# Defect energy levels in boron-doped silicon irradiated with 1-MeV electrons\*

P. M. Mooney, L. J. Cheng, M. Süli, J. D. Gerson, and J. W. Corbett §

Department of Physics and Institute for the Study of Defects in Solids, State University of New York at Albany, Albany, New York 12222 (Received 19 November 1976)

Using transient capacitance spectroscopy, we studied defect energy levels and their annealing behavior in boron-doped silicon of various resistivities irradiated with 1-MeV electrons at room temperature. Three levels located at  $E_v + 0.23$ ,  $E_v + 0.38$ , and  $E_c - 0.27$  eV consistently appear in various samples, showing they are characteristic defects in boron-doped silicon. Many properties of the  $E_v + 0.23$ -eV level and the divacancy are the same, according to the present study and others. We correlated the  $E_v + 0.38$ -eV level to the vacancy-oxygen-carbon complex recently identified by Lee and Corbett using the EPR technique. The  $E_c - 0.27$ -eV level could arise from an interstitial defect of oxygen and boron; and a new level at  $E_v + 0.30$  eV arising upon its disappearance could be a vacancy defect trapping an oxygen atom and a boron. Several additional defect levels are reported.

### I. INTRODUCTION

The self-interstitial and the vacancy in silicon are highly mobile at room temperature. Some secondary defects, created by trapping an interstitial or a vacancy at an imperfection site, such as the boron interstitial, the carbon interstitial,3 and the vacancy trapped at a next-nearest neighbor of a boron atom<sup>4</sup> are also mobile at room temperature. Consequently, stable defects in silicon created by irradiation at room temperature can be divided into three categories: (i) defects created directly by collision cascade, such as the divacancy; (ii) defects created by the interaction among radiation-induced intrinsic defects, such as the di-interstitial; and (iii) defects created by the interaction between an intrinsic defect and an imperfection originally in the crystal (usually an impurity), such as the vacancy-oxygen complex. Many experiments, primarily done with n-type silicon, have demonstrated that low-energy-electron irradiation (e.g., 1 MeV) with low fluence should produce defects of the third category. However, the literature contains much less information concerning impurity-associated defects in p-type silicon.

In this paper, we report results from an experimental study of defect energy levels in p-type boron-doped silicon created by 1-MeV electron irradiation at room temperature. These experiments reveal new information concerning impurity-associated defects in p-type silicon.

## II. EXPERIMENTAL

Our experimental method for the energy level measurements is similar to the transient capacitance spectroscopy reported by Lang. $^{5,6}$  The measured activation energies for carrier emission are accurate to about  $\pm\,0.02$  eV. The carrier

capture cross sections,  $\sigma_p$  (hole) and  $\sigma_n$  (electron), were measured at the temperature at which the signal from the level appeared. The cross sections were measured to within one significant figure. Electron irradiation was carried out at the 4-MeV Dynamitron at SUNY/Albany. The irradiation temperature was about 25-30 °C.

The samples used were diodes fabricated by phosphorous diffusion on boron-doped silicon wafers with nominal resistivities of 0.3, 1, 2, and 8  $\Omega$  cm. The samples were annealed in air to 200 °C and in a dry nitrogen atmosphere from 200 to 450 °C. Temperatures were measured to within 1 °C in the lower range and 2 °C in the upper range.

# III. EXPERIMENTAL RESULTS

Figure 1 shows typical transient capacitance spectra for 0.3, 2, and  $8-\Omega$  cm p-type silicon samples under the conditions of majority carrier pulse and injection pulse. Two majority carrier trapping centers and one minority carrier trapping center in the spectra are systematically observed. By measuring the thermal emission rates as a function of temperature, we found the locations of the energy levels of these trapping centers to be  $E_v + 0.23$ ,  $E_v + 0.38$ , and  $E_c - 0.27$  eV. The errors in these values are about  $\pm 0.02$  eV. As shown in Fig. 1, the additional majority carrier trapping levels located at  $E_n + 0.18$ ,  $E_n + 0.31$ , and  $E_n + 0.48$  eV with smaller concentrations were observed in  $0.3-\Omega$  cm samples, but not in others. Figure 2 shows the production rate of the  $E_c$  = 0.27= and the  $E_v + 0.38$ -eV levels under 1-MeV electron irradiation at room temperature as functions of the boron concentration of the sample. The production rate of the  $E_c - 0.27$ -eV level increases with boron concentration, but that of the  $E_n + 0.38$ eV level decreases with boron concentration. Furthermore, the increase of the production rate

