime spectra adequately. Values of the additional lifetime are shown in Fig. 2, top panel. Its value is close to 305 ps at 300 K, decreasing to 290 ps at 30 K, and its intensity decreases strongly with increasing temperature as shown in the middle panel. The two other lifetime components were the 0.65–1.3-ns component unaltered from the unirradiated case, and a shorter-lived component ranging between 100 and 200 ps. This latter lifetime component was consistent with the simple trapping model,[7] thus allowing the calculation of the positron trapping rate for the defects which give rise to our lifetime component. This trapping rate is shown in the bottom panel of Fig. 2.

From the lifetime data one can determine the trapped fraction of positrons according to

$$\alpha=\kappa/(\kappa+\lambda_B). \tag{1}$$

Here κ is the trapping rate, and λ_B the annihilation rate of positrons in the bulk ($=1/0.218$ ns^{-1} at 300 K). This allows a calculation of S_D, the parameter characteristic of the defect responsible for the 305-ps lifetime component according to

$$S=(1-\alpha)S_B+\alpha S_D. \tag{2}$$

Because the experimentally obtained values of S are arbitrary by virtue of the arbitrary definition of S within the

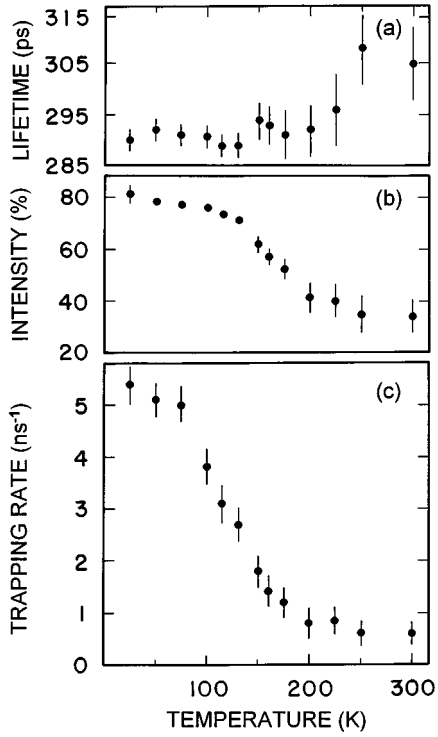

FIG. 2. Irradiation-produced positron lifetime (a), its intensity (b), and calculated trapping rate (c) as a function of sample temperature.

energy spectrum, only changes relative to S_B (the parameter characteristic of the bulk) are of physical importance. From Eq. (2) one obtains

$$S_D/S_B=(S/S_B+\alpha-1)/\alpha. \tag{3}$$

All quantities on the right-hand side of Eq. (3) are experimentally known in the present work, in contrast to the solitary Doppler experiments mentioned earlier,[1–3] where α was *assumed*—quite reasonably—to be 1 for high doses. Table I lists S_D/S_B values which prove essentially constant for large changes in the trapped fraction. This suggests, together with the near constancy of the defect lifetime, that a *single* type of defect is responsible for the trapping. This is most likely the divacancy in its singly negative state, as will be argued later in the discussion.

The irradiated sample was then isochronally annealed for 25 min at each temperature, following which lifetime and Doppler measurements were performed at 50 K. Figure 3 shows results for the defect lifetime (top panel) and the trapping rate, while the bottom panel shows the integrated absorption of the 1.8-μm infrared absorption band (obtained at 300 K). This absorption band arises, according to earlier works,[8,9] from divacancies in any of the charge states +, 0, and −, but not from the 2− charge state. Annealing of the positron trapping rate at 50 K deviates substantially from that of the infrared absorption, and the positron lifetime maintains a level close to 290 ps up to 515 °C, well beyond the temperature at which the infrared absorption has disappeared (one further annealing at 600 °C was conducted, and gave a lifetime of 365±20 ps).

