

## Aspects of the Defect Reactions Related to Carbon Impurity in Silicon

C. A. LONDOS

Physics Department, Solid State Section, University of Athens,  
104, Solonos Street, Athens 106 80, Greece

(Received May 9, 1988; accepted for publication July 23, 1988)

Deep-level transient spectroscopy (DLTS) measurements are reported for the well-studied carbon (C) and oxygen (O) related centers with activation energy around  $E_v + 0.36$  eV in irradiated p-Si. Comparisons of the concentrations of this defect state with those of the carbon interstitial (C<sub>i</sub>) defect state in pulled and float-zone material have been considered. The results yield some new insight concerning the C<sub>i</sub> involvement in reactions with primary defects and other impurities a) during and after low-temperature irradiation and b) after annealing around room temperature.

**KEYWORDS:** silicon, lattice, point defects, impurities, reactions, electron irradiation, DLTS (deep-level transient spectroscopy), C interstitial, C interstitial-C substitutional pair

### §1. Introduction

The two primary defects produced in Si by 1.5-MeV electron irradiation at 80 K are the isolated lattice vacancies (V) and self-interstitials (Si<sub>i</sub>). The V and the Si<sub>i</sub> which survive the recombination participate in various reactions forming secondary defects. In p-Si, V becomes mobile at ~150 K and combines with another V to form divacancies (V<sub>2</sub>), with O to form (O+V) pairs, with acceptor impurities (A) (where A stands for B, Al, ...) to form (A+V) associates. Si<sub>i</sub> has so far eluded direct experimental detection. However, it is well known that in p-Si, Si<sub>i</sub> is very mobile even at low temperatures and is selectively trapped by acceptor impurities with which it exchanges sites.<sup>1)</sup> This process, known as the Watkins replacement mechanism, is also valid between substitutional carbon atoms (C<sub>s</sub>) and Si<sub>i</sub> leading to the formation of the bonded C<sub>i</sub>.<sup>2)</sup> The latter defect<sup>3-5)</sup> gives a donor level at  $-E_v + 0.30$  eV and an acceptor level appearing only in n-Si at  $-E_c - 0.12$  eV. Interactions of Si<sub>i</sub> with O and the production of divacancy defects with adjacent Si<sub>i</sub> have also been proposed.<sup>6-8)</sup>

Near room temperature, C<sub>i</sub> begins to migrate. Among a variety of reactions in which C<sub>i</sub> participates the most dominant are with C<sub>s</sub>,<sup>3)</sup> O<sub>i</sub><sup>9)</sup> and (O+V)<sup>10)</sup> pairs. In this work, we have employed the unique performances of the DLTS technique to investigate possible interactions of C<sub>i</sub> with other defects at low temperatures and at room temperature after annealing.

### §2. Experimental

The Schottky diodes used in this study were fabricated by evaporation of aluminum on boron-doped, float-zone ( $\rho = 6.4-7.4 \Omega \cdot \text{cm}$ ) and pulled ( $\rho = 3-50 \Omega \cdot \text{cm}$ ) p-type Si wafers. The carbon concentration was  $2.5 \times 10^{16}$  atoms/cm<sup>3</sup> in both materials. Irradiations were performed *in situ* at 80 K with 1.5 MeV electrons from a Van der Graaf accelerator. The dosage was about  $2 \times 10^{16} e^-/\text{cm}^2$ . The measurements were carried out by a standard box-car spectrometer.<sup>11)</sup> They were performed at 5 V reverse bias and 5.7 V filling pulse amplitude to

eliminate the built-in voltage of the junctions.

Activation energies reported here were determined from Arrhenius plots ( $\log_{10} e_p/T^2$  versus  $1/T$ ) without allowing for the electric field effect or the temperature dependence of the capture cross sections on the thermal emission of the traps.

### §3. Results and Discussion

Figure 1 (solid curve) shows the majority of the DLTS spectrum of the float-zone Si after annealing at 315 K for 5 hours. The dotted curve depicts the C<sub>i</sub> peak immediately after the 80 K irradiation. Figure 2 is the corresponding diagram of Fig. 1 for the pulled material. Each peak is labelled with the letter H (for holes) and a number in brackets expressing the activation energy from the valence band.