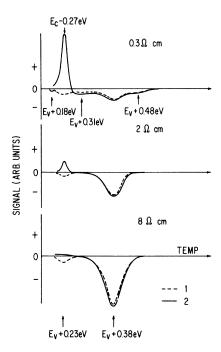


FIG. 1. Typical transient capacitance spectra after irradiation by 1-MeV electrons for boron-doped p-type silicon.

of the  $E_c-0.27$ -eV level seems to be proportional to the square root of boron concentration. Note that the  $E_c-0.27$ -eV trap is not clearly observed in the  $8-\Omega$  cm material, so we plotted the maximum possible production rate in Fig. 2. The production rates of the  $E_v+0.23$ -eV level in different samples vary around 0.002 cm<sup>-1</sup>; they are inde-

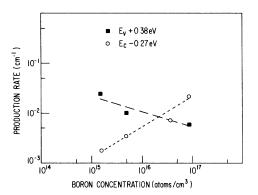


FIG. 2. Production rate vs boron concentration for the  $E_v$  +0.38- and  $E_c$  -0.27-eV energy levels in 1-MeV electron irradiated p-type silicon.

pendent of boron concentration. The production rates of the  $E_v$ + 0.18-,  $E_v$ + 0.31-, and  $E_v$ + 0.48-eV levels are about 0.001, 0.002, and 0.002 cm<sup>-1</sup>, respectively.

All the data presented here were taken a few weeks after irradiation. There is a majority carrier trapping level located at  $E_v + 0.29$  eV which always appears in all the samples just after room-temperature irradiation and which disappears completely within a few days when the sample is stored at room temperature. This level has been correlated with the carbon interstitial<sup>7,8</sup> which is mobile at room temperature.<sup>3</sup>

Table I gives the carrier capture cross sections of the energy levels measured in the present study. These values are calculated from the data obtained from the measurements of variations in the tran-

TABLE I. Capture cross sections of defects observed in present study of p-type silicon.

	Energy level (eV)	Capture cross section (cm <sup>2</sup> )
After	$E_{v} + 0.18$	$\sigma_p > 2 \times 10^{-17}$
irradiation	$E_v + 0.23$	$\sigma_{p} = 3 \times 10^{-16}$
	$E_v + 0.31$	$\sigma_p > 2 \times 10^{-17}$
	$E_v + 0.38$	$\sigma_{p_1}$ = 2 $ imes$ 10 $^{-16}$
		$\sigma_{p2} = 2 \times 10^{-19}$ (after irradiation)
		$\sigma_{p2} = 5 \times 10^{-18}$ (after 350 °C annealing)
		$\sigma_{p2} = 1 \times 10^{-18}$ (after 400 °C annealing)
	$E_v + 0.48$	$\sigma_{\hat{p}} > 2 \times 10^{-17}$
	$E_c-0.27$	$\sigma_n = 2 \times 10^{-13}$
After	$E_v$ + 0.30	$\sigma_p = 2 \times 10^{-16}$
annealing	$E_v + 0.26$	•••
	$E_v$ + 0.2	•••
	$E_v + 0.47$	$\sigma_p = 4 \times 10^{-16}$

sient signal as a function of the pulse width. A semilog plot of signal height versus pulse width can be fit by a single straight line, indicating one capture rate for all the levels except the  $E_v+0.38-eV$  level. Data for this level can be fit with two straight lines as shown in Fig. 3, which indicates two capture rates. This phenomenon implies that two different defects have a level at  $E_v+0.38\ eV$ : one defect (~80% of the signal) is a neutral trap, and the other (~20%) is positively charged when the Fermi level is below the trap level. The cross section for the minor portion seems to increase with annealing temperatures as shown in Table I.

The measured minority carrier capture cross section of the  $E_c = 0.27 - \text{eV}$  level,  $\sigma_n = 3 \times 10^{-13} \text{ cm}^2$ at 145 °K, shows that the trapping center must be positively charged before trapping an electron. We used the double pulsed technique<sup>5</sup> to measure the majority carrier capture cross section of the level after trapping the electron. The majority carrier capture cross section is on the order of 10<sup>-20</sup> cm<sup>2</sup>, which shows that the level is still positively charged after trapping the electron. Therefore the defect must be doubly charged before trapping an electron. The fact that the measured majority carrier cross sections of  $E_v + 0.18$ -,  $E_v + 0.24$ -, and  $E_v + 0.48$ -eV levels are on the order of  $10^{-16} \ \text{cm}^2$  suggests that the defects causing these levels are in their neutral states before they trap holes.

