

## Reversible room temperature interaction of impurities in Si

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2005 J. Phys.: Condens. Matter 17 S2185

(<http://iopscience.iop.org/0953-8984/17/22/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 129.252.86.83

The article was downloaded on 28/05/2010 at 04:55

Please note that [terms and conditions apply](#).

# Reversible room temperature interaction of impurities in Si

**E V Monakhov and B G Svensson**

Department of Physics, Physical Electronics, University of Oslo, PO Box 1048 Blindern, N-0316 Oslo, Norway

Received 6 October 2004, in final form 27 January 2005

Published 20 May 2005

Online at [stacks.iop.org/JPhysCM/17/S2185](http://stacks.iop.org/JPhysCM/17/S2185)

## Abstract

Impurity-related electronic states in high-purity high-resistivity n-type float-zone (FZ) Si have been studied by deep level transient spectroscopy (DLTS). FZ-Si with a doping concentration of  $\sim 1 \times 10^{12} \text{ cm}^{-3}$  was chemically etched in 10% diluted hydrofluoric acid (HF) prior to thermal deposition of a Schottky gold contact. DLTS measurements of the as-prepared diode reveal the presence of a deep electronic trap at 0.52 eV below the conduction band. Depth profiling measurements show that the trap concentration increases towards the surface, indicating that it is due to an impurity diffusing from the surface. Heat treatments for 15 min at 150–300 °C lead to annealing of the 0.52 eV trap and formation of a 0.17 eV trap that is uniformly distributed versus depth. A reverse formation of the 0.52 eV trap with a uniform depth distribution, accompanied by annealing of the 0.17 eV trap, is observed after storage of the sample at room temperature for 20–50 days. A subsequent heat treatment at 300 °C results in the repeated annealing of the 0.52 eV trap and formation of the 0.17 eV trap, which is followed by the reversed formation of the 0.52 eV trap and annealing of the 0.17 eV trap at room temperature (RT). Several such annealing/formation cycles can be performed with these centres with a good reproducibility of the data. It might be suggested that both centres are related to hydrogen, although the exact origin is not identified.

## 1. Introduction

Because of the advances of Si technology it is now possible to produce Si wafers with extremely low concentrations of impurities and as-grown defects. In combination with controlled low doping, this provides the possibility to investigate electrically active centres with concentrations down to  $10^{10} \text{ cm}^{-3}$ . One of the most interesting candidates for investigations at such a low concentration is hydrogen.

The remarkable properties of hydrogen in Si, such as the ability to passivate electrically active centres and high mobility even at room temperature, have been fuelling the research

interest for more than two decades [1]. Hydrogen can be introduced into Si by several techniques, such as ion implantation [2, 3], in-diffusion from the gas phase at high temperatures [4, 5], from plasma [6] and during wet chemical etch [7, 8]. However, the high reactivity and mobility [1], combined with the low solubility of hydrogen in Si [9], have made it difficult to distinguish between various forms of hydrogen in Si and the mechanisms of the interaction with other defects/impurities. In addition, the majority of studies are performed at concentrations well above the level of solubility of hydrogen in Si.

Metallic impurities in Si are also of great interest. The high mobility and electrical activity of such impurities as Cu and Fe are a serious concern for device technology [10]. Due to the low solubility of metallic impurities, it is normally difficult to reach concentrations high enough for spectroscopic studies. In these cases, special preparation of the samples, which includes fast quenching from elevated temperature, is required (see for instance [11]).

In this work we have performed deep level transient spectroscopy (DLTS) studies of high-purity n-type float-zone (FZ) Si with a doping concentration of  $\sim 1 \times 10^{12} \text{ cm}^{-3}$ . Because of the low doping level and high sensitivity of DLTS we have been able to investigate impurity-related centres at a concentration level below  $10^{10} \text{ cm}^{-3}$ .