The corresponding Doppler broadening parameters S_D/S_B as calculated from Eq. (3), are shown in Fig. 4. S_D/S_B de-

TABLE I. Trapped fraction α as calculated from the lifetime data and S_D/S_B values for various temperatures of the irradiated sample. Average value of S_D/S_B is 1.067 ± 0.002 when omitting data for the two highest sample temperatures because of the low-α values which could be influenced by additional defects.

Sample temperature (K)	Trapped fraction α	S_D/S_B
25	0.54	1.067
50	0.53	1.072
75	0.52	1.061
115	0.40	1.069
132	0.37	1.063
150	0.28	1.063
175	0.21	1.066
200	0.15	1.073
225	0.16	1.067
250	0.12	1.079
300	0.12	1.088

creases in the same temperature range as did the infrared absorption, attaining a nearly constant level of 1.038 above 300 °C. At temperatures above 500 °C the calculation of S_D/S_B becomes quite uncertain due to small values of the trapping rate.

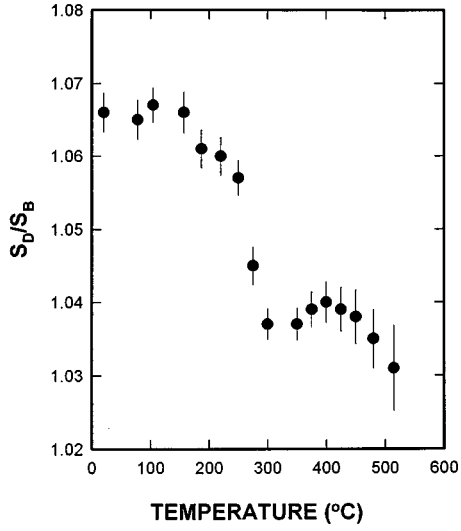

FIG. 4. Defect specific S_D/S_B as measured at 50 K for the isochronally annealed irradiated sample.

A temperature scan of the samples after annealing to 400 °C was done in order to compare with that for the as-irradiated sample. As shown in Fig. 5 the defect lifetime increases much more strongly with temperature than in the as-irradiated case. The trapping rate is still strongly tempera-

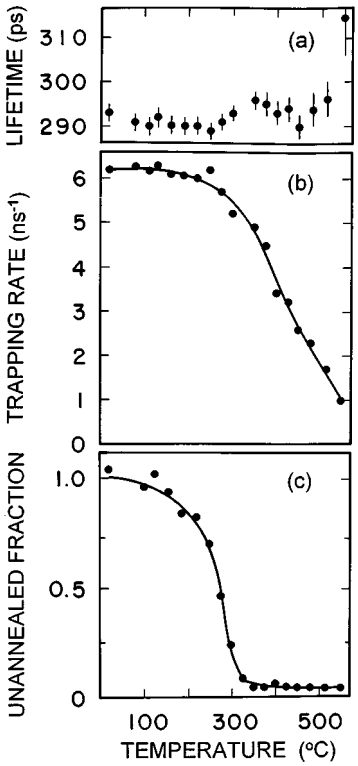

FIG. 3. Isochronal annealing data of an irradiated sample. In panel (a) is shown the irradiation-produced positron lifetime, and in (b) the trapping rate both for a sample temperature of 50 K. In panel (c) the normalized integrated (between 1.63 and 1.98 μm) infrared absorption is shown as measured at 300 K.

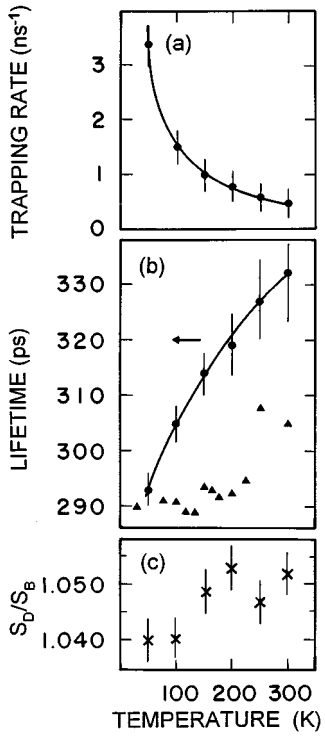

FIG. 5. Temperature scan of the irradiated sample isochronally annealed to 400 °C. In panel (a) the trapping rate is shown. In panel (b) the lifetimes after annealing (●) and before annealing (▲) are shown to facilitate direct comparison. In panel (c), S_D/S_B data are shown for this sample.

ture dependent, and S_D/S_B shows some (but not a dramatic) temperature dependence. It is clear that annealing has indeed modified the structure of the defects.

