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Charge-Dependent Defect Traces in the DLTS and MCTS Spectra of Silicon

By

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1.5 MeV electrons are used to irradiate boron-doped pulled silicon at 80 K and float-zone silicon at room temperature. In the pulled material a previously reported energy level $E_v + 0.13$ eV seems to acquire charge-dependent characteristics after annealing at 315 K. The A-center exhibits also a charge-dependent peak amplitude. In the float-zone material an $E_v + 0.09$ eV energy level is observed for the first time. This level is tentatively associated with one configuration of a metastable defect.

Aus der Schmelze gezogenes Silizium wird bei 80 K und zonengefloatetes Silizium bei Zimmertemperatur mit 1,5 MeV-Elektronen bestrahlt. In dem aus der Schmelze gezogenen Material scheint ein früher berichtetes Energieniveau $E_v + 0,13$ eV zu ladungsabhängigen Charakteristiken nach Temperung bei 315 K zu führen. Das A-Zentrum zeigt ebenfalls ein ladungsabhängiges Maximum. Im zonengefloateten Material wird erstmals ein Energieniveau bei $E_v + 0,09$ eV beobachtet. Dieses Niveau wird vorläufig mit einer Konfiguration eines metastabilen Defekts verknüpft.

1. Introduction

The study of defects is very important in semiconductor research. Since the defects control the charge carrier lifetime, it is necessary to know their formation, structure, and properties in order to improve the performance of semiconductor devices. Moreover, the study of defects is regarded today as a basic tool to understand the very nature of condensed matter. In this respect the study of metastable defects could provide additional information about the nature of semiconductors.

Recently some defects, exhibiting two metastable configurations [1, 2], have been studied with the method of deep level transient spectroscopy (DLTS) [3, 4]. These configurations are related to the charge state of the defect which in turn is controlled by the application or not of a reverse bias voltage to the samples at a certain temperature. The transformation from one configuration to the other is thermally (or electronically) activated. Therefore either configuration can be accessed experimentally by the proper use of temperature and junction bias conditions. Each configuration introduces its own levels in the energy gap and thus its own peaks in the DLTS spectrum.

2. Background

The basic procedure applied in order to reveal the two metastable configurations of a defect involves annealing at a certain temperature with the simultaneous application or not of a reverse bias voltage. A fast cooling of the samples, in order to freeze the

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²⁾ The experiment has been carried out in Reading University, England, during a leave of absence.

defect in the desired configuration, precedes the DLTS measurement. Let us consider a specimen which has been annealed under reverse bias conditions and the defects has been frozen in the first configuration, say A. The DLTS signal is obtained by superimposing forward voltage pulses on a steady reverse bias applied to the diode. Thus, for a time fraction depending upon the operating rate window, the junction is under forward bias. The charge state of the defect changes and the second configuration, say B, will be attained at a proper temperature. Therefore, configuration B can be detected during the first DLTS scan providing that the carrier emission rate, for the levels of this configuration, occurs at a temperature greater than the temperature $T_{A \rightarrow B}$ of the configurations transformation. In this case configuration A would not be observed unless its peaks appear in the spectrum at temperatures lower than $T_{A \rightarrow B}$.

3. Experimental

Schottky diodes were fabricated from boron-doped silicon. They were either of pulled kind with a 3 to 5 Ω cm resistivity or of float-zone kind with a 6.4 to 7.4 Ω cm resistivity. The specimen preparation procedure has been reported in detail previously [5].

Afterwards, the specimens were irradiated with 1.5 MeV electrons from the van der Graaf accelerator of Reading University (England). The pulled material has been irradiated at 80 K (using a liquid nitrogen cryostat) to a dose of $\approx 1.7 \times 10^{16}$ e⁻/cm² at a beam current of ≈ 0.15 μ A/cm². The float-zone material has been irradiated at room temperature to a dose of $\approx 1 \times 10^{16}$ e⁻/cm² at a beam current of ≈ 0.1 μ A/cm². The beam current was intentionally low to avoid undesired temperature rising during irradiation. To this end a cooling block using flowing water was mounted below the plate supporting the specimen.

The majority carrier traps introduced in the lower half of the forbidden gap of the p-type silicon were studied by means of the DLTS technique. A GaAs laser was used for the optical excitation of the minority carrier traps, introduced in the top half of the forbidden gap, during MCTS (minority carrier trap spectroscopy) measurements [6].

