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# Room-Temperature Irradiation of p-Type Silicon[2])

By

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Transient capacitance spectroscopy is used to study majority and minority traps introduced in pulled and float-zone boron-doped silicon, after 1.5 MeV electron irradiation at room temperature. In addition to familiar levels attributed to the positive charge state of the divacancy, the carbon interstitial, and the carbon-related defects, some other traps previously reported in solar cells are detected. In pulled silicon the minority trap $E_c - 0.26$ eV is studied and the results favour its attribution to the $(B_i-O_i)$ complex. Some differences exist between these results and those already reported by other authors for p-type silicon. In particular, the peak normally attributed to the carbon interstitial displays different annealing behaviour between the float-zone and the pulled material.

Nichtstationäre Kapazitäts-Spektroskopie wird benutzt, um die Majoritäts- und Minioritäts-trägerhaftstellen, die in aus der Schmelze gezogenem und zonengezogenem bordotierten Silizium nach Bestrahlung mit 1,5 MeV-Elektronen bei Zimmertemperatur eingeführt werden, zu untersuchen. Zusätzlich zu bekannten Niveaus, die den positiven Ladungszustand der Divakanz, der Kohlenstoffzwischengitterstörstelle und kohlenstoffverknüpften Defekten zugeordnet werden, werden einige andere Haftstellen, die früher in Solarzellen beobachtet wurden, nachgewiesen. In aus der Schmelze gezogenem Silizium wird die Minoritätshaftstelle $E_c - 0,26$ eV untersucht und die Ergebnisse deuten auf eine Zuordnung zum $(B_i-O_i)$-Komplex hin. Einige Differenzen bestehen zwischen diesen Ergebnissen und denen, die bereits von anderen Autoren für p-leitendes Si berichtet wurden. Insbesondere zeigt das Maximum, das normalerweise der Kohlenstoffzwischen-gitterstörstelle zugeordnet wird, ein unterschiedliches Temperungsverhalten in zonengezogenem und aus der Schmelze gezogenem Material.

## 1. Introduction

In this paper we have applied deep level transient spectroscopy (DLTS) and minority carrier trap spectroscopy (MCTS) [1, 2] in order to study defects in electron-irradiated silicon. We expect that electron bombardment of low energy and dose, at room temperature, should produce complexes comprising intrinsic defects and imperfections (such as impurity atoms) in the crystal. It may also produce complexes from interaction between impurity atoms, like the boron interstitial-oxygen interstitial structure.

## 2. Experimental Details

### 2.1 Specimen preparation

In DLTS experiments great care must be taken for the preparation of acceptable specimens. Surface damage or contamination of any kind give rise to strong peaks and render the results confused and unreliable.

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We have taken specimens from pre-polished wafers of about 0.4 mm thickness. The wafers were of ⟨111⟩ orientation for the float-zone and ⟨100⟩ for the pulled materials. We tried to produce by cleaving specimens with dimensions of approximately 5 × 5 mm².

A degrease procedure with ultrasonic bath in very pure trichloroethylene, acetone, methanol, and de-ionized water preceded the etching, which was made in a solution of acids $HNO_3:CH_3COOH:HF$ in the ratio 5:3:3 respectively, for 30 to 45 s. 1% gallium-doped gold was then evaporated under vacuum ($\approx 10^{-4}$ Pa) on the unpolished face of the specimens to produce the ohmic contact. Then a Schottky barrier from very pure aluminum was fabricated in two steps to provide a semitransparent metal film with the final aim to make feasible either electrical measurements for the study of majority traps, or optical measurements (after laser illumination) for the study of minority traps.

The samples used were diodes of boron-doped float-zone and pulled silicon with boron concentrations of $\approx 3 \times 10^{15}$ cm$^{-3}$ and $4.7 \times 10^{15}$ cm$^{-3}$, respectively.

