

Acceptor-related metastable defects in compensated n-type silicon

F. E. Rougieux¹, S. P. Phang¹, A. Shalav¹, B. Lim², J. Schmidt², D. Macdonald¹ and A. Cuevas¹

1. Research School of Engineering, College of Engineering and Computer Science, The Australian National University, Canberra, ACT 0200, AUSTRALIA
2. Institute for Solar Energy Hameln (ISFH), Am Ohrberg 1, D-31860 Emmerthal, GERMANY

ABSTRACT

This paper reviews the theory of metastable defect formation in compensated n-type silicon. By means of minority carrier lifetime measurements before and after defect activation we investigate the impact of 3 potential metastable defects relevant to the solar industry: Iron-boron pairs, chromium-boron pairs and the boron-oxygen defect.

1. INTRODUCTION

N-type silicon has been shown to be more immune to some metallic impurities than p-type silicon[1]. However new solar grade feedstocks not only contain higher concentrations of metallic impurities but also higher concentrations of dopants, making them compensated. Moreover with the advent of compensation engineering, different acceptor species such as gallium may be deliberately introduced to maximize ingot yield[2]. The presence of additional acceptors in n-type silicon may therefore potentially lead to the pairing of positively charged mobile interstitial impurities (iron, chromium) with such acceptors, and to a subsequent change in the minority carrier lifetime.

This paper aims to review some of

the important properties of metastable defects in compensated n-type silicon, based on theoretical considerations, and compare them with experimental data.

2. EXPERIMENTAL METHODS

The compensated samples used in this study came from intentionally compensated electronic grade silicon. For more information on the samples see Ref. [3]. All samples were damage etched and phosphorus gettered (predeposition 860 °C, 40 min and post-diffusion anneal at 600 °C, 2 hrs). This step effectively removes fast diffusing metallic impurities and anneals thermal donors. The diffused region was subsequently etched away. The first batch of samples were implanted with 50 keV Fe⁵⁶ ions to a dose of $6 \times 10^{11} \text{ cm}^{-2}$ on one surface. The second batch of samples were implanted with 100 keV Cr⁵² ions to a dose of $1.5 \times 10^{12} \text{ cm}^{-2}$ on one surface. The chromium dose was high in an attempt to compensate for precipitation of chromium at the surface during annealing. Both batches were annealed at 900 °C, 30 min in order to obtain respectively a maximum volume concentration (corresponding to the solubility limit) of iron of $4 \times 10^{13} \text{ cm}^{-3}$ and chromium of $2 \times 10^{12} \text{ cm}^{-3}$ in the

bulk of the material. The samples were then etched in order to remove any metallic impurities at the surfaces. The third batch of samples was not thermally

processed. All samples were then passivated using PECVD SiN deposited at 400 °C.

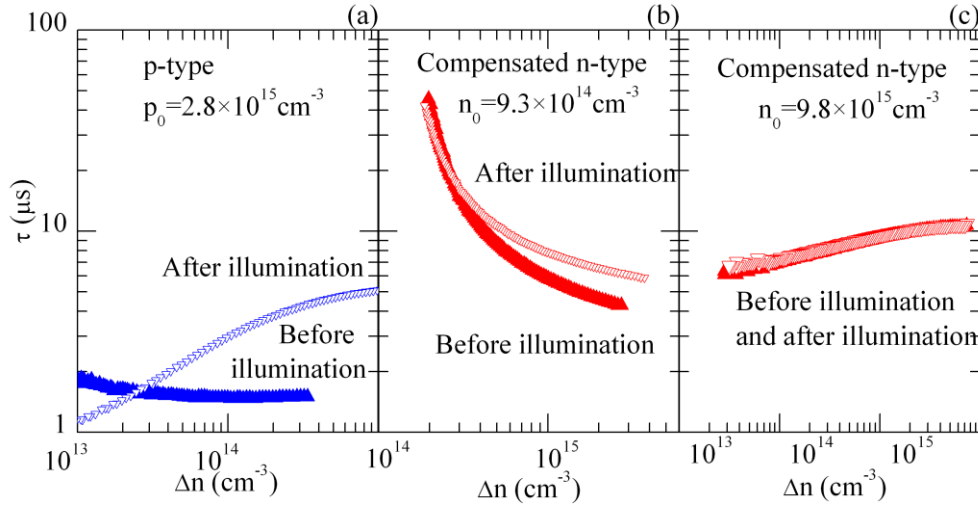


Fig. 1 Measured injection dependence of the minority carrier lifetime before and after illumination in iron implanted p-type and compensated n-type silicon.