DISCUSSION

The most likely defect type detected by the positrons in the as-irradiated sample is the divacancy. Monovacancies can be ruled out because (1) they are mobile well below room temperature, and (2) impurities which could trap monovacancies are too low in concentration to cause detection of possible impurity-monovacancy complexes by the positrons.

The positron lifetime of 290 ps (for $T \leqslant 200$ K) is indicative of trapping by divacancies.[10,11] The slightly larger value of 305 ps at 250 and 300 K might arise from a small admixture of longer lifetimes stemming from larger vacancy clusters whose contribution becomes perceptible when the divacancy trapping rate is low. The increase in S_D/S_B at 250 and 300 K (see Table I) supports this interpretation. The concentration of divacancies resulting from the dose of 1.2×10^{18} e^-/cm^2 agrees qualitatively with that estimated from the introduction rate of divacancies according to Corbett and Watkins.[12] The current results, together with the specific trapping rate for singly negative charged divacancies suggested by Mascher, Dannefaer, and Kerr,[13] yields a concentration of about $1.5\times10^{17}/\mathrm{cm}^3$, while a more recent estimate of the specific trapping rate by Kawasuso *et al.*[14] results in a smaller concentration, $0.6\times10^{17}/\mathrm{cm}^3$. For comparison, the introduction rate of Corbett and Watkins[12] (albeit for positively charged divacancies) suggests a concentration of $0.4\times10^{17}/\mathrm{cm}^3$. Kawasuso *et al.*[15] have furthermore found from isothermal annealing of their $\simeq$300-ps lifetime an activation energy of 1.3 eV, in good agreement with the divacancy interpretation based on earlier infrared[9] and electron paramagnetic resonance measurements.[12]

The next point to consider is the charge state of the divacancies. The strongly temperature-dependent trapping rate, as depicted in Figs. 2 and 5, is commonly taken as evidence of a negative charge of the defect,[13,16] but recently, Kawasuso *et al.*[11] have suggested a similar behavior for neutral divacancies. From a theoretical point of view it is difficult to understand how a neutral defect can behave as a negatively charged defect because the former lacks the attractive long-range Coulomb potential. We do also point out that Kawasuso *et al.*[11] assessed the charge state of the divacancies using the electronic level deduced from deep-level-transient spectroscopy,[17] which places the $0/-$ level at $E_C-0.4$ eV, where E_C denotes the bottom of the conduction band. Had the lower level of $E_C-0.54$ eV instead been used as deduced by Young and Corelli,[18] this would have led to the conclusion of a negative charge. In view of the above reservations, we maintain that the strong temperature dependence of the trapping rate indicates negatively charged divacancies. Since the doubly negative charged divacancy does not give rise to the 1.8-μm absorption band,[8] it is most likely that the divacancies observed in this work are singly negative.

In summary, the above discussion strongly suggests that in our samples 10-MeV electron irradiation introduced divacancies. The positron lifetime of 290 ps and the 1.8-μm absorption band are the main indicators therefore and, according to Table I, the line-shape parameter is 6.7% larger than that for the bulk. This value is nearly twice the value hitherto estimated from the solitary Doppler experiments.[1–3] A possible explanation for this discrepancy will be offered after discussing the implications of our annealing data.