### 2.2 Irradiation procedure

We irradiated the specimens with 1.5 MeV electrons from a Van der Graaff accelerator of Reading University (England) to a dose of $\approx 10^{16}$ e$^-$/cm$^2$ at a current of 0.1 μA/cm². The later was measured with a Faraday cup. The bombardment took place at room temperature under vacuum of $10^{-2}$ Pa.

The samples were placed on a plate on a water-cooled block to reduce the temperature increase during irradiation.

### 2.3 The DLTS apparatus

We used a DLTS commercial system from Polaron Ltd. A triple boxcar integrator with three sampling gates allowed the simultaneous implementation of two rate windows and hence the outputting of two spectra during one temperature scan. A GaAs laser, driven by the pulse generator, was used for the optical excitation of minority traps during the MCTS experiments. Unfortunately the filling pulses were not square for widths less than $\approx 500$ ns, a fact that imposed an upper limit on capture cross-section analysis.

The reported activation energies are accurate to about $\pm 0.02$ eV. Any given capture cross-section is referred to the temperature where the corresponding signal has appeared in the spectrum.

## 3. Experimental Results and Discussion

We have adopted a labelling system with the use of prefixes H or E and a number in brackets indicating the hole (H) energy from the valence band or the electron (E) energy from the conduction band.

The typical spectrum for the pulled silicon is shown in Fig. 1. Three main DLTS peaks are depicted there: $H_1$ (0.21 eV), $H_2$ (0.28 eV), and $H_3$ (0.39 eV). Judging from the energy levels, the position in the spectrum, the relative concentrations, and the annealing behaviour we may attribute $H_1$ and $H_2$ to the divacancy and the carbon interstitial, respectively. During repeated scans in the range 80 to 300 K we saw $H_2$ decay and $H_3$ grow at the same time, indicating that $H_3$ is carbon-related. In about five hours $H_2$ had completely vanished. The increase of $H_3$ is clearly smaller than the decrease in $H_2$. This fact has led Lee et al. [3] to suggest the possibility that the carbon interstitial may also go to some unknown defects, as observed in infrared studies [4]. A capture cross-section analysis for $H_3$ gave two straight branches for
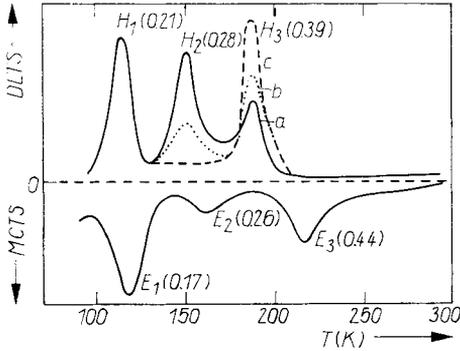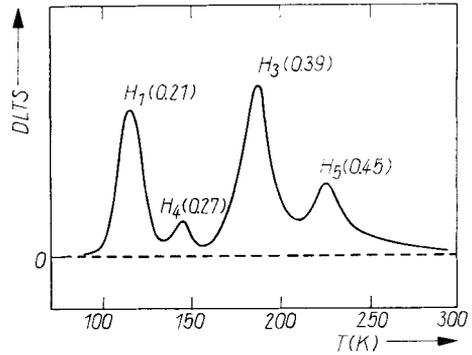
Fig. 1                                                    Fig. 2

Fig. 1. DLTS and MCTS spectrum of boron-doped, pulled silicon after 1.5 MeV electron irradiation at room temperature (r. w. = 40 s$^{-1}$). (a) 0.5 h, (b) 2 h, (c) 5 h after irradiation

Fig. 2. The DLTS spectrum of pulled silicon after annealing at 450 K for 90 min (r. w. = 40 s$^{-1}$)

the graphical representation of lg $(S_0 - S)/S_0 = f$ (pulse width), where $S_0$ is the maximum signal corresponding to a long enough pulse width for the trap to become saturated. This may suggest that two defects are associated with $H_3$. The corresponding capture cross-sections are $\sigma_1 \approx 6 \times 10^{-17}$ cm$^2$ and $\sigma_2 \approx 9.50 \times 10^{-19}$ cm$^2$. The defect with $\sigma_1$ has been attributed to the K-centre (V–O–C) [4, 5], but there are some doubts [3, 5], if we can correlate the second defect of $H_3$ with the carbon interstitial-carbon substitutional pair ($C_i$–$C_s$) as is suggested in [6].