## 2. Experimental details

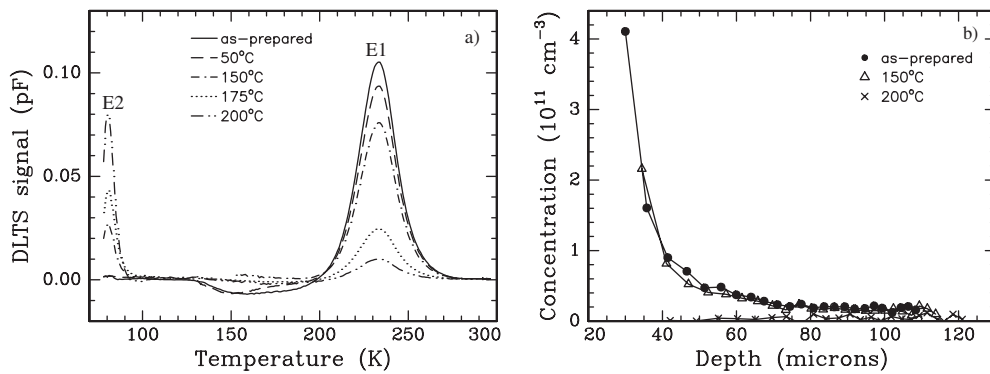
High-purity, high-resistivity float-zone (111) Si samples with a doping concentration of  $\sim 1 \times 10^{12} \text{ cm}^{-3}$  were chemically etched in 10% diluted hydrofluoric acid (HF) for 1 min at room temperature (RT). Such a treatment is known to result in the removal of the natural Si dioxide and passivation of the surface by hydrogen atoms. Gold Schottky diodes were subsequently deposited by thermal evaporation at a pressure of  $\sim 10^{-6}$  Torr.

DLTS measurements were performed, using a set-up described in detail elsewhere [12]. In short, the temperature of the sample was scanned between 77 and 280 K, and the measured capacitance transients were averaged in intervals of width 1 K. The DLTS signal was extracted by using a lock-in type of weighting function, and different spectra were obtained with rate windows in the range of  $20 \text{ ms}^{-1}$  to  $2.56 \text{ s}^{-1}$  from a single temperature scan. The concentration, energy level and capture cross-section of the traps were then evaluated from the spectra.

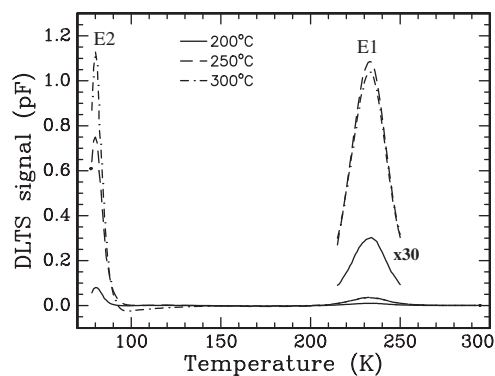
## 3. Results

A DLTS spectrum of the as-prepared diode is shown in figure 1(a). One dominating electron trap, labelled as E1, occurs with an activation energy of 0.52 eV. The depth distribution of E1 (figure 1(b)) shows that the concentration of the trap increases towards the surface. It should be noted that the strong increase in the concentration of E1 near the surface can affect the effective carrier concentration and therefore also the depth scale. An indication of hole injection with associated capture and emission is observed in the DLTS spectrum at  $\sim 150 \text{ K}$  (figure 1(a)). This may be due to the high concentration of electrically active centres in the near-surface region reducing the effective doping close to the surface.

After a heat treatment at  $50 \text{ }^\circ\text{C}$  for 15 min, a decrease in the amplitude of E1 is observed. Further decrease of the intensity of E1 and formation of a new centre, labelled as E2, with an activation energy of 0.17 eV occurs after annealing at  $150 \text{ }^\circ\text{C}$ . No indication of hole injection can be observed after the heat treatment at  $150 \text{ }^\circ\text{C}$ . This correlates with the decreased concentration of E1 in the near-surface region (figure 1(b)). Heat treatment at higher temperatures ( $175$  and  $200 \text{ }^\circ\text{C}$ ) leads to a considerable decrease of E1 and a corresponding increase of E2 (figure 1(a)), and the depth distribution of E1 becomes uniform (figure 1(b)).

