

## Photoluminescence on oxygen-rich acceptor-doped silicon

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**Abstract.** Oxygen-related centres in silicon containing the acceptors boron, aluminium, gallium or indium, were studied by photoluminescence. Only the O band showed a dependence on the kind of acceptor. In acceptor-implanted material the formation of the P luminescence was enhanced and we observed a new photoluminescence line at 1.117 eV which is attributed to a boron–oxygen complex.

### 1. Introduction

It is well known that a thermal treatment of oxygen-rich (Czochralski-grown) silicon introduces defects which are shallow donors. Since oxygen is present in a supersaturated solution after cooling the crystal from the growth temperature and at 450 °C the oxygen atoms are quite mobile, the generally accepted idea is that the so-called heat-treatment centres are due to the clustering of oxygen. The various subsequently formed complexes introduce shallow donor levels in the silicon band gap. For longer annealing times even large precipitates are formed, with typical dimensions near 1  $\mu\text{m}$ , that are observable with electron microscopy. Although a large amount of work, both theoretical and experimental, has been done with regard to this subject, the detailed structure of these defects and the mechanisms by which they are formed, have not yet been established. This is due to the fact that it is difficult to correlate the results obtained by various experimental techniques and to establish the influence of other impurities present in the starting material. Carbon especially plays an important role in the formation of thermal donors. Most of the existing experimental work was performed on samples with phosphorus or boron as a dopant. However, there are indications that the acceptor dopant can play an important role as well in the formation of heat-treatment centres [1] and in the annealing behaviour of silicon. For instance the so-called ‘reverse annealing’ after implantation is only observed in the case of boron and not with the other acceptors [2]. In this work we investigated the acceptor dependence of heat-treatment centres in Cz-grown silicon for both as-grown and implanted materials. The photoluminescence (PL) experiment was chosen here because of its high sensitivity and good applicability to

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thin surface layers. Many oxygen-related photoluminescence lines are reported in the literature. The first to mention photoluminescence of thermal donors were Tajima and co-workers [3]. Subsequently more lines were found. We mention the S<sub>i</sub> lines and the O band of Nakayama *et al* [4] and lines 1 to 10 of Minaev and Mudryi [5]. The more intense lines were studied in more detail. Stress studies were reported on the P line [6]. Optical detection of magnetic resonance (ODMR) of line 9 is described in [7]. However at present the origin of the lines is not clarified.

## 2. Experimental

In this study we used five different starting materials. The characteristics are listed in table 1. The set of samples 1 to 4 was used by Gregorkiewicz and co-workers to study the heat-treatment centres in EPR [8]. Material No 5 is oxygen-lean float-zone (FZ) material and was used as a reference to check the involvement of oxygen. As regards the heat treatments two different procedures were followed: (i) each heat treatment on a different sample, (ii) subsequent heat treatments on one sample. The results for equal total heat-treatment times were identical in both cases. Prior to the heat treatments the samples were heated to 1380 °C for 15 min to disperse the oxygen and subsequently quenched in order to obtain well defined starting conditions. The samples were mechanically polished or etched in a 1:3 mixture of HF and HNO<sub>3</sub>. Implantation of the samples with various acceptors (B, Al, Ga, In) was done with an energy of 100 keV, an equal dose of  $5 \times 10^{14} \text{ cm}^{-2}$  for all acceptors and a current of about 1  $\mu\text{A}$ . All heat treatments were done at a temperature of 450 °C.

