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Abstract. DLTS and MCTS studies are reported for boron-doped (about $3.5 \times 10^{15}\,cm^{-3}$) pulled silicon specimens which have been subjected to electron irradiation at 1.5 MeV at about 80 K. A number of previously reported and identified features are observed and two new peaks are reported, the first possibly dependent on oxygen content at an energy level of about $E_v + 0.13$ eV and with a capture cross section of about $10^{-18}\,cm^2$, the second with a charge-dependent peak amplitude at an energy of $E_v + 0.34$ eV—apparently a vacancy-dependent complex annealing out at around room temperature.

1. Introduction

As a continuation of recently reported studies of electron-irradiated boron-doped float-zone silicon (Bains and Banbury 1985, referred to here as I) we have made deep-level transient spectroscopy (DLTS) and minority-carrier-trap spectroscopy (MCTS) measurements for specimens from pulled crystals with boron-doping concentrations around $3.5 \times 10^{15}\,cm^{-3}$. In reporting further results here we adopt a labelling system for observed peaks compatible with and extending that used in I.

Some information on the effects of 1 MeV electron irradiation on rather more lightly doped diffused silicon junctions has been given by Kimerling *et al* (1979). They reported only features attributed to the vacancy, the carbon interstitial and a small feature arising from the donor state of the divacancy.

2. Experimental procedure

Schottky diodes were fabricated on slices of polished and etched boron-doped pulled silicon. The Schottky electrodes were applied by successive evaporations of aluminium through different masks to give an electrode semi-transparent over the larger part of its area—to permit laser illumination of the barrier for MCTS measurements—but thicker in a small region to facilitate electrical contact. Specimens were subjected to tests of capacitance against voltage and against temperature to verify near-ideal behaviour before acceptance for experimental use. DLTS and MCTS measurements before irradiation gave no significant signals for any of the specimens reported here.

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Diodes were mounted in a liquid nitrogen cryostat for irradiation and subsequent temperature cycling; irradiations by 1.5 MeV electrons at 0.15 μA cm^{-2} to a dose of 1.7×10^{16} electrons cm^{-2} were performed at about 80 K. Measurements by transient spectroscopy were then undertaken over temperature ranges at first restricted to below about 150 K, the threshold of vacancy migration (Watkins 1963); then, after annealing, they were restricted to below the temperature of the anneal.

DLTS and MCTS measurements were normally recorded under 5 V reverse bias with a DLTS forward-filling pulse amplitude ~5.7 V to eliminate the barrier during the filling operation. Excitation for MCTS was provided by a pulsed GaAs laser.

During annealing at 215 K, bias on the diode was set to 0 or −5 V as desired, to reveal charge-dependent metastable effects.

3. Results and discussion

The results obtained after irradiation are summarised in figures 1–3. Initial measurements below 155 K (figure 1) gave a peak H1 observed at a rate window of 2500 s^{-1} but outside the range of energy level measurement of the equipment; with a rate window of 0.4 s^{-1}, two other peaks labelled H9 and H3 were seen, for which we obtained energies

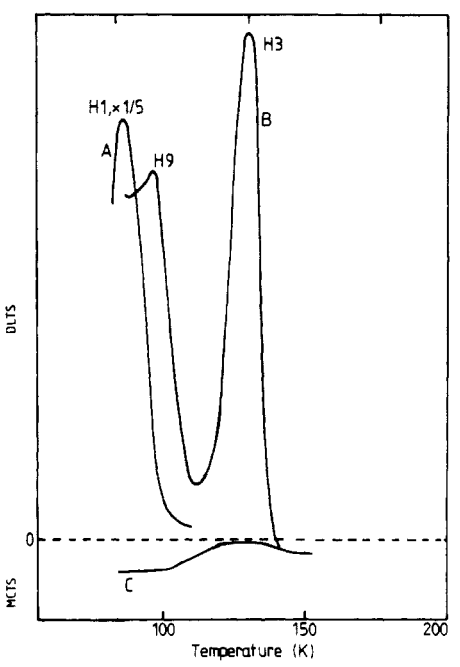

Figure 1. DLTS and MCTS signals (both given in arbitrary units) for the specimen after irradiation at about 80 K. (A) Rate window 2500 s^{-1} (DLTS). (B) Rate window 0.4 s^{-1} (DLTS). (C) Rate window 2 s^{-1} (MCTS).

