

# Deep level transient spectroscopy on proton-irradiated Fe-contaminated p-type silicon

C. K. Tang\*, L. Vines, B. G. Svensson, and E. V. Monakhov

University of Oslo, Physics Department/Center for Materials Science and Nanotechnology, P.O. Box 1048 Blindern, 0316 Oslo, Norway

Received 12 May 2012, revised 13 June 2012, accepted 14 June 2012

Published online 8 August 2012

**Keywords** silicon, iron, hydrogen, irradiation, defect DLTS

\* Corresponding author: e-mail [c.k.tang@smn.uio.no](mailto:c.k.tang@smn.uio.no)

Proton-irradiation has been realized on Fe-contaminated p-type Czochralski silicon and investigated for interaction between Fe and irradiation-induced defects using deep level transient spectroscopy. From isochronal thermal annealings, three distinctive Fe-related defects are observed with energy level position of 0.17, 0.28 and

0.34 eV above the valence band edge. From the evolution of the defect concentration at different annealing temperature, it is suggested that Fe has reacted with prominent irradiation-induced defects, such as the vacancy-oxygen complex and the divacancy center.

© 2012 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

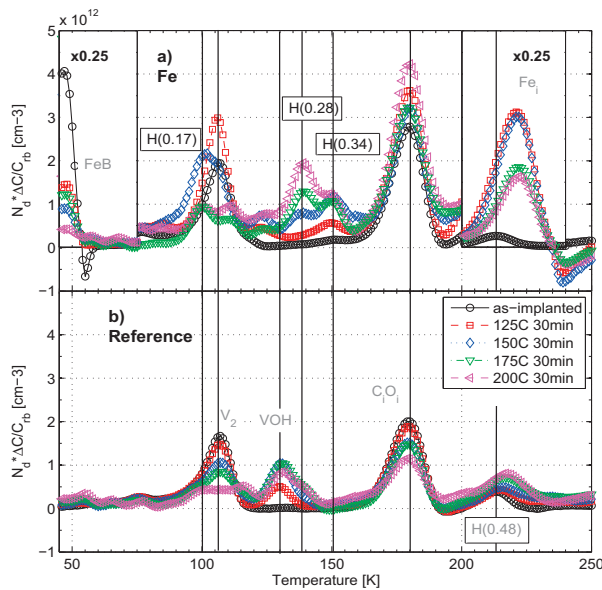
**1 Introduction** Iron is an important impurity in silicon due to its known harmful effects on the performance of both integrated circuits and solar cells [1]. In p-type silicon, improvement of solar cells by reducing the concentration of Fe can be achieved by performing a phosphorus in-diffusion step (gettering), which is essentially a part of the formation of the emitter layer. However, the mechanism of phosphorus gettering is not well understood. In addition, even with the standard phosphorus in-diffusion, a complete silicon-based solar cell may still exhibit light-induced degradation of 3–4 relative percentages with degradation characteristics of Fe contamination [2].

In order to improve the gettering efficiency of Fe, it is important to understand the underlying mechanism and the defects which are formed during the gettering process. In a recent report regarding phosphorus gettering, it has been shown that phosphorus atoms do not directly contribute to the gettering mechanism [3]. The authors propose a mechanism which involves reaction with injected vacancies and oxygen. Such interactions can also be investigated through generation of vacancies by irradiation of an Fe-contaminated sample and using an electrical characterization technique, such as deep level transient spectroscopy (DLTS), with the aid of theoretical predictions [4].

In this study, Fe-contaminated and Fe-lean float-zone (Fz) silicon samples have been irradiated by protons and investigated for possible reactions of Fe with irradiation-induced defects after subsequent isochronal annealings. Several defects are observed distinctively in the Fe-contaminated samples after annealing above 150 °C. Two of the Fe-related defects are possibly formed with divacancy and vacancy-oxygen complexes.

**2 Experiment** Samples were cut from Fz boron-doped silicon with doping concentration of  $2 \times 10^{14} \text{ cm}^{-3}$ , as confirmed by capacitance-voltage (CV) measurements. Cleaning of the samples was performed with an HF-dip before the introduction of Fe by ion-implantation at the back-side of the samples. The implantation energy and dose were 700 keV and  $2 \times 10^{12} \text{ cm}^{-2}$ , respectively. After implantation, the samples were heat treated in a tube furnace at 1000 °C for 1 h under nitrogen flow to distribute Fe uniformly in the sample [5]. Thereafter, the samples were further cleaned using the standard RCA-steps.