Three minority traps are present in the MCTS spectrum of Fig. 1; $E_1$ (0.17 eV), which we may attribute to the A-centre (V–O), $E_2$ (0.26 eV) and $E_3$ (0.44 eV). We shall defer the discussion of $E_2$ until we give the MCTS spectrum for the float-zone material.

Fig. 2 shows the DLTS spectrum of the pulled silicon after annealing at 450 K for 90 min. Two new peaks appear, $H_4$ (0.27 eV) with $\sigma_4 \approx 0.8 \times 10^{-18}$ cm$^2$ and $H_5$ (0.45 eV) with $\sigma_5 \approx 0.5 \times 10^{-18}$ cm$^2$. The MCTS spectrum after the annealing is the same as in Fig. 1 apart from a decrease in the peak height of $E_2$.

We have summarized the energy levels determined for the pulled silicon in Table 1.

Table 1

Energy levels of defects observed in this study for boron-doped pulled silicon

| | identification of the defects | energy levels | other remarks |
|---|---|---|---|
| after irradiation | $V_2$ | $E_v + 0.21$ eV | |
| | $C_1$ | $E_v + 0.28$ eV | |
| | K-center and | $E_v + 0.39$ eV | $\sigma_1 = 6 \times 10^{-17}$ cm$^2$ |
| | $(C_s–C_I)$ ( ?) | | $\sigma_2 = 9.5 \times 10^{-19}$ cm$^2$ |
| | A-center | $E_c - 0.17$ eV | |
| | $(B_i + O_i)$ | $E_c - 0.26$ eV | |
| | $V_2$ ( ?) | $E_c - 0.44$ eV | |
| after annealing at 450 K for 90 min ? | $(v + 0 + B)$ | $E_v + 0.27$ eV | $\sigma = 0.8 \times 10^{-18}$ cm$^2$ |
| | | $E_v + 0.45$ eV | $\sigma = 0.5 \times 10^{-18}$ cm$^2$ |
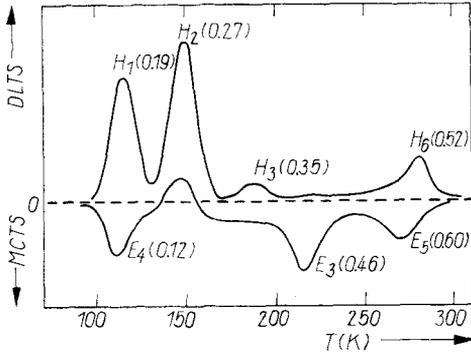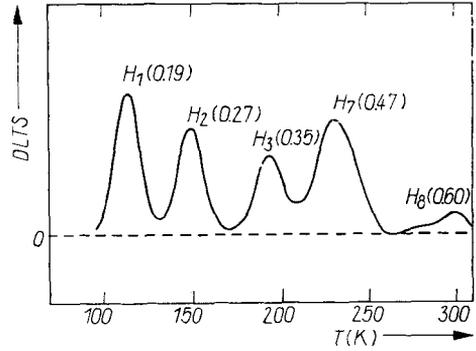
Fig. 3



Fig. 4

Fig. 3. The DLTS and MCTS spectrum of boron-doped, float-zone silicon after 1.5 MeV electron irradiation at room temperature (r. w. $= 40 \ s^{-1}$)

Fig. 4. The DLTS spectrum of float-zone silicon after annealing at 450 K for 90 min (r. w. $= 40 \ s^{-1}$)

Fig. 3 shows the typical spectrum for the float-zone silicon. The divacancy $H_1$ (0.19 eV), the carbon interstitial $H_2$ (0.27 eV), $H_3$ (0.35 eV), and $H_6$ (0.52 eV) are the DLTS peaks which appear here. We should notice that $H_2$ does not show any change in peak height during repeating scans in the range 80 to 300 K. $H_3$ is also unchanged during the above scans. Three traps again appear in the MCTS spectrum, $E_4$ (0.12 eV), $E_3$ (0.46 eV), and $E_5$ (0.60 eV). The labelling system in float-zone silicon is compatible with and an extension of that used for the pulled material.