Identification of the defect states was done on the basis of the energy positions in the gap, the introduction rates, the thermal stabilities and comparisons with previous assignments in the literature.<sup>3-5,10)</sup> Thus, peak H<sub>1</sub> in both figures is possibly related to V<sub>2</sub>. It is created during irradiation and increases its amplitude when V migrates. The level around  $E_v + 0.23$  eV was correlated<sup>3)</sup> with the positive charge state of V<sub>2</sub> in p-type Si. However, the measured activation energy from our experiments was systematically smaller than the above value. This fact might be taken as an indication that V<sub>2</sub> created by irradiation at low temperatures presumably traps some self-interstitials which in turn change its electronic state. In that case, peak H<sub>1</sub> may not arise from exactly the same defect structure in the two materials. This means that the measured equal activation energies in the float-zone and pulled Si may be accidental within the experimental errors. These ideas should also be considered when attempting to explain the observed differences in the line shape of the V<sub>2</sub> between the two materials.

Peak H<sub>2</sub> in both figures represents C<sub>i</sub>. It appears immediately after irradiation and begins to anneal out at around room temperature. The decay of the C<sub>i</sub> signal is accompanied by the concomitant growth of the H<sub>3</sub>(0.34) peak in the float-zone and the H<sub>3</sub>(0.37) peak in

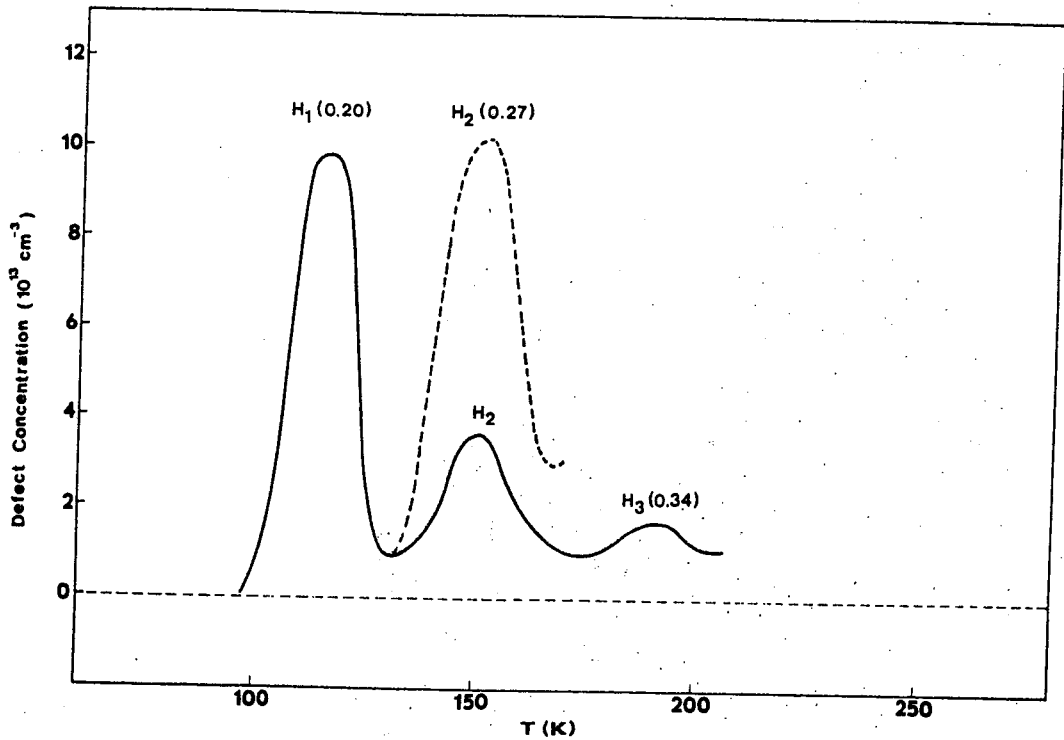


Fig. 1. The DLTS spectrum of float-zone Si irradiated at 80 K after annealing at 315 K for 5 hours (solid curve). The dashed curve depicts the  $C_1$  peak evoked immediately after the irradiation ( $e_p = 40 \text{ s}^{-1}$ ).