These data exhibit three unexpected features. (1) By associating the 290-ps lifetime component with divacancies, one would expect that the trapping rate should anneal in the same manner as does the 1.8-μm infrared-absorption band, but this is clearly not the case (see Fig. 3). (2) Upon annealing above 150 °C one would expect vacancy agglomeration arising from migration of divacancies, and hence an increase in lifetime. There is no indication for this according to Fig. 3, at least up to an annealing temperature of 515 °C. (3) Vacancy agglomeration would be expected to increase the value of S_D/S_B, but a decrease is in fact observed (see Fig. 4).

We suggest the following tentative defect model to explain these observations: Upon annealing above $\sim$150 °C, migrating divacancies form clusters, but they are initially ''loose'' in the sense that the individual vacancies have not coalesced completely. Only at sufficiently high temperature does final coalescense take place, to form a continuous multivacancy complex. The disappearance of the 1.8-μm absorption band, we then suggest, is a consequence of a significant distortion of the divacancy when becoming part of the loose cluster, perhaps to the degree that in such a cluster vacancies should rather be viewed as an assembly of individual monovacancies. The S_D/S_B data in Fig. 4 lend support to this suggestion, because a change from isolated divacancies to a loose cluster of monovacancies would decrease rather than increase S_D/S_B. This interpretation implies that the value of 1.038 for S_D/S_B might be comparable to that for monovacancies. The idea of a loose cluster of monovacancies (a ''sponge'' defect) was originally proposed by Hornstra[19] and discussed by Corbett and Bourgoin.[20]

For such a loose vacancy cluster one would expect the sample temperature to have a stronger influence on positron parameters than for a divacancy. This is observed (see Fig. 5). The positron lifetime and S_D/S_B increase substantially with temperature, in contrast to the case of the divacancy. It should be noted that, as judged from the trend of lifetime with temperature, a lower sample temperature than 50 K would have produced a lifetime *less* than that for the divacancy, which supports the idea of a monovacancy constituent of the cluster. Whether the change in lifetime is a result of a temperature-dependent configuration of the clusters or arises from a change in the localization of the positron within the cluster is not clear, although we do hold the latter possibility more likely than the former. Finally, we note that annealing at 550 °C results in a lifetime of 315 ps at 50 K (at 600 °C the lifetime was 365 ps, and independent of measurement temperature). This suggests that above $\sim$500 °C final coalescing of the loose vacancy clusters takes place.

Above we have presented a model which can explain the experimental results, but one item has not been discussed so far, namely the mechanism(s) by which the trapping rate decreases over the very wide temperature range of 150–550 °C. We have argued that the disappearance in the 150–300 °C range of the infrared-absorption band is due to coalescing of vacancies. This could well account for the rather small decrease in trapping rate of 20%. But when the coa-

lescing has been completed, long-range migration of vacancies seems unlikely, which then raises the question why the trapping rate continues to decrease. Three possibilities present themselves. The first invokes a release of the irradiation-produced interstitials from (unspecified) traps, whereupon the overall vacancy concentration would decrease. The second possibility is a gradual change in the charge state of the clusters. The third possibility is that even without a change in charge state a small binding energy for the positron could change slightly. This latter possibility presupposes that the clusters are negatively charged, for which there is a definite indication by virtue of the strongly temperature-dependent trapping rate shown in Fig. 5. Any of these possibilities could be invoked to explain the decrease in the trapping rate.

In closing this discussion, we return to the discrepancy between the here-advocated S_D/S_B value for divacancies of 1.067, and that suggested from the beam-based Doppler broadening experiments of 1.033–1.046.[1–3] This we suggest to arise from different irradiation conditions, (rather than from equipment differences, see Ref. 6) because in the beam-based Doppler experiments the defects were created by ion (or proton) irradiation to a concentration at least 100 times that utilized in our work. This could create many vacancy clusters of the type proposed here, so that the results from the beam-based Doppler experiments should rather be compared with our values obtained after annealing above 300 °C, in which case we obtain a remarkably good numerical agreement.