Fig. 4 displays the DLTS spectrum after annealing at 450 K for 90 min. $H_6$ (0.52 eV) has vanished and two new levels have arisen: $H_7$ (0.47 eV) and $H_3$ (0.60 eV). Remarkably, the defect we have attributed to the carbon interstitial is still present with relatively small loss in its concentration. The MCTS spectrum also remains unchanged. Table 2 summarizes the energy levels determined for the float-zone silicon.

Table 2

Energy levels of defects measured in this study for boron-doped float-zone silicon

| | identification of the defects | energy levels | others remarks |
|---|---|---|---|
| after irradiation | $V_2$ | $E_v + 0.19$ eV | |
| | $C_I$ | $E_v + 0.27$ eV | |
| | $(C_s–S_i–C_s)$ (?) | $E_v + 0.35$ eV | |
| | ? | $E_v + 0.52$ eV | |
| | ? | $E_c - 0.12$ eV | |
| | $V_2$ (?) | $E_c - 0.46$ eV | |
| | ? | $E_c - 0.60$ eV | |
| after annealing at 450 K for 90 min | ? | $E_v + 0.47$ eV | also appeared in Al-doped Si |
| | ? | $E_v + 0.60$ eV | |

We discuss first the behaviour of the carbon interstitial ($C_I$). The annealing characteristics of $C_I$ as found in our experiment for the pulled silicon are consistent with already published data [3, 6]. In float-zone silicon we found that $H_2$ remains, after annealing at 450 K for 90 min, in contrast with previous published data. EPR measurements, for example, in vacuum floating-zone-refined p-type silicon (B: $10^{15}$ cm$^{-3}$) have shown a conversion of $C_I$, after annealing at 65 °C for 30 min, to the Jahn-Teller-distorted $\langle 111 \rangle$ C–C interstitialy [7]. We repeated the experiment with float-zone specimens of different boron concentration in the range $1 \times 10^{15}$ to $1 \times 10^{16}$ cm$^{-3}$. We found the same annealing behaviour for $H_2$ as reported above. It is also noteworthy that $C_I$ produced after irradiation of similar float-zone specimens at 80 K has the normal annealing behaviour vanishing at room temperature after some hours [8] and giving rise to a defect with energy $E_v + 0.36$ eV which has been identified as the $C_s$–$Si_i$–$C_s$ complex [9]. The defect labelling $H_3$ (0.35 eV) may be associated with the $C_s$–$Si_i$–$C_s$ complex and not with the K-centre because of the low oxygen content in the float-zone material. Thus, if $H_2$ is correctly attributed to $C_I$, the latter is not annealed out completely after room temperature irradiation in our float-zone material.