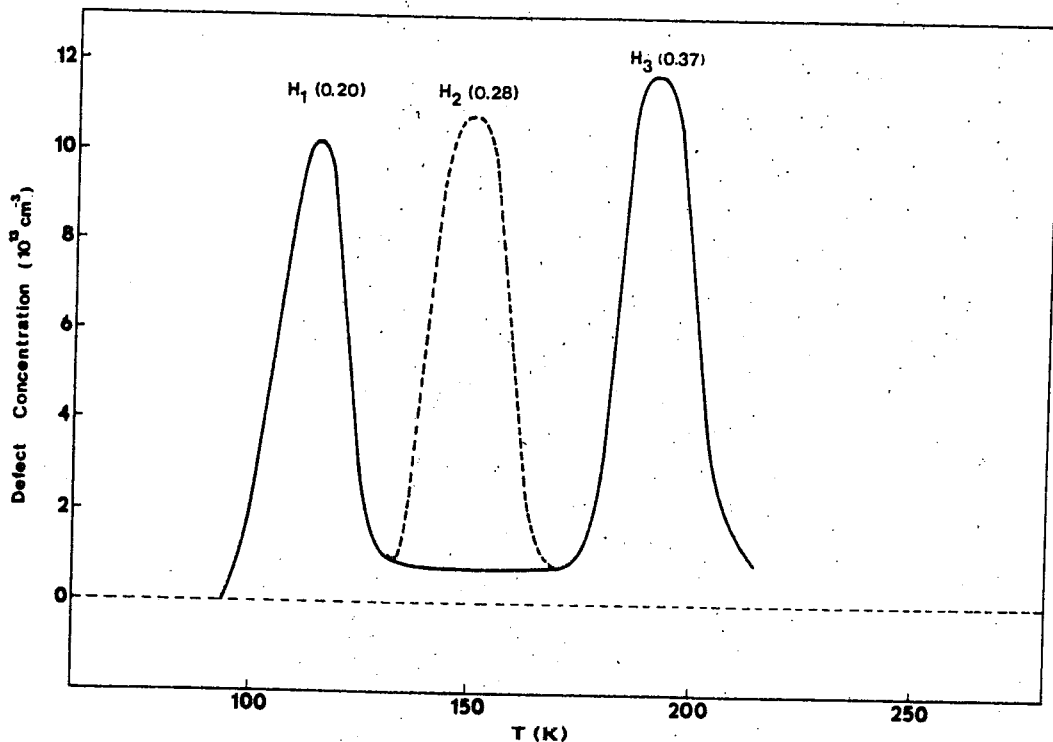


Fig. 2. The DLTS spectrum of pulled Si irradiated at 80 K after annealing at 315 K for 5 hours (solid curve). The dashed curve depicts the  $C_1$  peak evoked immediately after the irradiation ( $e_p = 40 \text{ s}^{-1}$ ).

the pulled Si. Therefore, in a preliminary assignment we could tentatively correlate peak  $H_3$  in both materials with a C-related centre. The observed faster disappearance of the  $C_1$  signal in the pulled material spectrum is consistent with its larger O content which could provide an increased number of trapping sites for the migrating  $C_1$  in

the Si network.<sup>12)</sup>

Comparing the peak amplitudes of  $H_2$  and  $H_3$ , it is obvious that the concentration of the C-related center in the float-zone Si is smaller than the decrease of the concentration of the  $C_1$ . In the pulled material, however, where the  $C_1$  signal completely disappears with the annealing, the

concentration of the  $H_3(0.37)$  peak is larger than that of the  $H_2(0.28)$  peak. We shall discuss the two Si materials separately.

### 3.1 $C_i$ -interactions in float-zone Si

In this case, since the emergence of  $H_3$  is simultaneous with the decay of  $H_2$ , we can assume that the  $C_i$  are not totally converted to the C-related centre. In other words, it is possible that part of the  $C_i$ 's join some unknown defect<sup>9</sup> which are presumably electrically neutral and thus elude detection by DLTS. Our observations are also consistent with IR studies which concluded<sup>13</sup> that a small fraction of the  $C_i$  defects must be lost at other traps.