**Table 1.** Specification of silicon samples.

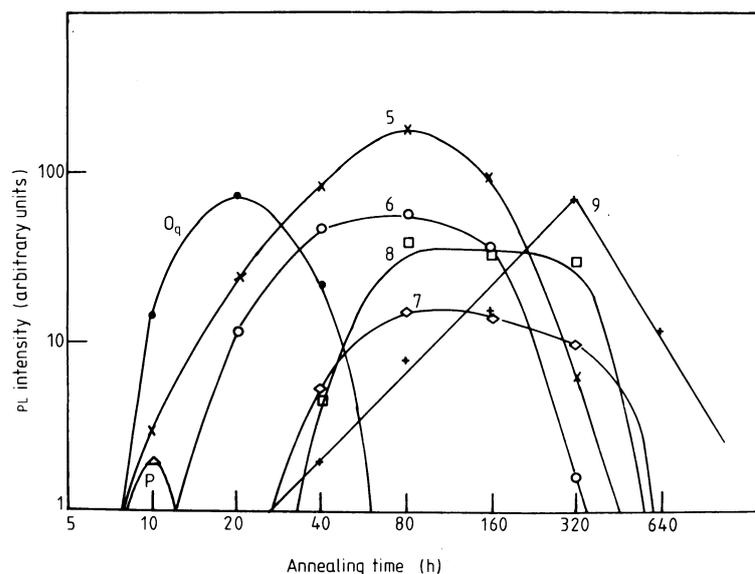
No	Type	Dopant	$\rho$ ( $\Omega \text{ cm}$ )	[O] ( $10^{18} \text{ cm}^{-3}$ )	[C] ( $10^{15} \text{ cm}^{-3}$ )
1	p Cz	In	7–11	1.4	<5
2	p Cz	Ga	1.8–2.1	1.4	<5
3	p Cz	Al	2.8–5	1.4	<5
4	p Cz	B	1.3	1.4	<5
5	p FZ	B	1000	0.01	<5

Photoluminescence was excited by an unfocussed cw mode Ar<sup>+</sup> laser operating at 514.5 nm. The incident power on the sample was 150 mW. The emission of the sample was analysed by a Jobin Yvon F/12 spectrometer with a 600 grooves  $\text{mm}^{-1}$  grating blazed at 1.5  $\mu\text{m}$  and detected by a liquid-nitrogen-cooled germanium detector (North Coast EO-817). The detector output was analysed by the usual lock-in techniques. The so-called voltage spikes of the detector (caused by an overload due to cosmic muons) were reduced by a sample-and-hold circuit as described in reference [9]. For the wavelength calibration of the spectrometer a mercury lamp was used. Most measurements were done at 4.2 K with the samples immersed in liquid helium.

## 3. Results

### 3.1. As-grown material

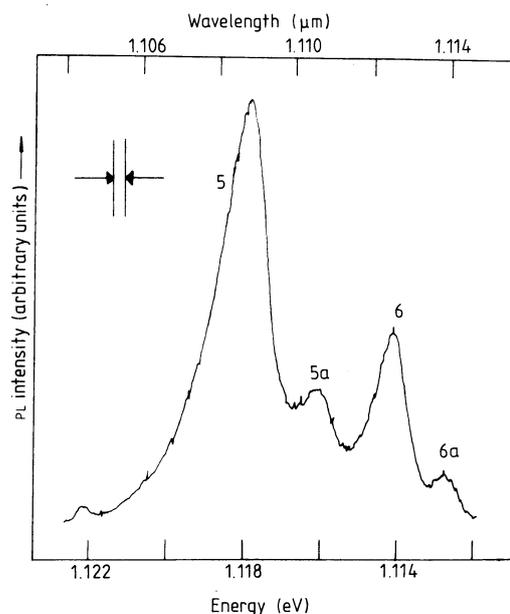
The annealing behaviour of the spectra is shown in figure 1 for boron-doped material.



**Figure 1.** The intensity of photoluminescence lines as a function of the time of annealing at 450 °C as observed in boron-doped silicon. The relative intensity of the  $O_q$  line must be multiplied by 10.

Apart from the acceptor bound exciton (BE) and bound multi-exciton-complexes (BMEC) other oxygen-related PL lines (labelled P,  $O_q$ , 5, 6, 7, 8, 9) show up as a function of the annealing time. All these lines were reported in the literature by various authors [4, 5]. Unfortunately several denotations for the same lines are used. We will use the numbering of [5]. Contrary to Minaev and Mudryi [5] we did not observe the PL lines H, 1, 2, 3, 4. This supports the observation of Nakayama *et al* [4] and Magnea *et al* [10] who investigated these lines and concluded that they were carbon related, and as such cannot be seen in carbon-lean material. The P line is observed for annealing times from 5–15 h in all samples, however with low intensity. Concentration of P centres was maximum at about 10 h annealing. This maximum is reached in a much shorter period of time than reported in [5]. Only Dörnen and Sauer [6] reported the observation of the P line after a few hours annealing but contrary to our measurements the intensity did not drop with longer annealing time. The reason for the different formation rates found by various authors is not understood. Perhaps the pre-anneal procedure (quenching from 1380 °C (this work) or 1 h at 700 °C [6]) is of importance.