Figures 4 and 5 show typical isochronal annealing data obtained from 0.3- and  $2-\Omega$  cm samples. Several interesting features are shown in Figs. 4 and 5. First, the  $E_c-0.27$ -eV level disappeared upon annealing around 170 °C. At the same time, a new majority carrier trapping level, located at  $E_v+0.30$  eV, appeared. Further isothermal annealing experiments have shown that the activation energies and the frequency factors for the disappearance of the  $E_c-0.27$ -eV level and for the growth of the  $E_v+0.30$ -eV level are the same, i.e.,  $E_A=1.2\pm0.1$  eV and  $f_0=(1.5\pm1)\times10^{11}$  sec<sup>-1</sup> (Fig. 6). Second, the  $E_v+0.30$ -eV level does not appear

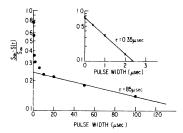


FIG. 3. Normalized signal vs pulse width for the  $E_{v}$ +0.38-eV energy level. Curve is fit with two straight lines indicating two capture rates.

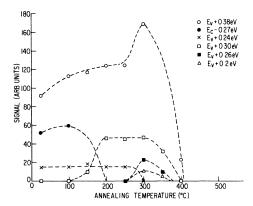


FIG. 4. Isochronal annealing data for 2- $\Omega$  cm samples of 1-MeV electron irradiated p-type silicon.

in the  $8-\Omega$  cm samples, in which the  $E_c-0.27$ -eV level was not clearly observed. These above results argue that the defect giving rise to the  $E_v+0.30$ -eV level evolves from the defect causing the  $E_c-0.27$ -eV level. Upon further annealing at higher temperatures, the  $E_v+0.30$ -eV level disappeared at about  $400\,^{\circ}\mathrm{C}$ .

Our isochronal annealing studies have also shown that the  $E_n + 0.38 - eV$  level disappeared upon annealing around 400 °C. The data from 2- and  $8-\Omega$  cm samples consistently indicate an increase in the intensity of this level upon annealing at lower temperatures, and a sizable increase around 300 °C. Upon annealing at 250-300 °C, the  $E_v$ + 0.23-eV level disappeared and two new levels  $(E_v + 0.2 \text{ and } E_v + 0.26 \text{ eV})$  appeared. The latter two annealed out around 400 °C. The  $E_n$ + 0.26-eV level was not observed in 0.3- $\Omega$  cm samples. In addition, the  $E_n + 0.48 - eV$  level, observed only in  $0.3-\Omega$  cm samples, disappeared upon annealing around 170 °C. Finally, several different majority carrier trapping levels were observed upon annealing  $8-\Omega$  cm samples at higher temperatures. A level located at  $E_v + 0.47$  eV, with

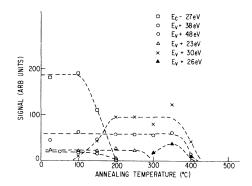


FIG. 5. Isochronal annealing data for  $0.3-\Omega$  cm samples of 1-MeV electron irradiated p-type silicon.

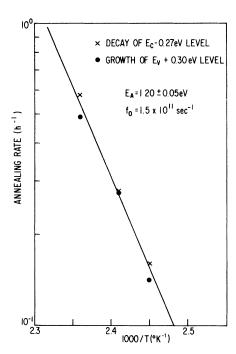


FIG. 6. Annealing rate as a function of temperature for the disappearance of the  $E_c$  -0.27-eV level and the growth of the  $E_v$  +0.30-eV energy level.

a cross section of  $\sigma_p = 4 \times 10^{-16}$  cm², appeared at 300 °C and disappeared around 450 °C. Another level with a very small concentration was observed after 350 °C annealing and disappeared around 450 °C. A sizable peak corresponding to a level located at  $E_v + 0.18$  eV appeared after 400 °C anneal and remained after 450 °C anneal.

### IV. DISCUSSION

The four defect energy levels observed in our study ( $E_v + 0.23$ ,  $E_v + 0.38$ ,  $E_c - 0.27$ , and  $E_v + 0.30$  eV) may have been previously reported by Kimerling<sup>8</sup> using a technique similar to ours and Walker

and Sah<sup>9</sup> using thermally stimulated capacitance measurements. The  $E_v$ +0.30-eV level appeared upon the annealing of the  $E_c$ -0.27-eV level. The reported locations of these levels are slightly different from our values, as shown with other levels appearing upon annealing in Table II. From the similar production and annealing properties of the levels reported by them and those we observed, we argue that all the workers have observed the same levels. The differences could be due to errors hidden in measurement and data analysis techniques which require further cooperative studies for clarification.