Prior to any discussion of this matter, we shall focus our attention on the observed decrease of the linewidth of  $H_2$  after annealing (Fig. 1). One may presume that two defect states contribute to the creation of peak  $H_2$ , one of which anneals out earlier than the other. However, such a conclusion is not supported by the facts. A capture cross-section analysis with the pulse-width variation method<sup>11</sup> gave only one branch in the plot of  $\log(S_0 - S)$  vs  $t_p$  ( $S$  is the DLTS output for a pulse-width  $t_p$ , and  $S_0$ , the saturated DLTS output for large pulse durations) indicating that only one defect contributes to the creation of  $H_2$ . Furthermore, the appearance of the transient from peak  $H_2$  in the screen of a very sensitive oscilloscope does not give the impression, as far as we can say, of a nonexponential one. During preliminary characterization of the samples prior to irradiation, the DLTS spectra were almost ideal showing almost no features, especially in the temperature region where the  $C_i$  signal appears. Additionally,  $C_i$  is a well-known defect and nowhere in the literature has any other defect been reported under the same conditions of irradiation, giving rise to a level in the same position in the gap.

Immediately after the irradiation a very strong peak appears in the spectra. This peak could be partially seen even with the two fastest available rate windows of  $1000\text{ s}^{-1}$  and  $2500\text{ s}^{-1}$ . The minimum temperature possible to achieve with our equipment prevented the determination of the energy level of the defect. The peak began to decay from  $\sim 160\text{ K}$  onwards. The decrease in the amplitude was accompanied by the increase of the amplitude of the  $V_2$ -related peak and the emergence of other peaks attributed to the  $(O+V)$  and the  $(B_s+V)$ <sup>14</sup> pairs. We have tentatively identified it as arising from the  $E_v + 0.13\text{ eV}$  level of the vacancy. However, it has been shown<sup>15</sup> that the  $V$  is a negative-U system and the signal related to its level is due to the simultaneous emission of two holes, thus it is twice the normal amplitude. Therefore, its real concentration is half the normally<sup>11</sup> calculated concentration. We found that this initial concentration of the  $V$  is larger than the sum of the concentrations of the  $V$ -related centers ( $V_2$ ,  $O+V$ ,  $B_s+V$ ) created after its migration. Thus, some of the vacancies should be trapped elsewhere. A possible candidate is carbon. Since  $C_i$  are immobile at low temperatures, a carbon-vacancy pairing would result from the migration of the  $V$ . Although this process is expected to appear in the spectra as a certain decrease of the amplitude of the  $C_i$  peak, such an effect was not observed here.  $(C+V)$  pairs could also be

formed at high temperatures. The possibility of a mobile  $C_i$  to combine with  $V_2$  has been previously considered and rejected on the grounds of Coulombic repulsion, since  $C_i$  and  $V_2$  are both in the positive charge state. However, there are indications that the divacancy may be highly distorted,<sup>16</sup> and thus the Coulombic factor in pairing with other defects is not as significant. We should note that in our experiments no changes of the  $V_2$  signal were observed during annealing of the  $C_i$ . Obviously, the creation of an electrically inactive center comprising  $C$  and  $V$  would also be consistent with the results in pulled Si where the formation of such a pair is expected to be suppressed by the competitive presence of oxygen in trapping the vacancies. The possible trapping of  $C_i$  from boron atoms, preferentially of the interstitial-type which are mobile below room temperature,<sup>17</sup> cannot be ruled out.

It is worth noting the interesting suggestion that small dislocation loops<sup>18</sup> created by the irradiation could act as sinks for the  $C_i$ . It is also possible that when the  $C_i$ -Si bond is breaking up at around room temperature, a small fraction of the liberated  $C_i$  is repositioned at the substitutional sites. This idea has been tested by infrared absorption studies with negative results.<sup>6</sup> From photoluminescence and absorption studies a conversion of the  $C_i$ -Si configuration to a  $C_s$ -Si configuration during annealing has also been postulated.<sup>19</sup>

### 3.2 $C_i$ -interactions in pulled Si

In this case, we have the seemingly contradictory results that the final number of  $C_i$  atoms is larger than the initial number measured prior to annealing. Thus, the question of where these excess  $C_i$ 's come from immediately arises. In the following, a number of possible causes will be discussed in an attempt to interpret the observed phenomenon.