3. IRON-ACCEPTOR PAIRS

In compensated n-type silicon at thermal equilibrium, the charge state of interstitial iron is neutral[4], hence iron is not able to pair with acceptors and theoretically iron-boron, iron-indium, iron-gallium and iron aluminum pairs cannot form in compensated n-type silicon [5, 6]. Such behavior has been observed before in negatively biased p-type silicon[6].

Fig. 1 shows the measured injection dependence of the minority carrier lifetime before and after illumination with a flash in iron implanted p-type and compensated n-type silicon. Due to the higher capture cross section for electrons compared to holes the p-type samples (Fig. 1(a)) exhibit a lower minority carrier lifetime than the n-type samples (Fig. 1(b) and Fig. 1(c)) as seen before[4]. The minority carrier lifetime

of the low resistivity compensated n-type silicon sample (Fig. 1(c)) does not change after illumination, in agreement with previous results[6]. However for the higher resistivity compensated n-type sample (Fig. 1(b)), the lifetime increases slightly at high injection after illumination. The measurements were repeated many times and the sample always showed a similar change in lifetime.

To our knowledge this effect has not been observed before. As measured by SIMS measurements and ECV the sample is indeed n-type. This could reflect the fact that not all iron atoms are neutral in this material and therefore a minute amount of positively charged interstitial iron is able to pair with the boron atoms. Using Fermi-Dirac statistics, one finds that at a doping $n_0 = 1 \times 10^{15} \text{ cm}^{-3}$, less than $1 \times 10^6 \text{ cm}^{-3}$

iron atoms should be ionized assuming the level of interstitial iron to be at $E_v+0.38$ eV[1]. Although the formation and binding energy of iron-boron pairs is mainly determined by electrostatic interaction, it is possible that a minute amount of neutral iron atoms pairs with boron atoms due to steric effects in the dark. In such a tentative scenario, illumination although not changing the charge state of interstitial iron could lead

the interstitial iron atoms to be more mobile and therefore overcome the weak binding energy induced by steric effects. Another possibility is that large inhomogeneities in the sample lead to a few localized p-type regions. Those regions could in turn affect the lifetime of the whole sample. However we were not able to see these regions through MW-PCD mapping of the wafer.

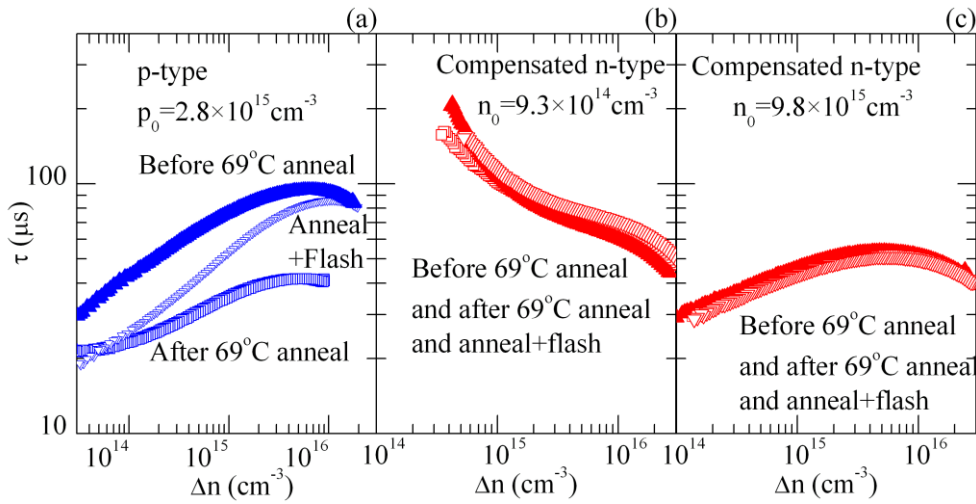


Fig. 2 Measured injection dependence of the minority carrier lifetime before 69 °C annealing (full upright triangles), after a 100 hours 69 °C anneal (empty squares) and after a subsequent flash to break the iron-boron pairs (empty downright triangles) in chromium implanted p-type and compensated n-type silicon. The samples were annealed at 250 °C, 30 min prior to measurements to dissociate the chromium-boron pairs[7, 8].