Aluminium contacts were deposited onto the front-side to form Schottky barrier contacts for CV-measurements and DLTS. Ohmic contacts were formed at the back-side by scratching on silver-paste. For DLTS, six rate-windows

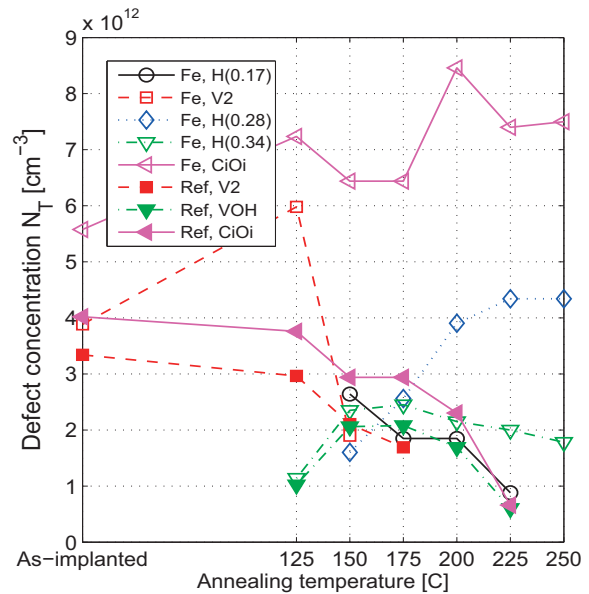


**Figure 1** Spectra of DLTS measurements, with GS4 weighting function, on proton-irradiated Fe-contaminated and reference samples after different subsequent annealing temperature for 30 min. It shows three distinctive peaks (H(0.17), H(0.28) and H(0.34)) which are only found in the Fe-contaminated samples. These spectra are extracted from rate-window of  $(320 \text{ ms})^{-1}$ .

were used ranging from  $(20 \text{ ms})^{-1}$  to  $(640 \text{ ms})^{-1}$  and the signals were extracted by the GS4 weighting function [6]. The reverse and pulse bias voltages were 15 and -15 V, respectively.

After DLTS measurements, which confirmed that the Fe-contaminated samples only contained the Fe-B pair and/or interstitial Fe ( $\text{Fe}_i$ ) deep levels, proton-irradiation was performed with an energy of 1.8 MeV and a dose of  $3 \times 10^{11} \text{ cm}^{-2}$ . The reference samples, which were not intentionally contaminated with Fe, received the same proton-irradiation. As estimated by SRIM [7], the projected range of  $\text{H}^+$  is  $\sim 40 \mu\text{m}$  which is a factor of  $\sim 3$  deeper than the region investigated with CV and DLTS. The proton-irradiated samples were stored for more than two weeks at room temperature before commencing the measurements and the isochronal annealing (30 min).

**3 Results and discussion** Figure 1 shows the DLTS spectra for Fe-contaminated (Fig. 1a) and reference (Fig. 1b) samples at as-implanted state and after subsequent isochronal annealings up to  $200^\circ\text{C}$ . The well-known irradiation-induced defects can be observed in the as-implanted samples, such as the divacancy ( $\text{V}_2$ ) [8–10] and the interstitial carbon-interstitial oxygen pair ( $\text{C}_i\text{O}_i$ ) [9, 11] with the respective energy level positions of 0.18 eV and 0.36 eV above the valence band edge ( $E_V$ ). A minor peak caused by the irradiation at 213 K can also be seen with

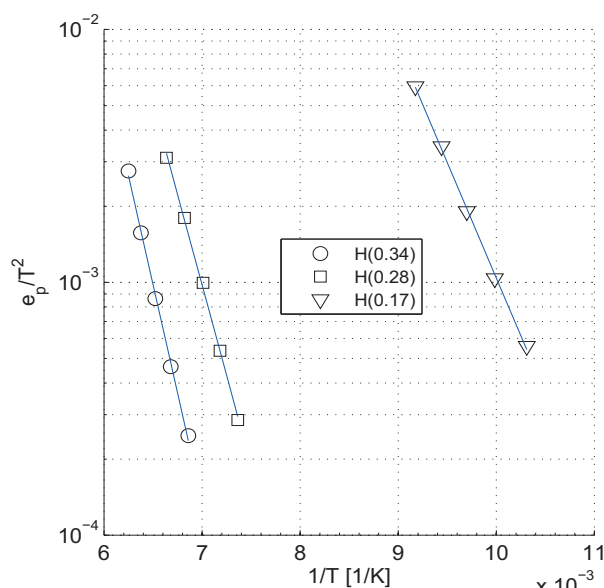


**Figure 2** Evolution of the defect concentrations in Fe-contaminated and reference samples to subsequent annealings of 30 min.

energy level of  $E_V + 0.48 \text{ eV}$ , labelled as H(0.48). However, the origin of this defect is still under investigation.