#### 3.2.1 $C_i$ -related complexes

According to this model, an electrically neutral carbon-related complex forming at low temperatures breaks up at around room temperature and the liberated  $C_i$  contribute to the formation of the  $H_3$  peak. A reasonable candidate would again be the  $(C+V)$  pair. Previously we had minimized the possibility of its formation from processes involving the migration of  $V$  or  $C_i$ . In the context of the present interpretation, we consider the creation of a different kind of  $(C+V)$  pair produced during irradiation. It is possible that a number of vacancies created during the primary radiation damage are able to carry out enough jumps to reach the  $C_i$ . It is also possible that some of the initial  $Si_i$  may not have sufficient energy to eject carbon atoms to interstitial sites. In these cases<sup>20</sup> the replacement process is not efficient enough and  $(C+V)$  pairs may be formed. Obviously, the above creation mechanism of the  $(C+V)$  defect is also possible in the float-zone grown Si. However, the liberation of  $C_i$  from the presumable dissociation of the  $(C+V)$  pairs could not be seen in the DLTS spectrum of this material, since  $C_i$ 's prefer being captured by unknown defects.

Another complex consistent with the discussed model is the carbon-oxygen pair. Absorption bands observed at  $922$  and  $932\text{ cm}^{-1}$  after low temperature irradiation were

ascribed to the vibrations of the (C+O) defect centers<sup>21)</sup> which are unstable at room temperature.

### 3.2.2 Si-related complexes

The formation of the short-lived, fast-diffusing metastable defect configurations in low-temperature irradiated Si was put forward previously.<sup>22)</sup> Based on this information, we believe that Si interstitials released by dissociation of some defects could interact with carbon atoms in normal lattice sites to provide the excess carbon interstitials. This idea has also been proposed previously<sup>23)</sup> to account for the increase in the strength of the C(1) band, attributed to  $C_i$ , in n-type Si around 200 K. One possible defect is that comprising a silicon interstitial trapped by an interstitial oxygen atom.<sup>6)</sup> It is also known<sup>7)</sup> that mobile Si interstitials can be captured by divacancies which are formed by the direct radiation process when the energy of the incident electrons is in excess of some threshold value. It has been found<sup>7)</sup> that a fraction of these divacancy-Si interstitial complexes anneal below room temperature. A model invoking metastable vacancy-interstitial pairs<sup>24)</sup> has also been proposed and successfully used to explain the irradiation temperature dependence of some defects. However, preliminary annealing studies of the  $C_i$  at temperatures up to 260 K have not revealed any growth of the corresponding DLTS signal.

### 3.2.3 $C_i$ at electrically neutral configuration

The  $E_c - 0.12$  eV level of the  $C_i$  in n-type Si is not observed after the low-temperature irradiation<sup>4)</sup> but at higher temperatures without complementary changes of the peaks in the DLTS spectrum to be detected. Growth stages for this level below room temperature have also been reported.<sup>7)</sup> Kimerling, based on the Jackson model,<sup>25)</sup> has postulated that a certain fraction of the  $C_i$  are locked in the silicon lattice in an electrically inactive configuration. Presumably, the associated defect state is pushed outside the energy gap. At higher temperatures these interstitials convert back to normal and the concentration of the  $C_i$  increases. Changes of the configuration of the  $C_i$  have also been proposed in another case to account for its annealing behaviour. Localized vibrational mode (LVM) spectroscopy studies<sup>23)</sup> show that a centre, labelled C(2) and tentatively attributed to the  $C_i$  in  $T_d$  symmetry, is produced immediately after the C(1) centre assigned to the normal interstitial in  $C_3v$  symmetry starts to decay. Based on the above considerations, we would suggest that a small fraction of the  $C_i$  created by the irradiation forms an electrically neutral configuration which, at around room temperature, transforms to the normal one contributing to a further increase of the amplitude of the  $H_3$  peak. It should be remembered that infrared absorption studies<sup>26)</sup> on high-dose electron irradiated Si at room temperature have shown that the removal of carbon atoms from normal lattice sites is not exactly correlated with the formation of the other observed C-related defects. This then leads to the question of the destination of the carbon.