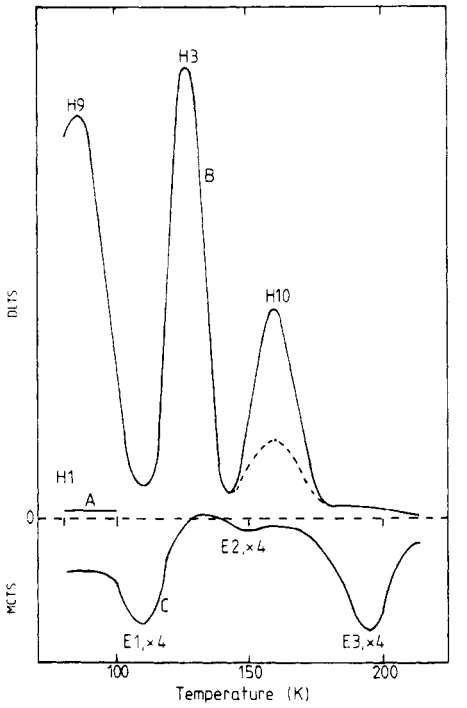

Figure 2. DLTS and MCTS signals (both given in arbitrary units) for the specimen after irradiation and annealing at 215 K for 30 min. (A) Rate window 2500 s^{-1} (DLTS). (B) Rate window 0.4 s^{-1} (DLTS): full curve, after zero-bias anneal; broken curve, after anneal under reverse bias of 5 V. (C) Rate window 2 s^{-1} (MCTS).

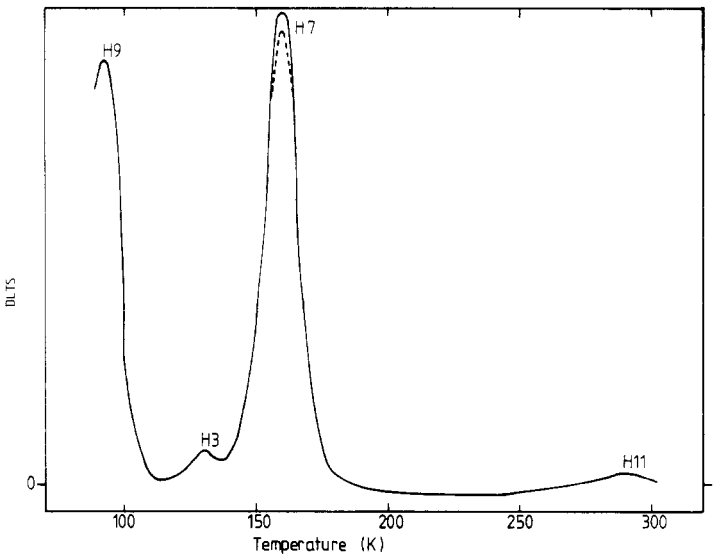

Figure 3. DLTS signals (in arbitrary units) for the specimen after irradiation and annealing at 315 K for 1 h (rate window 0.4 s^{-1}). The MCTS signal was unchanged from that for figure 2, with no features between 215 and 315 K.

of $E_v + 0.13$ eV and $E_v + 0.27$ eV. H1 and H3 have been attributed to the vacancy and the carbon interstitial respectively (I). MCTS results have no structure at this stage.