In addition to the irradiation defects, the Fe-contaminated samples contain a peak at 48 K with energy level of  $E_V + 0.10 \text{ eV}$  and defect concentration of  $3 \times 10^{13} \text{ cm}^{-3}$ . This defect arises from the Fe-B pair and it can be dissociated in a reversible reaction by illumination, minority carrier injection or heat treatment into  $\text{Fe}_i$  and B [5, 12]. The energy level position of  $\text{Fe}_i$  is  $E_V + 0.40 \text{ eV}$  and it is clearly visible in Fig. 1 at 221 K after annealing at  $125^\circ\text{C}$  for 30 min. It can also be noted that the sum of the concentration of the Fe-B pair and  $\text{Fe}_i$  is decreasing by subsequent annealing. Several reasons can explain the decrease. Interstitial Fe is highly mobile and can diffuse to the surface. It can also undergo reactions with other defects such as the irradiation-induced defects, forming electrically active or inactive defects.

Figure 2 shows the evolution of the concentration of defects by subsequent isochronal annealings. Focusing on the reference samples, both  $\text{V}_2$  and  $\text{C}_i\text{O}_i$  are observed to anneal out at an earlier stage than normally reported [13]. In addition, a peak appears after annealing at  $125^\circ\text{C}$  with energy level of  $E_V + 0.25 \text{ eV}$  and capture cross-section of  $3 \times 10^{-15} \text{ cm}^2$ . This peak has previously been identified as vacancy-oxygen-hydrogen complex (VOH) [9, 14], which indicates that hydrogen has diffused either from the surface or from the implantation region to the DLTS probing region. Within this assumption, the early annealing of  $\text{V}_2$  and  $\text{C}_i\text{O}_i$  can thereby be explained by passivation by hydrogen. Passivation of the  $\text{C}_i\text{O}_i$  center by H have both been experi-



**Figure 3** Arrhenius plot of the peaks which are distinctive to Fe-contaminated samples.

mentally demonstrated [15, 16] and theoretically predicted [17].

For the Fe-contaminated samples, the same trend for the annealing behaviour for  $V_2$  and  $C_iO_i$  is not observed. On the contrary, the concentrations increase after annealing at 125 °C. For  $V_2$ , further annealing leads to a reduction in the concentration which is a similar trend as the reference samples. Whereas for  $C_iO_i$ , the concentration evolution differs from that observed for the reference samples throughout the annealing series; for example, even an increase in the concentration is observed after 200 °C annealing. From the above observations, it is shown that a different and more complex annealing behavior of irradiation-induced defects exist in the presence of Fe. The interaction with Fe will be discussed later.

Apart from the intrinsic irradiation-induced defects and the prominent Fe defects discussed previously (the  $Fe_i$  and the Fe-B pair), three peaks are distinctive to Fe-contaminated samples, and observed at 101, 139 and 150 K. Figure 3 shows the Arrhenius plots of these defects and the extracted energy level positions are 0.17, 0.28 and 0.34 eV above  $E_V$  with capture cross-sections of  $4 \times 10^{-16}$ ,  $6 \times 10^{-15}$  and  $4 \times 10^{-14}$  cm<sup>2</sup>, respectively. The defects are correspondingly labelled as H(0.17), H(0.28) and H(0.34).

The generation of H(0.34) is similar to the generation of VOH in the reference sample (see Fig. 2). In addition, it should be noted that the VOH complex has not been detected in the Fe-contaminated sample. These observations indicate that H(0.34) and the VOH complex have a common precursor, the vacancy-oxygen pair (VO or A-center),

or, that the VOH complex is the precursor of H(0.34) resulting in a defect configuration of VOH-Fe.

Interestingly, the VO-Fe defect has previously been reported by You *et al.* [18] in n-type Si with energy level position of 0.36 eV below the conduction band edge ( $E_C$ ). The formation of VO-Fe was found to occur after annealing between 100 and 150 °C which agrees with the appearance of H(0.34) in this study. Furthermore, an Fe-related defect with energy level position of  $E_V + 0.33$  eV has been reported by Wünstel and Wagner after slowly cooling of heat treated Fe-indiffused Si-samples [19]. From the comparison between Czochralski and Fz Si-samples, it was found that the defect concentration was reduced in the Fz samples. Hence, the authors suggested that the defect is a complex of Fe and oxygen. Thus, previous literature data support the finding in this study that the H(0.34) center can involve a vacancy, Fe and oxygen, and it may possess multiple levels in the band gap.

The hole trap H(0.28) appears after annealing at 150 °C for 30 min and increases steadily for higher temperature until it reaches a maximum at 250 °C. This converged concentration is similar to the initial concentration of  $V_2$  which puts a question of whether  $Fe_i$  has reacted with  $V_2$ . The evolution of the concentrations of H(0.28) and  $V_2$  during the annealing series do not show an unambiguous correlation; however, several other reactions may have occurred simultaneously giving rise to passivation of defects and/or creation of overlapping signals.