The  $O_q$  lines (q denotes a momentum-conserving phonon) were first reported by Nakayama *et al* [4] and Tajima *et al* [11] in B-doped material. Contrary to their observations we detected lines 5 and 6 in the same samples as the  $O_q$  lines. Minaev and Mudryi [5] did not report the  $O_q$  line. This is most probably due to the fact that they measured at a temperature of 15 K instead of 4.2 K and the  $O_q$  band intensity diminishes at higher temperatures. In our experiment the maximum of the  $O_q$  is reached after 20–40 h annealing which is shorter than the time reported in [4]. Also in Al-doped material we detected an  $O_q$  band, however with lower intensity. In In-doped material no  $O_q$  band appeared and in Ga-doped material only traces of  $O_q$  could be detected. The  $O_q$  band has disappeared when lines 5 and 6 are reaching their maximum. When comparing our



**Figure 2.** Photoluminescence of aluminium-doped oxygen-rich silicon after 80 h heat treatment at 450 °C.

annealing times with [5] we conclude that we need less annealing. This was to be expected as in comparison to [5] we had more oxygen and much less carbon, which is known to inhibit the formation of thermal donors. When measuring lines 5 and 6 with higher resolution (3 Å), which is shown in figure 2, we detected two extra lines, which we labelled 5a and 6a. This structure was present for all acceptors. The spectral positions of the lines are given in table 2. The peak positions did not show any variation with the kind of acceptor dopant. Different samples showed a different intensity ratio for lines 5 and 6. Because there is no direct correlation between the intensities of 5 and 6 and temperature or time of annealing we conclude that, although often observed as a pair, the lines originate from different centres. Figure 2 shows that the lines are asymmetric: a broad tail at the high-energy side and a steep slope at the low-energy side indicating an optical transition involving free particles. A similar line structure in B- and P-doped material was reported by Weber and Queisser [12] who labelled the lines O<sub>1</sub> to O<sub>4</sub> and described them as new photoluminescence lines. There is a small energy difference (0.0014 eV) between the line positions O<sub>1</sub>, O<sub>3</sub> [12] and 5, 6 of Minaev and Mudryi [5].

**Table 2.** Energies of thermally induced luminescence lines.

Line	<i>E</i> (eV)
5	1.1180
5a	1.1163
6	1.1143
6a	1.1128

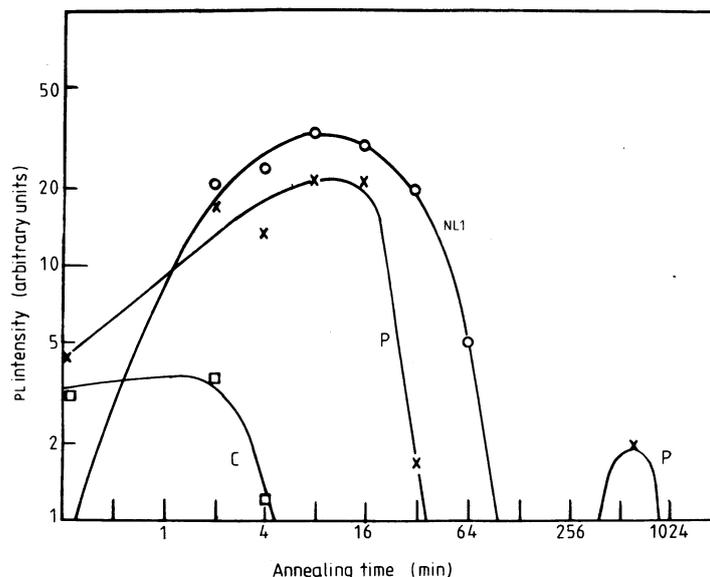
However we think this alone is not a decisive proof that the lines are different. Moreover the energy difference between the lines is exactly the same. Unfortunately in [12] there is no detailed information as to why  $O_1$ ,  $O_3$  are considered to be different from lines 5 and 6 of [5].

Lines labelled 8 and 9 were observed in all materials. No acceptor-related shift could be detected. The lineshape showed the asymmetry similar to that of lines 5 and 6: broader high-energy side and steeper low-energy side. At higher temperature lines 8 and 9 showed a more complicated structure which could not be resolved.

In summary, the PL lines P,  $O_q$ , 5, 6, 7, 8, 9 were observed for shorter annealing times than earlier reported. The lines  $O_q$  were much stronger in B- and Al-doped material than for Ga- and In-doping. Lines 5 and 6, which are probably identical to the O lines of [12], showed a similar structure.