CONCLUSION

This work has reaffirmed the lifetime value of 290 ± 5 ps for isolated singly negative divacancies in silicon, and the Doppler parameter S_D/S_B was found to have a value of 1.067 ± 0.002. Annealing between 150 and 300 °C is proposed to create loose multivacancy complexes in which the positron can be localized at low temperatures in the monovacancy part. Upon this annealing, the 1.8-μm infrared-absorption band vanishes, and the value of S_D/S_B decreases to 1.038 ± 0.003. Annealing above $\simeq$515 °C is necessary for the formation of actual vacancy clusters.

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[1] J. Mäkinen, E. Punkka, A. Vehanen, P. Hautojärvi, J. Keinonen, M. Hautala, and E. Rauhala, J. Appl. Phys. **67**, 990 (1990).

[2] B. Nielsen, O. W. Holland, T. C. Leung, and K. G. Lynn, J. Appl. Phys. **74**, 1636 (1993).

[3] R. D. Goldberg, P. J. Schultz, and P. J. Simpson, Appl. Surf. Sci. **85**, 287 (1995).

[4] In this technique the original aqueous 100-μCi ^{22}NaCl solution is first dried out completely in the supplied vial having a conically shaped bottom. Then, using a micropipet, five microliters of water is added to form a highly concentrated solution which is then deposited on the source envelope material. Usually two drops ($\sim$0.5 microliters) are sufficient to produce a 10-μCi source which dries forming an evenly distributed layer of ^{22}NaCl with a diameter close to 1 mm. 80% of active material in the vial can be retrieved in this manner.

[5] P. Kirkegaard, N. J. Pedersen, and M. Eldrup, PATFIT-88, Risø-M-2740 (Risø, DK-4000 Roskilde, Denmark).

[6] The beam investigation was done with a Doppler spectrometer with a resolution of 1.5 keV, whereas ours had 1.2 keV. This raises the question of systematic resolution-induced effects. From computer simulations we have found that although S itself decreases significantly with increasing width of the resolution function, *relative* changes in S are decreased by only $\sim$5% upon a change from 1.2 to 1.5 keV in the spectrometer resolution.

[7] R. N. West, Adv. Phys. **22**, 263 (1973).

[8] H. Y. Fan and A. K. Ramdas, J. Appl. Phys. **30**, 1127 (1959).

[9] L. J. Cheng, J. C. Corelli, J. W. Corbett, and G. D. Watkins, Phys. Rev. **152**, 761 (1966).

[10] S. Dannefaer, G. W. Dean, D. P. Kerr, and B. G. Hogg, Phys. Rev. B **7**, 2709 (1976).

[11] A. Kawasuso, M. Hasagawa, M. Suezawa, S. Yamaguchi, and K. Sumino, Hyperfine Interact. **84**, 397 (1994).

[12] J. W. Corbett and G. D. Watkins, Phys. Rev. **138A**, 555 (1965).

[13] P. Mascher, S. Dannefaer, and D. Kerr, Phys. Rev. B **40**, 11 764 (1989).

[14] A. Kawasuso, M. Hasagawa, M. Suezawa, S. Yamaguchi, and K. Sumino, Jpn. J. Appl. Phys. **34**, 2197 (1995).

[15] A. Kawasuso, M. Hasagawa, M. Suezawa, S. Yamaguchi, and K. Sumino, Appl. Surf. Sci. **85**, 280 (1995).

[16] M. J. Puska, C. Corbel, and R. M. Nieminen, Phys. Rev. B **41**, 9980 (1990).

[17] A. O. Evwaraye and E. Sun, J. Appl. Phys. **47**, 3776 (1976).

[18] R. C. Young and J. C. Corelli, Phys. Rev. B **5**, 1455 (1972).

[19] J. Hornstra, Philips Research Laboratory Report No. 3497, 1959 (unpublished).

[20] J. W. Corbett and J. C. Bourgoin, in *Point Defects in Solids*, edited by J. H. Crawford, Jr. and L. M. Slifkin (Plenum, New York, 1975), Vol. 2, pp. 8 and 9.