According to calculations by Estreicher *et al.* [4],  $Fe_i$  can form several stable configurations with  $V_2$  where one configuration possess one donor and one acceptor state with their respective energy level position of  $E_V + 0.25$  eV and  $E_V + 0.36$  eV ( $E_C - 0.75$  eV). Thus, if the donor state is identified as H(0.28), a second signal with similar amplitude is expected in the DLTS-measurement. An additional peak with the suggested energy level position is not observed. However, one may speculate that the peak is overlapping with  $C_iO_i$  which is located closely to  $E_V + 0.36$  eV. Interestingly, the amplitude of  $C_iO_i$  in DLTS shows an increase during the annealing, in contrast to that of the reference sample. Hence, it may be speculated that the second level of the predicted  $Fe_i-V_2$  is overlapping with  $C_iO_i$ .

H(0.17) exists only in a narrow temperature interval of  $\sim 50^\circ$ . Its relation to other irradiation-induced defects are not unambiguous and the literature on Fe-related defect with such energy level position is scarce. However, the defect is associated with Fe but shows no relation to H(0.28) and H(0.34) which presumably indicates an independent defect and, thus, unlikely to involve  $V_2$  or VO.

**4 Conclusion** Boron-doped Fe-contaminated Fz silicon has been proton-irradiated and investigated for Fe-related defects using DLTS after subsequent isochronal annealings. Three distinctive Fe-related deep levels have been observed after different annealing temperatures. The Fe-

related defects H(0.28) and H(0.34) are likely complexes formed with  $V_2$  and VO, respectively.

**Acknowledgements** This work was funded by the Norwegian Research Council through the project “Hydrogen in solar-grade p-type Si (HydSil)” (RENERGI program).

## References

- [1] A. A. Istratov, H. Hielsmair, and E. R. Weber, *Appl. Phys. A* **70**, 489–534 (2000), and references therein.
- [2] J. H. Reiss, R. R. King, and K. W. Mitchell, *Appl. Phys. Lett.* **68**(23), 3302 (2008).
- [3] M. Syre, S. Karazhanov, B. R. Olaisen, A. Holt, and B. G. Svensson, *J. Appl. Phys.* **110**, 024912 (2011).
- [4] S. K. Estreicher, M. Sanati, and N. G. Szewacki, *Phys. Rev. B* **77**, 125214 (2008).
- [5] C. K. Tang, L. Vines, B. G. Svensson, and E. V. Monakhov, *Appl. Phys. Lett.* **99**, 052106 (2011).
- [6] A. A. Istratov, *J. Appl. Phys.* **82**, 2965 (1997).
- [7] J. F. Ziegler, *Nucl. Instrum. Methods Phys. Res. B* **219**, 1027 (2004).
- [8] B. G. Svensson, A. Hallén, J. H. Svensson, and J. W. Corbett, *Phys. Rev. B* **43**(3), 2292 (1991).
- [9] H. Malmbeck, L. Vines, E. V. Monakhov, and B. G. Svensson, *Solid State Phenom.* **178-179**, 192–197 (2011).
- [10] P. M. Mooney, L. J. Cheng, M. Süli, J. D. Gerson, and J. W. Corbett, *Phys. Rev. B* **15**, 3836 (1977).
- [11] J. Lalita, N. Keskitalo, A. Hallén, C. Jagadish, and B. G. Svensson, *Nucl. Instrum. Methods B* **120**, 27–32 (1996).
- [12] A. A. Istratov, H. Hielsmair, and E. R. Weber, *Appl. Phys. A* **69**, 13–44 (1999), and references therein.
- [13] B. G. Svensson and J. L. Lindström, *Phys. Status Solidi A* **95**, 537 (1986).
- [14] O. Feklisova, N. Yarykin, E. B. Yakimov, and J. Weber, *Physica B* **308-310**, 210–212 (2001).
- [15] S. Fatima, C. Jagadish, J. Lalita, B. G. Svensson, and A. Hellen, *J. Appl. Phys.* **85**(5), 2562 (1999).
- [16] O. Feklisova, N. Yarykin, E. Yakimov, and J. Weber, *Physica B* **273-274**, 235–238 (1999).
- [17] J. Coutinho, R. Jones, P. R. Briddon, S. Öberg, L. I. Murin, V. P. Markevich, and J. L. Lindström, *Phys. Rev. B* **65**, 014109 (2001).
- [18] Z. P. You, M. Gong, J. Y. Chen, and J. W. Corbett, *J. Appl. Phys.* **62**, 2 (1988).
- [19] K. Wünnel and P. Wagner, *Solid State Commun.* **40**, 797–799 (1981).