4. Results and Discussion

4.1 Pulled silicon

After irradiation at liquid nitrogen temperature the specimen has been allowed to warm up to room temperature. Annealing for some hours, under zero bias conditions, at room temperature, was performed to facilitate the migration of the carbon interstitial and the formation of the $E_v + 0.36$ eV level. However, another main peak with energy $E_v + 0.13$ eV is of particular interest in this study. This peak appears in the spectrum immediately after the low-temperature irradiation and behaves normally with all the available rate windows for DLTS scans in the range 80 to 300 K [7]. The fact is that this defect seems to acquire charge-dependent characteristics after annealing at 315 K. These characteristics are exhibited only for the slow rate windows. Fig. 1a shows the DLTS spectrum obtained with a rate window of 8 s⁻¹. The specimen had been annealed previously at 315 K for 30 min with bias off. The first scan (solid line) was recorded during an increasing temperature ramp. The second scan (dashed line) was recorded immediately after the first during a decreasing temperature ramp. In the latter scan the $E_v + 0.13$ eV level has disappeared. This level appears again only after a new annealing at 315 K. A repetition of the above procedure after an annealing at 315 K with a 5 V reverse bias has provided similar results. This phenomenon was repeated for all rate windows operating in the range from 0.4 to 100 s⁻¹. Fig. 1b

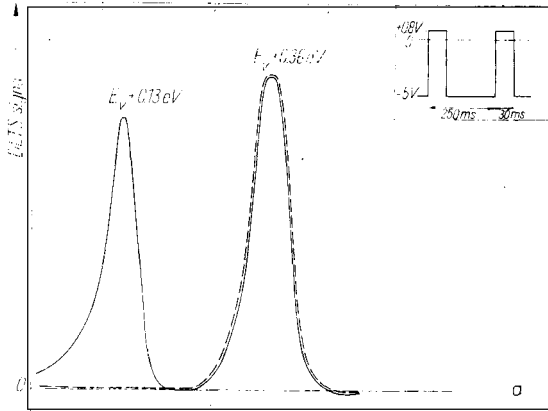
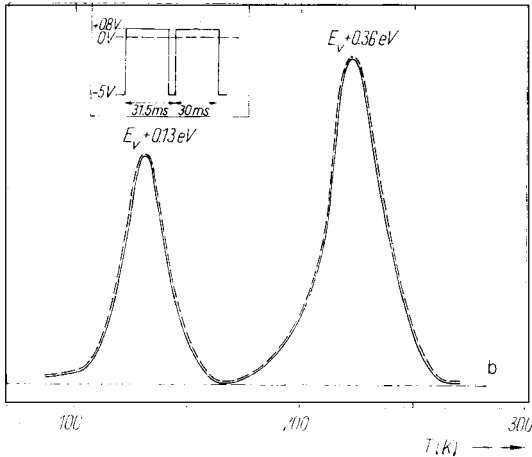


Fig. 1. The DLTS spectrum of the 1.5 MeV electron irradiated at 80 K, boron-doped pulled silicon, obtained after annealing at 315 K for 30 min with bias off a) rate window of 8 s^{-1} and b) 1000 s^{-1} . The solid curve is for increasing temperature and the dashed curve is for decreasing temperature. The obtained spectrum is quite the same for annealings with bias on



is a repetition of Fig. 1a but with a fast rate window operating at 1000 s^{-1} . The $E_v + 0.13 \text{ eV}$ level is always present with either temperature scanning modes. Similar results to Fig. 1b were obtained with the fastest available rate window of 2500 s^{-1} . The bias conditions (e.g. 0 or 5 V reverse voltage) during annealing do not seem to affect the obtained DLTS spectrum. However, on occasions when the fast rate windows of 1000 and 2500 s^{-1} are used the concentration of the $E_v + 0.13 \text{ eV}$ level is always decreased and that of the $E_v + 0.36 \text{ eV}$ increased (in comparison with the corresponding traces for slow rate windows). The increase of the latter is less than the decrease of the former.

These results cannot be explained by the simple model which suggests the existence of two metastable defect configurations, one attained by annealing under zero bias and the other under reverse bias. Moreover, the mere fact that this behaviour of the $E_v + 0.13 \text{ eV}$ level appears after the annealings at 315 K is most intriguing. Unfortunately, no detailed measurements have been performed to allow a clear explanation. However, it is obvious that this behaviour depends crucially on the used rate window. With slow rate windows the specimens are most of the time under reverse bias during the DLTS scanning. Conversely, with fast rate windows the specimens are most of the

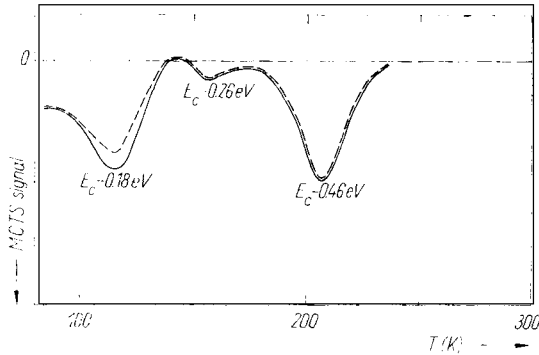


Fig. 2. The MCTS spectrum of the 1.5 MeV electron irradiated at 80 K, boron-doped pulled silicon. The solid curve is taken after cooling with bias off and the dashed curve after cooling with bias on (rate window 8 s^{-1})

time under forward bias. The insets in Fig. 1 a and b show the applied voltage pulsing schemes across the junction for the corresponding rate windows.

In the course of this investigation the $E_c - 0.18 \text{ eV}$ level observed in the MCTS spectrum was found to exhibit a charge-dependent peak amplitude. In Fig. 2 the solid line is obtained after cooling with bias off and the dashed line with bias (5 V) on. From the energy value, the position on the temperature axis and the annealing behaviour we attribute this level to the A-centre (O-V). We should notice, for the sake of comparison, that the arb. unit on the MCTS axis of Fig. 2 is five times larger than that on the DLTS axis of Fig. 1 a and b.