A capture cross-section analysis gave two branches, and consequently, two capture cross sections ( $\sigma_1 = 1.2 \times 10^{-16}$  cm<sup>2</sup>,  $\sigma_2 = 5 \times 10^{-18}$  cm<sup>2</sup>) for the peak  $H_3(0.37)$  in the pulled material and one branch giving

( $\sigma = 5 \times 10^{-18}$  cm<sup>2</sup>) for the peak  $H_3(0.34)$  in the float-zone Si. These results are consistent with the aforementioned models. Since  $C_s$  is the main trap for the mobile  $C_i$ , we believe that the center with the capture cross section  $5 \times 10^{-18}$  cm<sup>2</sup>, present in both Si materials, is the  $C_i-C_s$  pair. In the float-zone material, some of the  $C_i$ 's are lost to unknown traps. In the pulled material, there is a competition between oxygen and the unknown traps for capturing the  $C_i$  where oxygen prevails. Consequently,  $(C_i+O_i)$  or  $(C+O+V)$  complexes are formed giving the corresponding  $\sigma_1 = 2 \times 10^{-16}$  cm<sup>2</sup> branch. We shall see in the next paragraph that the validity of these correlations has recently been in doubt.

### 3.2.4 One of the defects giving the $E_v + 0.37$ eV level does not contain C

Lately, experiments performed on electron-irradiated n-Si<sup>27)</sup> have revealed that the  $C_i-C_s$  pair is a bistable defect with two configurations and two corresponding levels,  $E_c - 0.10$  eV and  $E_c - 0.17$  eV. In p-Si,<sup>28)</sup> only one configuration of the above defects has been seen by DLTS giving a donor level at  $E_v + 0.09$  eV, in agreement with previous assignments.<sup>29)</sup> Obviously, the correlation<sup>3)</sup> of the  $E_v + 0.33$  eV with the  $C_i-C_s$  pair is seriously challenged. Furthermore, recent measurements<sup>30)</sup> have concluded that the G15 electron paramagnetic resonance spectrum associated with the (C+O+V) center,<sup>31)</sup> the 0.97 eV photoluminescence line, the C(3) infrared absorption band and the DLTS level at  $E_v + 0.38$  eV have a common origin, the  $C_i-O_i$  pair. Thus, based on the above information, only the  $C_i-O_i$  defect could be considered to contribute to the DLTS peak  $H_3$  with  $E_v + 0.37$  eV energy. The nature of the second component of  $H_3$  is not certain. Nevertheless,  $H_3$  appears to grow in our spectra simultaneously with the  $C_i$  decay. It might be argued that C only indirectly helps the formation of the second component of the  $H_3$  peak by participating in some intermediate reactions but is not involved in its structure. A (partial) chemical identification would refer to the second component of  $H_3$  as an oxygen-related, carbon-dependent centre.

## §4. Conclusions

Irrespective of the fine detail and the operative mechanism which governs the movement of C atoms through the Si network, our data indicate that the interaction of the C impurity with other defects in the Si lattice might be much more complicated than previously thought. Carbon follows different and more intricate reaction patterns in the oxygen-rich Si material than in the oxygen-lean Si material. The complete understanding of the carbon interplay with other defects in Si requires further investigation with a combination of experimental techniques.

## References

- 1) G. D. Watkins: Phys. Rev. **B12** (1975) 5824.
- 2) G. D. Watkins and K. L. Brower: Phys. Rev. Lett. **36** (1976) 1329.
- 3) L. C. Kimerling: *Radiation Effects in Semiconductors, Dubrovnik, 1976*, eds. N. B. Urli and J. W. Corbett, IOP Conf. Proc. No 31 (Institute of Physics, Bristol and London, 1979) p. 221.
- 4) L. C. Kimerling, P. Blood and W. N. Gibson: *Defects and Radiation Effects in Semiconductors, Nice, 1978*, ed. J. H. Albany,