### 3.2 Implanted material

The spectra obtained after implantation of acceptor ions are dominated by the well known irradiation-induced PL band. Superimposed on this band are narrow PL lines like C, W and, in boron-doped material, the  $I_2$  line. Monitoring of these lines indicates that at our annealing temperature of 450 °C the primary radiation defects are annealed out in about 8 min. The observed spectra are essentially the same for all materials. The most interesting feature of the implanted material was the quick appearance of a P line and the observation of a new PL line which we labelled PL-Si-NL1. The intensity of these lines as a function of annealing time is depicted in figure 3. It is seen that the intensity of the P line reaches a maximum at about 10 min, disappears with longer annealing time and reappears for 10 h annealing as for the as-grown material. To explain the annealing behaviour of the P line, one can consider that the P line is formed already during implantation. The initial increase in intensity is then explained by annealing of an



**Figure 3.** The intensity of photoluminescence lines, observed in boron-implanted silicon, as a function of the time of annealing at 450 °C.

amorphous layer caused by the implantation. This argument is contradicted by the following: the implantation dose is rather low, therefore no amorphous layer is expected, the acceptor-related lines are rather constant with annealing and the C line starts to decrease whereas the P line starts to increase. So we conclude that the P centres are formed upon annealing of the material. It is well established that the P line is related to oxygen complexing. The enhancement of the formation rate can be explained by assuming that a nucleation centre is needed for the clustering of oxygen. In as-grown Cz silicon oxygen itself is the defect with highest concentration ( $\approx 10^{18} \text{ cm}^{-3}$ ). At 450 °C the diffusion coefficient is typically  $D = 1 \times 10^{-18} \text{ cm}^2 \text{ s}^{-1}$  [13]. For a random diffusion mechanism we have an associated diffusion length  $l = (6Dt)^{1/2}$  [14]. For 10 h  $l \approx 50 \text{ \AA}$ . The average distance between neighbouring oxygen atoms is of the order of 100 Å. We conclude that oxygen can form complexes in a time scale of 10 h. As regards the implanted material, the difference from the as-grown material is the concentration of acceptors in the implanted layer, typically of the order of  $10^{20} \text{ cm}^{-3}$ . This gives an average distance between acceptor impurities of about 20 Å. In 10 min the diffusion length of oxygen is of the order of 6 Å and it is likely that the complexing of oxygen will start in the vicinity of an acceptor ion. Trapping of oxygen atoms at the acceptor seems the most reasonable explanation for the enhanced formation rate of the P centre. Interactions of implantation-induced defects such as vacancies and interstitials can be ruled out as these defects are not present at 450 °C. Furthermore, the diffusion rates of other defects such as B or C do not have the correct order of magnitude to account for the observed formation time. The measurements indicate that the optimal formation time in the implanted material increases in the sequence In, Ga, Al, B. According to the atomic stopping theory (LSS) [15] the implanted layer will be thinnest for indium and thickest for boron and the local concentration of acceptors will show the same sequence In, Ga, Al, B.

As indicated in figure 3 we observed a PL spectrum called NL1 from 2 to 60 min annealing, with a maximum intensity after 10 min. Contrary to other PL lines this line was not observed for all acceptor dopants. Only boron-doped material showed the NL1 line at the energy 1.117 eV. In the as-grown material, annealed from 0 to 600 h, this line was not detected. Implantation was necessary for the formation of the spectrum. Annealing of oxygen-lean float-zoned material, with boron implanted, did not produce the 1.117 eV line either. It is therefore concluded that the NL1 centre needs both oxygen and boron for its formation. Nakayama *et al* [4] report the SB line in carbon-lean, boron-doped Cz silicon after 100 h annealing at 500 °C. Judging from its energy NL1 could be the SB line, were it not for its different temperature behaviour. The SB line has maximum intensity at temperatures higher than 10 K while the intensity of NL1 drops upon raising the temperature above 4.2 K. Moreover NL1 was also present in material with higher carbon concentration, while SB shows only in carbon-lean material.