Because the energy levels (listed in Table II) have been observed in a wide range of samples by different investigators, we believe they are associated with major defects in boron-doped silicon. The defect giving rise to the  $E_v + 0.23 - eV$ level has been correlated with the positively charged divacancy.8 Our results are consistent with this correlation. The divacancy can be produced by a collision cascade during irradiation or by a combination of two vacancies. Under 1-MeV electron irradiation with light fluences, the former process should be the dominant one, as is evident from the experiment of Corbett and Watkins.10 However, the production rate varies from sample to sample with different crystal origins, as is evident in our measurements, presumably because the availability of the self-interstitial to be trapped at the divacancy can vary.

The other three levels appear to arise from three impurity-associated defects (as indicated by our results). The major impurities in our samples as well as those used by Kimerling<sup>8</sup> and Walker and Sah,<sup>9</sup> are oxygen and carbon, in addition to the dopant boron. The oxygen concentration should be in the order of 10<sup>18</sup> atoms/cm<sup>3</sup>, because the samples used are diffused diodes. It is known that carbon very often exists in silicon crystals; its content in our samples is not known, but is

TABLE II. Energy levels in p-type silicon obtained by the present studies and by Kimerling (Ref. 8) and Walker and Sah (Ref. 9).

Present study (eV)	Kimerling (eV)	Walker and Sah	Annealing properties
$E_v$ + 0.30	$E_v + 0.27$	$E_v$ + 0.28 eV	out 30 °C
$E_{v} + 0.23$	$E_v + 0.21$	$E_v$ + 0.182 eV	out 250-300 °C
$E_v + 0.38$	$E_v + 0.33$	$E_v$ + 0.354 eV	in 30 °C, out 400 °C
$E_c - 0.27$	$E_c = 0.26$	Not observed because of limitations of the technique	out 170°C
$E_v^{}+0.30$	$E_v^{+} 0.29$	$E_v$ + 0.302 eV	in 170 °C, out 400 °C

probably on the order of 10<sup>16</sup> atoms/cm<sup>3</sup>. Other impurities could also appear in silicon crystals, but their appearance is not as consistent as those of oxygen and carbon.<sup>11</sup> In Sec. IV A, we shall present the information available up to the present which we believe is relevant to the defects giving rise to the three levels and discuss possible correlations.

# A. $E_v + 0.38$ -eV level

This level appears at about room temperature upon the annealing of the  $E_v + 0.29 - eV$  level, which Lee et al., using the photo-EPR technique as well as the transient capacitance method, associated with the carbon interstitial. Consequently, the  $E_v + 0.38$ -eV level should also be associated with carbon. Recently, using the EPR technique, Lee and Corbett<sup>12</sup> have identified the K center in irradiated p-type silicon as a positively charged vacancycarbon-oxygen complex, [V+C+O], in which a carbon and oxygen form a "CO molecule" nested in a divacancy. They have found that (i) this defect appears upon the annealing of the carbon interstitial; (ii) it has a level at  $E_n + 0.33(\pm 0.02)$  eV; (iii) it is neutral when the Fermi level is above the level; and (iv) it disappears upon annealing around 400 °C. Of the defects giving rise to the  $E_n$ + 0.38-eV level most (~ 80%) have these same properties, and can therefore be correlated with this vacancy-carbon-oxygen complex.

According to Almeleh and Goldstein, <sup>13</sup> the production rate of the K center in p-type silicon under 1-MeV electron bombardment was about 0.025 cm<sup>-1</sup>. The production rates of the  $E_v$ +0.38-eV level in p-type silicon of various resistivities obtained by the present study, Kimerling, <sup>8</sup> and Walker and Sah<sup>9</sup> were also in this range as shown in Fig. 7. The data in Fig. 7 also indicate that the production rate of this level decreases with increasing boron concentration in the range higher than  $10^{16}$  atom/cm<sup>3</sup>. This trend is reasonable,

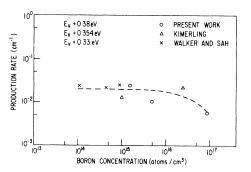


FIG. 7. Production rate vs boron concentration for 1-MeV electron irradiated boron-doped silicon from the present study, Kimerling, and Walker and Sah.