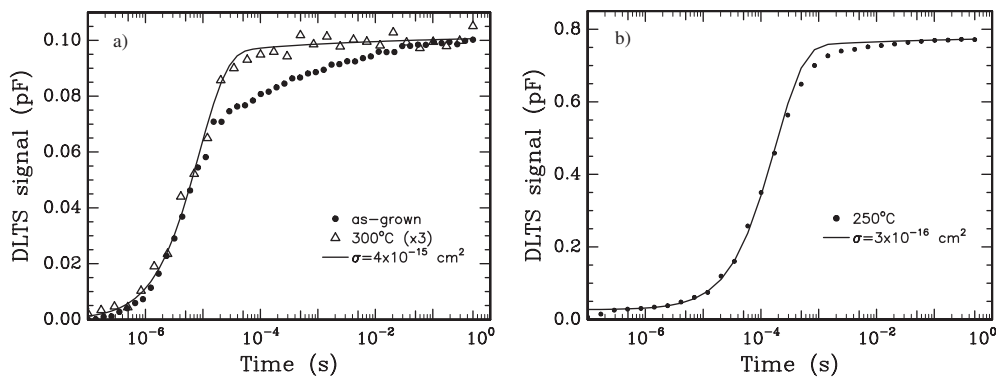


**Figure 1.** DLTS spectra (a) for FZ-Si and the depth distribution of the 0.52 eV trap (b) after preparation of the Schottky diode and 15 min isochronal annealing at  $\leq 200$  °C.

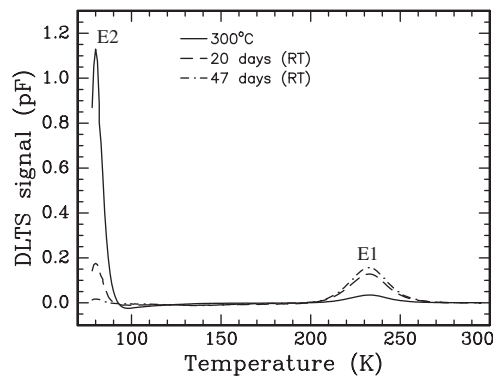


**Figure 2.** DLTS spectra for FZ-Si after 15 min isochronal annealing at  $\geq 200$  °C. The region of the spectra around the 0.52 eV peak is also shown multiplied by a factor of 30.

Heat treatment at higher temperatures (250 and 300 °C) results in a dramatic increase of E2 (figure 2). An increase in the amplitude of E1 can also be seen (for better visibility it is shown multiplied by a factor of 30). Several DLTS measurements have been performed with different reverse bias voltages in the range of 1–10 V (measurements with higher bias voltages reveal an increased leakage current that affected the experimental results), and no variation of the activation energy of E1 and E2 has been observed. Capture kinetics studies of E1 have been performed on the as-grown and 300 °C-annealed samples (figure 3(a)). It can be seen that the capture cross-sections of the peaks are almost identical for the two samples ( $4 \times 10^{-15}$  cm<sup>2</sup>). This confirms that E1 after the 300 °C annealing is indeed related to the same centre as E1 in the as-prepared sample. Figure 3 also shows a theoretical curve for the peak amplitude versus the filling pulse width calculated within the Pons model [13]. A deviation from the theoretical curve can be seen for the as-grown sample in the signal saturation region. This is due to the high trap concentration in the near-surface region of the samples (figure 1(b)). The effect is previously known and described in detail elsewhere [14]. In short, as the traps of high concentration become filled, the carrier concentration decreases. The decreased carrier concentration reduces the capture rate that is proportional to the carrier concentration. A similar capture cross-section measurement for E2 yields a value of  $3 \times 10^{-16}$  cm<sup>2</sup> (figure 3(b)).



**Figure 3.** DLTS signal as a function of filling pulse width for the 0.52 eV trap after preparation of the Schottky diode and 15 min of annealing at 300 °C (a), and for the 0.17 eV trap after 15 min of annealing at 250 °C (b). The solid line shows the dependence for a trap with a capture cross-section of  $4 \times 10^{-15} \text{ cm}^{-2}$  (a) and  $3 \times 10^{-16} \text{ cm}^{-2}$  (b) calculated within the Pons model.