We believe that the spectrum at 1.117 eV, present only in B-implanted Cz-grown material is reported here for the first time and label it PL-Si-NL1. The production characteristics are quite similar to those observed for the P line after implantation. Then the possibilities of forming the NL1 centre in this short period of time are analogous to those of the P centre. This leads again to the model of oxygen diffusion and complexing. Together with the fact that NL1 is only observed in B-implanted material we postulate that NL1 is most probably due to a B-O complex. Measured with higher resolution and at higher temperatures ( $\approx 9 \text{ K}$ ) it shows that NL1 consists of three components, labelled 0, 1, 2. This is shown in figure 4. The energies are listed in table 3. A more direct proof of the involvement of B in the defect is shown in figure 5. The  $^{10}\text{B}$ - $^{11}\text{B}$  isotope shift is seen for components 0 and 1. From this isotope shift we conclude that boron is actually

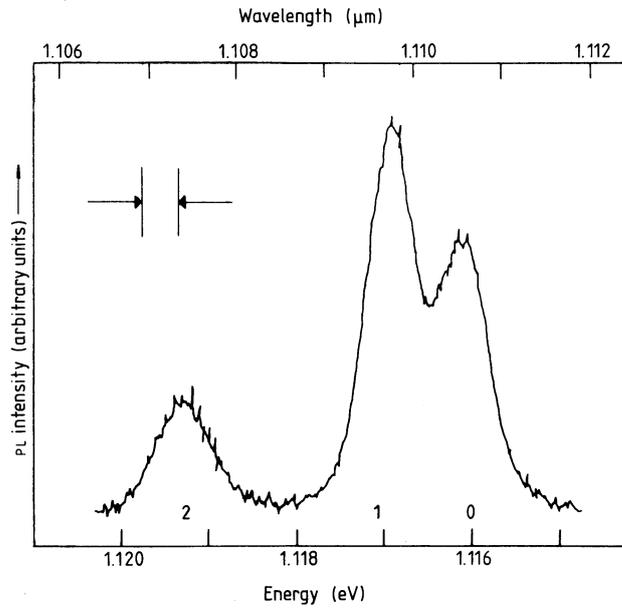


Figure 4. The photoluminescence spectrum PL-Si-NL1 in boron-implanted oxygen-rich silicon after heat treatment.

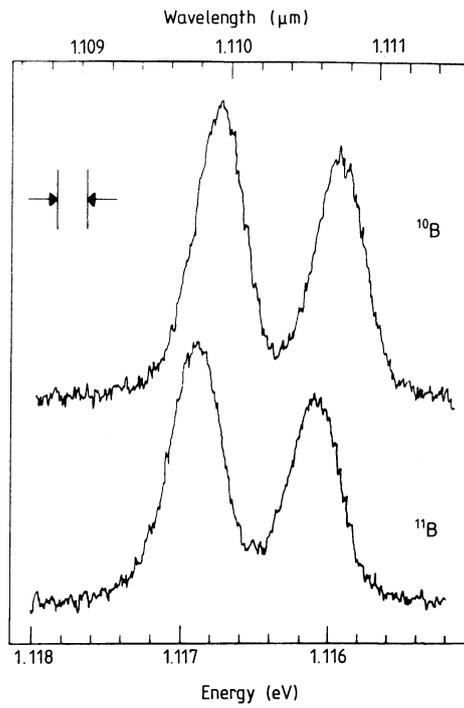


Figure 5. Isotope shift of the components 0 and 1 of the NL1 photoluminescence spectrum.

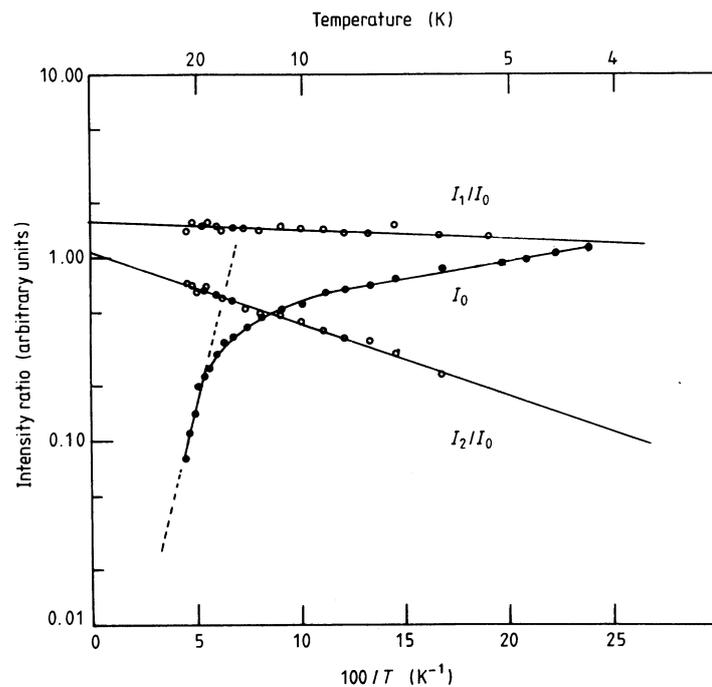
**Table 3.** Energies of the components of the NL1 photoluminescence.