because in this range the boron atoms could start to compete for the vacancy or the self-interstitial with other impurities (oxygen or carbon) which are necessary constituents for the vacancy-carbon-oxygen complex. The scatter of the data shown in the figure can be explained by differences in the impurity content from one sample to

The annealing temperature of the  $E_n + 0.38 - eV$ level, observed by the present study to be around 400 °C, is the same as that of the vacancy-carbonoxygen complex reported by Lee and Corbett.12 In our cross-section experiments we have observed that  $\sim 80\%$  of the defects giving rise to the  $E_n + 0.38$ -eV level are in a neutral state when the Fermi level is above the defect level, which is also consistent with the finding of the EPR work of Lee and Corbett. From the onset of their photo-EPR signal, Lee and Corbett concluded that the vacancy-oxygen complex has a level at  $E_{\nu}$ + 0.33( $\pm$  0.02) eV, which is smaller than that of  $E_n + 0.38 (\pm 0.02)$  eV. Due to the difference in process between the photoexcitation and the thermal emission, we do not consider the difference in the level position to be inconsistent. Alternatively, the vacancy-carbon-oxygen complex and a second unknown defect could together cause an apparent  $E_n + 0.38 - eV$  level.

Several possible mechanisms for the formation of the [V+C+O] defect have been discussed. The first is

$$[C_s+O_t]+[V]+[V+C+O],$$

where [V] represents the vacancy and  $[C_s+O_i]$  represents a complex consisting of a substitutional carbon and an interstitial oxygen. Newman and Smith, is using infrared absorption measurements, presented evidence that the  $[C_s+O_i]$  defect may exist prior to irradiation. Also Sieverts  $et\ al.^{15}$  have observed [V+C+O] in heat treated samples. The simplicity of this mechanism also argues for it. One difficulty is that the vacancy migrates at  $\sim 200\ ^{\circ}$ K, indicating that [V+C+O] should form at that temperature; however, it forms at room temperature upon the annealing of the interstitial carbon. Nevertheless, this mechanism is a reasonable one for [V+C+O] formation during heating process.

The favorable mechanism under irradiation at room temperature is the one in which [V+C+O] is formed by trapping an interstitial carbon at a vacancy-oxygen complex (the A center) with a simultaneous ejection of a silicon atom from a neighboring site, as

$$[C_i] + [V + O] - [V + C + O] + [Si_i]$$

The silicon atom becomes a self-interstitial which

is highly mobile at room temperature. Several arguments support this mechanism. The first is the observation that [C<sub>i</sub>] anneals out at room temperature<sup>12</sup> when [V+C+O] appears. The second is that the A center, [V+O], is known to exist in our samples although we have not observed any energy level which can be attributed to this defect. [V+O] has one energy level at  $E_c = 0.17$  eV and is neutral when the Fermi level is below that level. Therefore, it is not surprising that [V+O] does not play a role in majority carrier trapping in p-type silicon and is also electrically inactive. On the other hand, [V+O] could be an effective minority carrier trapping center because in its neutral state it has an electron capture cross section as large as  $1 \times 10^{-14}$  cm<sup>2.8</sup> Our observation of the defect depends on the hole capture cross section of the defect. Our failure to observe [V+O] enables us to set a lower limit for the hole capture cross section of the negatively charged vacancy-oxygen complex at 10<sup>-14</sup> cm<sup>2</sup>. This is a reasonable limit, as the typical cross section of a Coulomb attractive center is in the range of 10<sup>-12</sup>-10<sup>-14</sup> cm<sup>2</sup>. Experimental evidence that the hole capture cross section of [V+O] is  $\geq 10^{-14}$  cm<sup>2</sup> has frequently appeared in the literature.16-19 In addition, many workers have indicated the existence of [V+O] in p-type silicon using the minoritycarrier lifetime technique.  $^{18,19}$  Therefore, [V+O]may exist in the samples used in the present study but cannot be observed under our experimental conditions. The third argument in favor of this mechanism is that the ejection of the silicon atom is energetically possible, because the chemical bonding energy between carbon and oxygen (257 kcal/mole) is more than three times larger than that between silicon and silicon (76 kcal/mole).<sup>20</sup>

The observed increase in the intensity of the  $E_v+0.38$ -eV level after annealing around 300 °C in some samples is also consistent with the correlation with [V+C+O], because [V+O] is mobile at that temperature and [V+C+O] can be formed by trapping a [V+O] at a substitutional carbon site.