In MCTS we shall discuss the levels $E_2$ (0.26 eV) and $H_7$ (0.27 eV), the latter produced after annealing at 450 K, together. $E_2$ has been attributed by Mooney et al. [5] to the boron interstitial–oxygen ($B_i$–$O_i$) complex and by Kimerling [6] to the boron interstitial–boron substitutional ($B_i$–$B_s$) pair. $H_7$, rising after the dissociation of $E_2$, has been associated either with the (V–O–B) complex [5] or with the di-interstitial silicon ($Si_i$–$Si_i$) pair [6]. In our results the total absence of $E_2$ from the float-zone spectrum (the boron concentration in float-zone Si was slightly lower than in pulled material) may be taken as an indication that the ($B_i$–$O_i$) complex is the likely candidate for this defect as suggested in [5]. The results from solar cells [10, 11] point to similar identification. A more detailed analysis with diffused n$^+$–p solar cells [12] has shown that the mobile boron interstitial ($B_i$) can interact either with the interstitial oxygen (when B $\approx 2 \times 10^{16}$ cm$^{-3}$) to form the ($B_i$–$O_i$) pair as in our case, or with the substitutional boron (for higher boron concentrations, e.g. $7 \times 10^{16}$ cm$^{-3}$, where the competition between $B_s$ and $O_i$ for $B_i$ becomes apparent) to form the ($B_i$–$B_s$) pair. In the latter case $E_2$ is depressed and a majority trap with energy $E_v + 0.30$ eV appears. The fact that we have not detected the latter is compatible with the relatively small boron concentration of our specimens. It is noteworthy from our results that $E_2$ does not disappear completely after 90 min at 450 K.

The fact that the peak $H_6$ (0.52 eV), seen only in the float-zone material, disappears after the annealing while $H_7$ (0.47 eV) appears is in accordance with the results for solar cells [10]. A defect level similar to our $H_7$ observed in aluminum-doped float-zone material [6, 13], has been associated with the (Al–V) pair. Such an association is unlikely here, for the boron–vacancy pair has already been identified by EPR [14] and DLTS [8] measurements and has different annealing properties.

We note that $E_1$ (0.12 eV) has been detected with other techniques in n-type silicon [15, 16]. Finally, the level $E_3$ (0.45 eV) common in room and liquid nitrogen temperature irradiation of pulled and float-zone silicon may be one of the manifestations of the divacancy.

## References

[1] D. V. Lang, J. appl. Phys. **45**, 3023 (1974).

[2] G. L. Miller, D. V. Lang, and L. C. Kimerling, Ann. Rev. Mater. Sci., 377 (1977).

[3] Y. H. Lee, L. J. Cheng, J. D. Jerson, P. M. Mooney, and J. W. Corbett, Solid State Commun. **21**, 109 (1977).

[4] A. Brelot and J. Charlemagne, in: Irradiation Effects in Semiconductors, Ed. W. Corbett and G. D. Watkins, Gordon & Breach, New York 1971 (p. 161).

[5] P. M. Mooney, L. J. Cheng, M. Süli, J. D. Jerson, and W. Corbett, Phys. Rev. B **15**, 3836 (1977).

[6] L. C. Kimerling, Radiation Effects in Semiconductors, 1974, Inst. Phys. Conf. Ser. No. 31. 221 (1977).

[7] G. D. Watkins and K. L. Brower, Phys. Rev. Letters **22**, 1329 (1976).

[8] S. K. Bains and P. C. Banbury, J. Phys. C **18**, L109 (1935).

[9] K. P. O'Donnell, K. M. Lee, and G. D. Watkins, Physica (Utrecht) **116B**, 257 (1983).

[10] J. T. Schott, H. M. De Angelis, and R. J. Drevinsky, J. Electronic Mater. **9**, 419 (1980).

[11] M. Roux, J. Bernard, and R. Renlet, J. appl. Phys. **56**, 531 (1934).

[12] P. J. Drevinsky and H. M. DeAngelis, 13th Internat. Conf. Defects in Semiconductors, Coronado (CA), August 12 to 17, 1984, Proc. to be published in J. Electronic Mater., December 1984.

[13] Y. H. Lee, K. L. Wang, A. Jaworowski, P. M. Mooney, L. J. Cheng, and J. W. Corbett, phys. stat. sol. (a) **57**, 697 (1980).

[14] G. D. Watkins, Phys. Rev. B **13**, 2511 (1976).

[15] G. K. Werthein and D. N. E. Buchaman, J. appl. Phys. **30**, 1232 (1959).

[16] H. J. Stein and F. L. Vook, Phys. Rev. **163**, 790 (1967).