Recently, a metastable defect has been reported [8] in phosphorous-doped silicon. The first configuration of this defect introduces an $E_c - 0.105 \text{ eV}$ level and the second an $E_c - 0.172 \text{ eV}$ level. The latter is probably related to the A-centre. In another experiment [1] the metastable $E_c - 0.1 \text{ eV}$ level is reported without exhibiting complementary behaviour to the A-centre. Moreover, some indications exist for a signal which overlaps the (O-V) signal and causes a shift of its energy to the higher value of $E_v + 0.20 \text{ eV}$. In our experiment, the shape of the capacitance transient of the A-centre, obtained on the screen of an oscilloscope simultaneously with the peak on the MCTS spectrum, is not exactly exponential. This might be in accord with the presence of two overlapping signals. In conclusion, we think that our small charge-dependent A-centre peak amplitude changes in p-type silicon may be due to the same aforementioned phenomenon [1, 8] for n-type silicon. This is consistent with the identification of the complex as a carbon-modified A-centre without any correlation to the group V dopant. The level $E_v + 0.1 \text{ eV}$ is not recorded in this study because of the temperature limit of our equipment to operate below 80 K.

4.2 Float-zone silicon

Fig. 3 shows the DLTS spectrum obtained immediately after the room temperature irradiation and with a rate window operating at 500 s^{-1} . The defect which introduces the peak labelled H^* , with $E_v + 0.09 \text{ eV}$, energy, has a puzzling property. On day later, after many scans had been performed, the H^* peak had vanished. Then, the specimen was kept in a refrigerator (-12°C) for a couple of weeks. When the measurements were repeated the H^* peak reappeared. The application of the standard procedure to reveal metastable configurations (e.g. annealing at 220 K with bias off or on for 10 min) has shown that the H^* peak appears only when we cool with bias off. A possible reason we have not seen previously [5] this level is the following. The H^* peak appears for the fast rate windows at temperatures above 80 K, while for the slow rate windows, applied in [5], this peak would appear below the available low-temperature

Table 1
Summary of defects with charge-related characteristics in Silicon

material	irradiation conditions	identity	energy levels	remarks	references
1 boron-doped, float-zone	1.5 MeV electrons, at 80 K	boron substitutional-vacancy pair	$E_v + 0.31$ eV $E_v + 0.37$ eV $E < E_v + 0.13$ eV	bistable defect; the first two levels belong to the one configuration and the third level to the other	[9]
2 boron-doped, pulled	1.5 MeV electrons, at 80 K	a vacancy-related complex	$E_v + 0.34$ eV	charge-dependent peak amplitude	[7]
3 boron-doped, pulled	1.5 MeV electrons, at 80 K	(?)	$E_v + 0.13$ eV	the peak disappears for scans taken with decreasing temperature when slow rate windows are operated; this behaviour emerges after annealing at 315 K	this paper
4 phosphorus-doped, float-zone and pulled	1 or 1.5 MeV electrons, at room temperature	carbon-modified A-centre	$E_c - 0.105$ eV $E_c - 0.172$ eV	bistable defect; the first level belongs to the one configuration and the second level to the other	[1, 8], this paper
5 boron-doped, float-zone	1.5 MeV electrons, at room temperature	(?)	$E_v + 0.09$ eV	evidence of a metastable defect; this level belongs to the one configuration	this paper

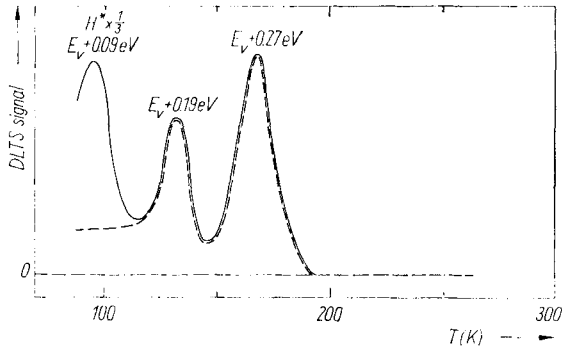


Fig. 3. The DLTS spectrum of the 1.5 MeV electron irradiated at room temperature, boron-doped, float-zone silicon. The solid curve is taken immediately after irradiation and the dashed curve after one day of measurements (rate window 500 s^{-1})

limit of 80 K. We may tentatively propose that this defect alternates between two geometrical configurations (the first introducing an $E_V + 0.09 \text{ eV}$ level) although a level belonging to the second configuration has not been traced. However, the restriction of our temperature range to values above 80 K and the lack of detailed and systematic measurements for this particular defect prevented us from drawing any definite conclusion. The defects exhibiting charge-related characteristics have been summarized in Table 1.

In summary, this work demonstrates that many defects in silicon exhibit charge-dependent characteristics. The available data do not enable models for the above centres to be derived. A more detailed picture may come from a correlation of the DLTS results with those from EPR and TSCAP experiments.

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