In conclusion we believe we have successfully correlated the major fraction (~80%) of the  $E_v$ +0.38-eV level with [V+C+O]. The defect causing the remaining fraction (~20%) of the level is still not known. Kimerling<sup>8</sup> has observed a level of  $E_v+0.33$  eV which we believe is the same as the  $E_v+0.38$ -eV level mentioned before. He has tentatively attributed this to the carbon-carbon pair, identified by Brower<sup>21</sup> using the EPR technique. We note that the carbon-carbon pair disappears upon annealing around 300 °C, which is much lower than annealing temperature of the  $E_v+0.33$ -eV level reported by Kimerling.<sup>8</sup> In addition, silicon samples similar to some of those used in the

present study have been examined by Lee<sup>22</sup> using the EPR technique; he did see the signal from [V+C+O], but none from the carbon-carbon pair.

# By $E_c = 0.27$ - and $E_v = 0.30$ -eV levels

Our experimental results show that the defect giving rise to the  $E_v + 0.30 - \mathrm{eV}$  level evolves from the defect causing the  $E_c - 0.27 - \mathrm{eV}$  level. We shall discuss these two levels together.

The production rate of the defect causing the  $E_c-0.27$ -eV level increases with boron concentration. Kimerling<sup>8</sup> has also observed this phenomenon. In Fig. 8, we plotted Kimerling's data along with ours. Considering our data alone would indicate that the production rate is proportional to the boron concentration to the one-half power. If Kimerling's data are included, the one-half-power dependence becomes uncertain. Nevertheless, all the data in Fig. 8, including Kimerling's data from 10-MeV irradiation, indicate that the production rate increases with the boron concentration and that the power of the dependence is in the range of  $\frac{1}{2}$  to 1.

Because of the boron dependence, we believe that the defect causing the  $E_c-0.27~{\rm eV}$  is a boron-associated defect. The information for boron-associated defects available from the literature is summarized below. Using the EPR and electron-nuclear-double-resonance techniques, Watkins² observed an interstitial boron in silicon irradiated with 1.5-MeV electrons at 20.4 °K. Interstitial boron is unstable at room temperature, disappearing in ~30 min with an activation energy of 0.6 eV. Watkins⁴ also identified the Si-G10 spectrum as due to a lattice vacancy trapped by a substitutional boron in silicon. He did not observe any hyperfine spectrum caused by the

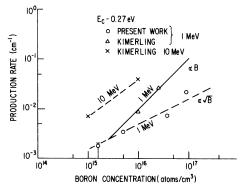


FIG. 8. Production rate vs boron concentration for the  $E_c$  -0.27-eV energy level in 1- and 10-MeV electron irradiated samples. Kimerling's data are plotted with data from the present study.

boron atom in his study. Because the G10 spectrum is observed only in boron-doped floatingzone material, he has concluded that the boron atom is a next-nearest neighbor to the vacancy. These two studies indicate that neither of the first generation complexes produced by the trapping of primary defects is present in room-temperature irradiated silicon.

Using infrared absorption techniques, Bean et al.23 studied electron irradiation damage in silicon containing high concentrations of boron. They observed two absorption lines at 733.0 and 760.0 cm<sup>-1</sup>, labeled Q lines, which arise from vibrational modes of <sup>11</sup>B and <sup>10</sup>B in a center which still has to be identified. They reported that the intensity of the Q lines did not change upon annealing until 220 °C. Obviously, the  $E_c - 0.27 - eV$ level observed by us cannot be correlated to the Q lines. Some other boron-associated defects have been reported by Cherki and Kalma<sup>24</sup> using the photoconductivity technique and by Tan et al.25 using the internal friction technique. We are not able to establish any correlation between these defects and the  $E_c = 0.27 - \text{eV}$  level observed by us.

Using electrical measurements, Vavilov, Mukashev, and Spitsyn<sup>26</sup> observed annealing stages at 360-500 °K in boron-doped silicon and 460-560 °K in aluminum- and gallium-doped samples. They also reported a deep donor level at  $E_v + 0.45$  eV in p-type silicon associated with the annealing stage, irrespective of the type of acceptor impurity. They suggested that the defects in question were complexes consisting of vacancies and acceptor impurity atoms. Their annealing stage in borondoped sample occurred at roughly the same temperature as the  $E_n = 0.27$ -eV level. A small annealing stage in carrier recovery at ~170 °C was observed by Stein and Gereth<sup>27</sup> in their annealing study of  $10-\Omega$  cm boron-doped pulled silicon. These results from electrical measurements are consistent with our results that an electrically active defect in boron-doped material disappears upon annealing around 170 °C.