**Figure 4.** DLTS spectra for FZ-Si after 15 min of isochronal annealing at 300 °C and storage at room temperature for 20 and 47 days.

After storage for 20 days at RT, E1 recovers with a correlated decrease of E2 (figure 4). After 47 days, E2 is almost completely annealed out and E1 reaches the maximum amplitude. Depth profiling measurements reveal a uniform distribution of E1 over the depth. A subsequent heat treatment at 300 °C for 15 min results in restoration of E2 and loss of E1. Furthermore, after storage for several days at RT, E1 is observed to increase again while E2 decreases. The growth and annealing of E1 and E2 have been cycled several times with excellent reproducibility of the results.

#### 4. Discussion

Although deep levels, similar to those observed in the present study, have been reported previously in as-grown high-resistivity FZ-Si [15–19], little is known on the exact origin of these centres. Firstly, it was suggested that a level at  $E_c - 0.49 \text{ eV}$ , where  $E_c$  is the conduction band edge, is related to Si self-interstitials [15, 16]. Secondly, an impurity-related origin, presumably involving sulfur, has been proposed for an electronic level at  $E_c - 0.54 \text{ eV}$  [18].

However, to the best of our knowledge, no reversible room temperature behaviour of the levels has been reported.

The observed evolution in the DLTS spectra can be interpreted as follows. E1 and E2 are presumably related to an impurity mobile at RT, which is introduced during Schottky contact preparation (involving HF etching). Two possible identifications can be proposed for this impurity: a metallic impurity and atomic hydrogen (H). It has been reported, for example, that a level at  $E_c - 0.15$  eV is observed in Cu-diffused Si [11]. This level anneals at RT and is tentatively identified as interstitial Cu. One should note, however, that this level is observed after Cu in-diffusion at 600 °C and quenching at a cooling rate of 1000 K s<sup>-1</sup>. Besides this, no formation of a mid-gap level has been reported during annealing of the 0.15 eV level [11]. To the best of our knowledge, there are no reports on a metallic impurity that can account for the observed electronic levels E1 and E2 and their correlated behaviour.

A more probable identification may be H. Treatment of Si samples in HF is known to result in absorption of hydrogen atoms on the surface and incorporation of hydrogen in a near-surface region. Moreover, a trap similar to E1 with an activation energy of 0.51 eV has been observed previously by DLTS in plasma-hydrogenated Si [6]. Although this 0.51 eV trap has not been assigned to a specific complex, it has been conclusively identified as hydrogen related. It should be mentioned that the doping level of Si in [6] was  $7 \times 10^{15}$  cm<sup>-3</sup>, which is almost four orders of magnitude higher than that in the present study ( $\sim 1 \times 10^{12}$  cm<sup>-3</sup>). This implies that the HF treatment has to introduce only  $10^{-4}$  of the amount of hydrogen introduced by the plasma treatment in order to obtain a similar effect in the present DLTS studies.

The activation energy of E2 (0.17 eV) is similar to that of the donor state of atomic hydrogen (H(0/+)) [20]. Further evidence in favour of the identification of E2 as H(0/+) is the annealing of E2 at RT with the correlated formation of E1, which is considered to involve hydrogen. This implies mobility of E2 at RT. Although it is tempting to identify E2 as H(0/+), there is an argument against this identification: the absence of a Poole–Frenkel effect for E2. Indeed, the rate of electron emission from a donor-like centre, such as H(0/+), is expected to exhibit a dependence on the electric field. The absence of a Poole–Frenkel effect can, however, be explained by taking into account the low doping of the Si samples used. Because of the low concentration of donors, the depletion region is relatively large ( $\sim 30$  μm for zero bias and  $\sim 100$  μm for a reverse bias of 10 V). This results in a weak electric field in the depletion region and, thus, a weak Poole–Frenkel effect.

Finally, an assignment of the E2 level to the carbon–hydrogen centre (CH) [21] should also be discussed. CH is known to be a deep acceptor with a level at  $E_c - 0.17$  eV, which can explain the absence of a Poole–Frenkel effect. On the other hand, CH is established to already anneal at around RT in samples doped with  $\sim 5 \times 10^{15}$  cm<sup>-3</sup> [21].