Line	$E$ (eV)
0	1.1161
1	1.1169
2	1.1193

incorporated in the defect. The isotope shift,  $E(^{11}\text{B}) - E(^{10}\text{B}) \approx +0.15$  meV, is both in sign and magnitude comparable to the isotope shifts reported for other centres in silicon [16, 17]. Data on the temperature dependence of components 0, 1, 2 are plotted in figure 6. From the intensity ratios it follows that the components are thermalising. The activation energies are 0.09 and 0.8 meV for  $I_1/I_0$  and  $I_2/I_0$ , respectively. The thermal activation energies differ from the spectroscopic spacing between the lines which are 0.9 and 3.2 meV, respectively. The intensities of the lines can be fitted with the formula:

$$I(T) = I(0)[1 + \sum_i c_i \exp(-E_i/kT)]^{-1}. \quad (1)$$

The overall intensity of luminescence NL1 is quenched with a deactivation energy of about 10 meV and degeneracy factor of about 3000, indicating a transition to the conduction band. These numbers are subject to inaccuracies because, due to insufficient signal intensity, not enough measuring points could be gathered to monitor the steep quenching of intensity at higher temperatures. The deactivation energy of 10 meV is



**Figure 6.** Intensity  $I_0$  and intensity ratios  $I_1/I_0$  and  $I_2/I_0$  for the components of the photoluminescence spectrum NL1 as a function of the temperature  $T$ .

significantly smaller than the localisation energy (53 meV), a result indicating that the centre is of the iso-electronic type. Further investigations are necessary to reveal the structure of the centre.

#### 4. Conclusions

Most oxygen-related PL centres are not influenced by the kind of acceptor dopant. A new PL line at 1.117 eV is reported. The line originates from a boron–oxygen complex. It is demonstrated that acceptors can act as nucleation centres for oxygen complexes. The formation of the  $O_q$  lines showed a dependence on the acceptor. The formation times for various heat treatment PL lines are shorter than commonly reported.

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#### References

- [1] Muller S H, Sieverts E G and Ammerlaan C A J 1979 *Defects and Radiation Effects in Semiconductors 1978*. (Inst. Phys. Conf. Ser 46) p 297
- [2] Gregorkiewicz T and Ammerlaan C A J 1985 *Radiat. Eff. Lett.* **85** 249
- [3] Tajima M, Kanamori A and Iizuka T 1979 *Japan. J. Appl. Phys.* **18** 1401
- [4] Nakayama H, Nishino T and Hamakawa Y 1981 *Appl. Phys. Lett.* **38** 623
- [5] Minaev N S and Mudryi A V 1981 *Phys. Status Solidi a* **68** 561
- [6] Dörnen A, Sauer R and Weber J 1985 *J. Electron. Mater.* **A 14** 653
- [7] Weber J and Watkins G D 1985 *J. Electron. Mater.* **A 14** 661
- [8] Gregorkiewicz T, van Wezep D A, Bekman H H P Th and Ammerlaan C A J 1987 *Phys. Rev. B* **35**
- [9] Collins A T and Jeffries T 1982 *J. Phys. E: Sci. Instrum.* **15** 712
- [10] Magnea N, Lazrak A and Pautrat J L 1984 *Appl. Phys. Lett.* **45** 60
- [11] Tajima M, Kishino S, Kanamori M and Iizuka T 1980 *J. Appl. Phys.* **51** 2247
- [12] Weber J and Queisser H J 1987 *Proc. Symp. Mater. Res. Soc. (Boston), 1985* vol 59
- [13] Newman R C, Tucker J H and Livingston F M 1983 *J. Phys. C: Solid State Phys.* **16** L151
- [14] Flynn C P 1972 *Point Defects and Diffusion* (Oxford: Clarendon)
- [15] Mayer J W, Eriksson C and Davies J A 1970 *Ion Implantation in Semiconductors* (New York: Academic)
- [16] Davies G, Lightowers E C, Woolley R, Newman R C and Oates A S 1984 *J. Phys. C: Solid State Phys.* **17** L499
- [17] Thonke K, Burger N, Watkins G D and Sauer R 1985 *J. Electron. Mater.* **A 14** 823