Since we are unable to correlate the  $E_c-0.27{\text{-eV}}$  level to any known boron-associated defect, there is room for speculation. Two experimental findings obtained from our study are important to this speculation: (i) the defect causing the  $E_c-0.27{\text{-eV}}$  level anneals out by dissociation at 170 °C as indicated by our values for the activation energy and the frequency factor: and (ii) this defect is in a positively charged state with an energy level close to the conduction band. The latter indicates that the defect could be interstitial type. Since the boron interstitial is mobile at room temperature, the defect has to be a second generation defect. After careful consideration, we suggest that the

defect is a complex formed by the trapping of an interstitial boron by an interstitial oxygen. This model seems to fit the experimental data well. There are a lot of oxygen atoms available in our sample for the trapping of the mobile interstitial boron. In addition, the chemical bonding energy between oxygen and boron (~192 kcal/mole) is slightly higher than that between silicon and oxygen (~188 kcal/mole), 20 showing that the formation of the interstitial boron-oxygen complex,  $[B_i + O_i]$ , is energetically possible. This  $[B_i + O_i]$ defect dissociates itself by emitting an interstitial boron at 170 °C. The interstitial boron is then trapped by a multivacancy-oxygen complex to form a vacancy-oxygen-boron complex. The reasons for suggesting this process are (i) the high concentration of the vacancy-oxygen complexes available, and (ii) the high chemical bonding energy between oxygen and boron. This vacancy-oxygenboron complex gives rise to the  $E_v + 0.30$ -eV level appearing upon the disappearance of the  $E_c = 0.27 - eV$ level and disappearing upon annealing around 400 °C. It is known that the vacancy-oxygen complex disappears upon annealing around 300 °C. It seems reasonable that the additional trapping of a boron at the vacancy site requires a higher annealing temperature. The experimental data in Fig. 2 show a competition for a primary defect in the formation of the defects causing the  $E_v + 0.38$ - and  $E_{\it c}$  -0.27-eV levels. We think that the competition is for the self-interstitial by the substitutional carbon and substitutional boron.

Kimerling<sup>8</sup> has speculated that the  $E_c = 0.27 - eV$ level is associated with a boron-boron pair which is formed by the trapping of the interstitial boron at a substitutional boron site, similar to the carbon-carbon pair in silicon reported by Brower.21 If it is so, the production rate of the level ought to be proportional to the square of the boron concentration. However, the data available (see Fig. 8) indicate a dependence on the boron concentration to a power of  $\frac{1}{2}$  to 1. He has also speculated that the  $E_v + 0.30$ -eV level formed upon the disappearance of the  $E_c - 0.27$ -eV level is associated with the di-interstitial identified by Brower. However, that the annealing of the di-interstitial occurs around 500 °C, about 100 °C higher than that of the  $E_v + 0.30$ -eV level, argues against this association.

Our suggestion that the  $E_c-0.27-$  and  $E_v+0.30-$ eV levels are associated with the interstitial oxygen-boron complex and the vacancy-oxygen-boron complex, respectively, agrees with the experimental data available. However, we would like to emphasize the speculative nature of the suggestion. Further studies should pursue these possibilities.

#### C. Other trapping levels

In the present study, we have observed several other levels appearing upon irradiation or annealing at higher temperature in one sample or the other. Because of the lack of more detailed information concerning these levels, we shall not discuss them further than the report of their existence.

#### V. SUMMARY

The  $E_c-0.27$ -,  $E_v+0.38$ -, and  $E_v+0.23$ -eV levels are the dominant levels observed in p-type boron-doped silicon irradiated with 1-MeV electrons at room temperature. The experimental data for these three levels obtained by the present study as well as by others are consistent with a

model in which the  $E_c$  – 0.27-,  $E_v$ +0.38-, and  $E_v$ +0.23-eV levels are associated with the interstitial oxygen-boron complex, the vacancy-carbon-oxygen complex, and the divacancy, respectively. The  $E_v$ +0.30-eV level, which appears upon the disappearance of the  $E_c$ -0.27-eV level at 170 °C, may arise from the vacancy-oxygen-boron complex. Several additional majority carrier trapping levels have been observed upon irradiation or upon annealing at higher temperatures in p-type silicon.