## 5. Conclusion

We have performed DLTS studies of the impurity interaction at a concentration of  $10^{10}$ – $10^{11}$  cm<sup>-3</sup> in n-type FZ-Si with doping of  $\sim 1 \times 10^{12}$  cm<sup>-3</sup>. A mid-gap level at  $E_c - 0.52$  eV with increasing concentration at the surface is observed in the as-prepared samples. Heat treatment at 150–300 °C results in annealing of the mid-gap level and gives rise to a shallower one at  $E_c - 0.17$  eV. A reverse transformation with annealing of the 0.17 eV level and formation of the 0.52 eV level occurs after storage at RT for several weeks. The correlated formation and annealing of both of the peaks can be repeated during several annealing/storage series. It is discussed that the 0.17 and 0.52 eV levels are related to a fast diffusing impurity, like hydrogen, introduced during the contact preparation. Further work is being pursued to obtain a more firm identification of the two levels.

## Acknowledgment

Partial financial support by the Norwegian Research Council (Strategic University Programme on Microtechnology) is gratefully acknowledged.

## References

- [1] See e.g. Pearson S J, Corbett J W and Stavola M 1991 *Hydrogen in Semiconductors (Semiconductors and Semimetals vol 34)* (New York: Academic)
- [2] Irmscher K, Klose H and Maass K 1984 *J. Phys. C: Solid State Phys.* **17** 6317
- [3] Holm B, Bonde Nielsen K and Bech Nielsen B 1991 *Phys. Rev. Lett.* **66** 2360
- [4] Markevich V P, Murin L I and Litvinko A G 1993 *Pis. Zh. Tekh. Fiz.* **19** 39
- [5] McQuaid S A, Binns M J, Londos C A, Tucker J H, Brown A R and Newman R C 1995 *J. Appl. Phys.* **77** 1427
- [6] Johnson N M, Ponce F A, Street R A and Nemanich R J 1987 *Phys. Rev. B* **35** 4166
- [7] Endrös A 1989 *Phys. Rev. Lett.* **63** 70
- [8] Yoneta M, Kamiura Y and Hashimoto F 1991 *J. Appl. Phys.* **70** 1295
- [9] van Wieringen A and Warmoltz N 1956 *Physica* **22** 849
- [10] See e.g. Schröter W, Seibt M and Gilles D 1991 *Electronic Structure and Properties of Semiconductors (Materials Science and Technology: a Comprehensive Treatment vol 4)* ed R W Cahn, P Haasen and E J Kramer (New York: VCH) p 539
- [11] Istratov A A, Hieslmair H, Flink C, Heiser T and Weber E R 1997 *Appl. Phys. Lett.* **71** 2349
- [12] Svensson B G, Ryden K-H and Lewerentz B M S 1989 *J. Appl. Phys.* **66** 1699
- [13] Pons D 1984 *J. Appl. Phys.* **55** 3644
- [14] Monakhov E V, Wong-Leung J, Kuznetsov A Yu, Jagadish C and Svensson B G 2002 *Phys. Rev. B* **65** 245201
- [15] Lefèvre H 1980 *Appl. Phys.* **22** 15
- [16] Lefèvre H 1982 *Appl. Phys. A* **29** 105
- [17] Alietti M, Nava F, Tonini R, Cantoni P, Stagni L and Cavallini A 1994 *Nucl. Instrum. Methods Phys. Res. A* **337** 394
- [18] Astrova E V, Voronkov V B, Kozlov V A and Lebedev A A 1998 *Semicond. Sci. Technol.* **13** 488
- [19] Simoen E, Claeys C, Job R, Ulyashin A G, Fahrner W R, De Gryse O, Clauws P and Tonelli G 2003 *J. Electrochem. Soc.* **150** G520
- [20] Herring C, Johnson N M and Van de Walle C G 2001 *Phys. Rev. B* **64** 125209
- [21] Endrös A 1989 *Phys. Rev. Lett.* **63** 70