After annealing at 215 K for 30 min under zero bias (figure 2), H1 has disappeared, as expected for the vacancy; H9 and H3 remain and a new signal H10 ($E_v + 0.34$ eV) appears in the extended temperature range now available. In MCTS results after the 215 K anneal, two main peaks labelled E1 and E3 are seen with energies $E_c - 0.18$ eV and $E_c - 0.47$ eV, together with another faint signal E2.

In figure 3, results after annealing to 315 K show H9 unchanged and H3 almost absent; a new peak H7 (I) is seen at $E_v + 0.36$ eV, with properties distinct from those of H10, as discussed later, and another very weak signal H11 corresponding to an energy near the centre of the gap. The MCTS spectrum of figure 2 is unaltered by the 315 K anneal, and shows no further features between 215 and 315 K.

In a further anneal to 425 K for 30 min, H9 was unchanged and H7 slightly increased with the final disappearance of H3. After a final anneal of 60 min at 470 K, H9 and H7 are still present, and a new peak H12 ($E_v + 0.5$ eV) of small amplitude has appeared. The MCTS spectrum was unaffected by the above annealings.

The peak labelled H9 would appear to be the same as that reported by Brabant *et al* (1977) at $E_v + 0.12$ eV, obtained from thermally stimulated capacitance studies in similar material after 1.5 MeV electron irradiation at liquid helium temperature; the fact that a further anneal of 60 min at 470 K did not cause any change in H9 is consistent with this postulated identity and the annealing of results of Brabant *et al* (1977). A capture cross section analysis in our case gave rather poor linearity with a value of the order of 10^{-18} cm^2. Brabant *et al* (1977) debate and leave open the possibility that this defect is the isolated divacancy, despite the rather large discrepancy in energy from that normally accepted, around $E_v + 0.23$ eV. The fact that the feature seen in I with energy $E_v + 0.19$ eV, attributed to the divacancy, was small compared with H9 seen here would suggest that the presence of oxygen is relevant to the appearance of the feature. The

dependence of divacancy formation on the presence of interstitial oxygen, reported and discussed by Oehrlein *et al* (1983), would provide a correlation of the right sense here. In our experiments the peak H9 was seen to have risen by 7% on average after vacancy migration.

The peak labelled H10 appears to rise from a vacancy-related defect. Its maximum amplitude was similar on different specimens and gave a trap concentration around one third of that obtained from the pre-annealing vacancy peak, allowing for the negative-U property of the latter. However, H10 was found on further investigation to show a variable amplitude, with the following systematic behaviour. In many observations for the lowest-rate window ($0.4\ s^{-1}$) curves similar to the full curve in figure 2 were obtained after a five-minute anneal at 215 K under zero bias and quenching to 80 K. The same temperature sequence under 5 V reverse bias gave the broken curve with a peak amplitude of less than half its previous value. In every case the peak could be regenerated by a zero-bias 215 K anneal and quenching; without the quench and with a downward temperature ramp for DLTS the peak was much reduced, as expected under the occupancy condition of the trap (full in the case of this p-type material) which prevails for most of the time under the negatively biased measurement cycle at the low-rate window ($0.4\ s^{-1}$) at temperatures above the temperature of the peak signal. If we regard this peak as being associated with the centre when in one of two possible configurations, the alternative form, favoured under reverse bias, has not been seen in these studies.

Difficulties arise however, when we try to examine the spectrum for higher-rate windows to determine the trap energy. At a rate window of $1\ s^{-1}$ the results are all in agreement with those described above, but for higher-rate windows (for which the DLTS feature is centred above 170 K) the peak is usually small and then charge dependence evidence becomes unclear. Further work is required here.

An attempt to study the annealing out of the defect giving rise to H10 was complicated by the appearance of H7 at a similar position, emerging with anneals from 294 K upwards. The charge-dependent component (figure 3) of the composite peak reduces as the temperature of the anneal increases; if we attribute all charge dependence to H10 this property may be used to estimate the strength of the latter as a function of annealing treatment. On this basis the zero-bias-regenerated H10 is found to begin to decay at about 270 K and to have been reduced by a factor of six in 60 min at 315 K.