### ACKNOWLEDGMENT

We thank Dr. Y. H. Lee for many helpful discussions. We also thank Dr. L. C. Kimerling for his beneficial advice in the initial stage of our capacitance measurements.

- \*Supported in part by the ONR under Contract No. N00014-75-C-0919.
- †Permanent address: Dept. of Physics and Astronomy, Vassar College, Poughkeepsie, N. Y. 12601.
- ‡Permanent address: Hiradåstechnikai Ipari Kutató Intézet., Félvezető Főosztály, Budapest IV, Foti-u 56, Hungary.
- §Supported in part by the John Simon Guggenheim Memorial Foundation.
- <sup>1</sup>G. D. Watkins, in *Radiation Damage in Semiconductors* (Dunod, Paris, 1965), p. 917.
- <sup>2</sup>G. D. Watkins, Phys. Rev. B <u>12</u>, 5824 (1975).
- <sup>3</sup>G. D. Watkins and K. L. Brower, Phys. Lett. <u>36</u>, 1329
- <sup>4</sup>G. D. Watkins, Phys. Rev. B 13, 2511 (1976).
- <sup>5</sup>D. V. Lang, J. Appl. Phys. <u>45</u>, 3014 (1974).
- <sup>6</sup>D. V. Lang, J. Appl. Phys.  $\overline{45}$ , 3023 (1974).
- <sup>7</sup>Y. H. Lee, L. J. Cheng, J. D. Gerson, P. M. Mooney, and J. W. Corbett, Solid State Commun. 20, 109 (1976).
- <sup>8</sup>L. C. Kimerling, IEEE Trans. Nucl. Sci. NS-23, 1497 (1976); Proceedings of the International Conference on Radiation Effects in Semiconductors, Dubrovnik, Yugoslavia, Sept. 1976 (unpublished).
- <sup>9</sup>J. W. Walker and C. T. Sah, Phys. Rev. B <u>7</u>, 4587 (1973).
- <sup>10</sup>J. W. Corbett and G. D. Watkins, Phys. Rev. <u>138</u>, A555 (1965).
- <sup>11</sup>A. Mayer, Solid State Technol. <u>15</u>, 38 (1972).
- <sup>12</sup>Y. H. Lee and J. W. Corbett (unpublished).
- <sup>13</sup>N. Almeleh and B. Goldstein, Phys. Rev. <u>149</u>, 687 (1966).

- <sup>14</sup>R. C. Newman and R. S. Smith, J. Phys. Chem. Solids 30, 1493 (1969).
- <sup>15</sup>E. G. Sieverts, M. Sprenger, and C. A. J. Ammerlaan (private communication).
- <sup>16</sup>G. N. Galkin, N. S. Rytova, and V. S. Vavilov, Sov. Phys.-Solid State 2, 1819 (1961).
- <sup>17</sup>R. H. Glaenzer and C. J. Wolf, J. Appl. Phys. <u>36</u>, 2197 (1965).
- <sup>18</sup>K. Nakashima and Y. Inuishi, J. Phys. Soc. Jpn. <u>29</u>, 1500 (1970).
- <sup>19</sup>B. L. Gregory and C. W. Gwyn, Sandia Laboratories Report No. SC-M-71 0887, 1971 (unpublished).
- <sup>20</sup> Handbook of Chemistry and Physics, 52nd ed. (Chemical Rubber Co., Cleveland, Ohio, 1971), p. F-177.
- <sup>21</sup>K. L. Brower, Phys. Rev. B <u>14</u>, 872 (1976).
- $^{22}$ Y. H. Lee (private communication).
- <sup>23</sup>A. R. Bean, S. R. Morrison, R. C. Newman, and R. S. Smith, J. Phys. C <u>5</u>, 379 (1972).
- <sup>24</sup>M. Cherki and A. H. Kalma, Phys. Rev. B <u>1</u>, 647 (1970)
- <sup>25</sup>S. I. Tan, B. S. Berry, and W. F. J. Frank, *Ion Implantation of Semiconductors and Other Materials*, edited by B. L. Crowder (Plenum, New York, 1973), p. 19.
- <sup>26</sup>V. S. Vavilov, B. N. Mukashev, and A. V. Spitsyn, Radiation Damage and Defects in Semiconductors, edited by J. E. Whitehouse (Institute of Physics, London, 1973), p. 191.
- <sup>27</sup>H. J. Stein and R. Gereth, J. Appl. Phys. <u>39</u>, 2890 (1968).