- Inst. Phys. Conf. ser. 46 Inst. Phys, Bristol and London, 1979) p. 273.
- 5) Y. H. Lee, L. J. Cheng, J. D. Gerson, P. M. Mooney and J. W. Corbett: *Solid State Commun.* **21** (1977) 109.
  - 6) A. Brelot and J. Charlemaque: *Int. Conf. Radiation Effects in Semiconductors, Albany, New York, 1970*, eds. J. W. Corbett and G. D. Watkins (Gordon and Breach, New York, 1971) p. 161.
  - 7) R. D. Harris and G. D. Watkins: *Int. Conf. Defects in Semiconductors, Coronado, 1984*, eds. L. C. Kimerling and J. M. Parsey (Metallurgical Society, AIME, Warrendale Pennington, 1985) p. 759.
  - 8) C. A. Londos: *Phys. Rev.* **B35** (1987) 7511.
  - 9) G. Davies, A. S. Oates, R. C. Newman, R. Woolley, E. C. Lightowers, M. J. Binns and J. G. Wilkes: *J. Phys.* **C19** (1986) 841.
  - 10) P. M. Mooney, L. J. Cheng, M. Suli, G. D. Gerson and J. W. Corbett: *Phys. Rev.* **B15** (1977) 3836.
  - 11) D. V. Lang: *J. Appl. Phys.* **45** (1974) 3014.
  - 12) R. Woolley, E. C. Lightowers, A. K. Tipping, M. Claybourn and R. C. Newman: *Defects in Semiconductors, Paris, 1986*, ed. H. J. von Bardeleben, *Material Science Forum* vol. 10-12 (Tras Tech Publications, 1986) p. 929.
  - 13) A. K. Tipping and R. C. Newman: *Semicond. Sci. Technol.* **2** (1987) 315.
  - 14) S. K. Bains and P. C. Banbury: *J. Phys.* **C18** (1985) L109.
  - 15) G. D. Watkins and J. R. Troxell: *Phys. Rev. Lett.* **44** (1980) 593.
  - 16) A. O. Ewwaraye and E. Sun: *J. Appl. Phys.* **47** (1976) 3379.
  - 17) G. D. Watkins: *Phys. Rev.* **B13** (1976) 2511.
  - 18) J. A. Van Vechten: *Phys. Rev.* **B35** (1987) 864.
  - 19) K. Thonke, H. Klemisch, J. Weber and R. Sauer: *Phys. Rev.* **B24** (1981) 5874.
  - 20) A. R. Been, R. C. Newman and R. S. Smith: *J. Phys. Chem. Sol.* **31** (1970) 739.
  - 21) F. L. Vook and H. J. Stein: *Appl. Phys. Lett.* **13** (1986) 343.
  - 22) G. D. Watkins: *Radiation Effects in Semiconductor Components*, ed. F. Cambou (Journées de Electronique, Toulouse, 1976) vol. I, p. A<sub>1</sub>.
  - 23) R. C. Newman: *Infrared Studies of Crystal Defects* (Taylor and Francis, London, 1973) p. 87.
  - 24) R. E. Whan and F. L. Vook: *Phys. Rev.* **153** (1967) 814.
  - 25) L. C. Kimerling: *Defects and Radiation Effects in Semiconductors, Nice, 1978*, ed. J. H. Albany, *Inst. Phys. Conf. ser.* 46 (Inst. Phys., Bristol and London, 1979) p. 56.
  - 26) R. C. Newman: *Rep. Prog. Phys.* **45** (1982) 1163.
  - 27) M. T. Assom, J. L. Benton, R. Sauer and L. C. Kimerling: *Appl. Phys. Lett.* **51** (1987) 256.
  - 28) L. W. Song, X. D. Zhan, B. W. Benson and G. D. Watkins: *Phys. Rev. Lett.* **60** (1988) 460.
  - 29) L. I. Murin: *Phys. Status Solidi (a)* **93** (1986) K147.
  - 30) J. M. Trombetta and G. D. Watkins: *Appl. Phys. Lett.* **51** (1987) 1103.
  - 31) Y. Lee, J. W. Corbett and K. Brower: *Phys. Status Solidi (a)* **41** (1977) 673.