H7 is a carbon-related defect arising in the spectrum simultaneously with the disappearance of interstitial carbon. This peak gave a single value of the capture cross section of $4.4 \times 10^{-17}\ cm^2$. However, the final assignment for this defect is not certain since there are two main candidates—the C_i–C_s pair (Kimerling 1977) and the C–O–V complex (Mooney *et al* 1977).

The MCTS spectra obtained after the five-minute anneal at 215 K under zero and under 5 V reverse bias and quenching to 80 K have not shown significant changes in the concentrations of the minority traps. We conclude that no complementary behaviour exists between any of the traps in the MCTS spectrum and the majority trap H10 in the DLTS spectrum.

E1 may be taken to be the A centre appearing after the disappearance of the isolated vacancy. Its magnitude is less than might be expected judging by that of the DLTS vacancy peak, but the magnitudes of peaks seen in DLTS and MCTS in our case prevent simple comparisons because of the limitations in the effective areas of optical excitation in the trap filling for MCTS. The amplitudes of the peaks in the MCTS spectrum are dependent on the sample. Notwithstanding this fact, E1 seems to be the same as that which Kimerling (1977) has attributed to the vacancy–oxygen centre, using comparisons of the

defect's introduction, its thermal stability and impurity dependence, together with EPR and IR absorption identifications. The amplitude of E1 is unaltered after the 315 K anneal—an indication that H7 might be correlated with the C_i–C_s pair (Kimerling *et al* 1979) and not the K centre which is thought to be created when a mobile carbon interstitial is captured by the V–O pair.

E2 is not sufficiently well resolved from background to permit an energy level determination. Because of the small amplitude and the broadness of the peak any precise determination of its activation energy is very difficult. From measurements on different samples we found that E2 has an activation energy in the range of 0.24–0.29 eV below the conduction band. Three traps obtained earlier give energy levels in this range: the B_i–B_s pair (Kimerling 1977), the B_i–O_i pair (Mooney *et al* 1977) and one of the charge states of the divacancy (Kimerling 1977). Watkins (1975) has proposed that silicon interstitials originally created as partners of Frenkel pairs in the primary irradiation damage effect somehow acquired mobility, so some pairs dissociated and the free interstitial injects a boron atom from its lattice site, creating a boron interstitial. The mobile boron interstitial can interact with either an interstitial oxygen or a substitutional boron. The doping impurity level (B: 4.7×10^{15} cm^{-3}) in our pulled material is much lower than the oxygen concentration (O: 10^{18} cm^{-3}). This rules out any possible assignment of E3 to the B_i–B_s pair. On the other hand since the carbon concentration (of order 10^{16} cm^{-3}) in our material exceeds that of boron we may surmise that the production of the boron interstitials is reduced in favour of the interstitial carbon. This is reflected by the fact that the boron interstitial has not been traced in our studies. Thus we may also reject the possibility of the identification of E3 with the B_i–O_i complex. Further support for this argument is the following: we know (Mooney *et al* 1977) that the B_i–O_i pair becomes unstable at around 150–200 °C giving rise to V–O–B complexes which introduce a majority level at $E_v + 0.28$ eV. This level has not been observed in our spectra. Furthermore, from the fact that E2 persists after annealing for 60 min at 470 K we might possibly attribute it to one manifestation of the divacancy.

We have also seen E3 in similarly doped specimens of float-zone material after the same irradiation and annealing treatment. The boron interstitial is a defect giving rise to at least one electrical level, 0.45 eV below the conduction band (Troxell and Watkins 1980), and anneals rapidly at room temperature (Watkins 1975). However, this is not the case for E3 which persists at temperatures of 470 K. It is worth noticing that a level 0.39 eV below the conduction band has been observed in slightly doped, pulled n-type silicon and attributed to a negatively charged centre correlated with the divacancy (Kimerling 1977).

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