4. CHROMIUM-ACCEPTOR PAIRS

For heavily doped n-type silicon ($n_0 > 1 \times 10^{16} \text{ cm}^{-3}$), the charge state of chromium is also neutral, therefore the formation of chromium-acceptor pairs is not possible[9]. However for lower net doping (below $n_0 = 2.5 \times 10^{15} \text{ cm}^{-3}$) the charge state of interstitial chromium becomes positive and therefore chromium-boron (CrB), chromium-gallium and chromium-aluminum pairs can form.

The creation of CrB pairs is likely to lead to an overall decrease of the lifetime in compensated n-type silicon. This lifetime degradation can be explained due to the larger capture cross section for holes of CrB pairs compared to interstitial chromium[10].

Fig. 1 shows the measured injection dependence of the minority carrier lifetime before 69 °C annealing (full upright triangles) and after 100 hours 69 °C anneal. The samples were initially

annealed at 250 °C, 30 min in order to dissociate the chromium-boron pairs[7, 8] and further light soaked for 5 min in order to partially activate the boron-oxygen defect. This avoids the creation of further BO defects when subsequently flashing the samples in order to dissociate potential iron-boron pairs. Even though the 900 °C, 30min anneal was carried out in a clean furnace after a 4 hours TCA clean, metal contamination is likely to happen. When flashing the p-type samples (Fig. 2(a)) in order to dissociate potential iron-boron pairs, the lifetime increased drastically, saturating at almost the initial value, especially at higher injection levels. Therefore unfortunately, in our chromium implanted samples, the iron contamination from the furnace masks, at least partly, the impact of the implanted chromium. Note that implanted chromium often migrates to the surface when annealed[11].

Even though we see no significant change in the minority carrier lifetime before and after anneal in the compensated n-type samples (Fig. 2(b) and (c)) we cannot prove nor disprove the existence of chromium-boron pairs in such material at this stage. More conclusive experiments with a higher implanted dose need to be carried out to confirm the existence, or otherwise of such pairs in high resistivity compensated n-type silicon.

5. BORON-OXYGEN DEFECT

In compensated n-type silicon the formation of the boron-oxygen defect (BO) also been shown to lead to a strong decrease of the minority carrier lifetime [3, 12, 13]. While in p-type silicon two different degradation mechanisms are

created during illumination, the fast stage center (FRC) and the slow stage center (SRC), only the FRC center has been shown to form in compensated n-type silicon. Moreover the formation kinetics of the defect upon illumination has been shown to be slower in compensated n-type when compared to p-type silicon and increases with higher illumination intensities [3, 13, 14].

Note that contrary to metallic defects the BO defect does not form through the migration of a mobile species (such as oxygen dimers) towards negatively charged acceptors[15]. It is now believed that a latent form of the BO defect is created upon ingot cooling at relatively high temperature[15]. The defect is subsequently activated through injection of carriers and particularly holes (either through illumination or bias)[15].

It is the lower hole concentration in compensated n-type silicon that slows the BO formation kinetics and does not allow the formation of the SRC[14].

Fig. 3 shows the measured injection dependence of the minority carrier lifetime after different lengths of illumination in compensated n-type silicon. In this sample ($n_0=9.8 \times 10^{15} \text{ cm}^{-3}$ and interstitial oxygen concentration $[O_i]=7.5 \times 10^{17} \text{ cm}^{-3}$), the minority carrier lifetime drops from 1000 μs to 90 μs (at $\Delta n=1 \times 10^{15} \text{ cm}^{-3}$) after BO activation.

Note that the lifetime of such degraded samples is only marginally higher than the minority carrier lifetime of the samples implanted with an iron concentration of $4 \times 10^{13} \text{ cm}^{-3}$. Hence the BO defect is likely to be the dominant defect in relatively pure compensated solar grade feedstocks[16].

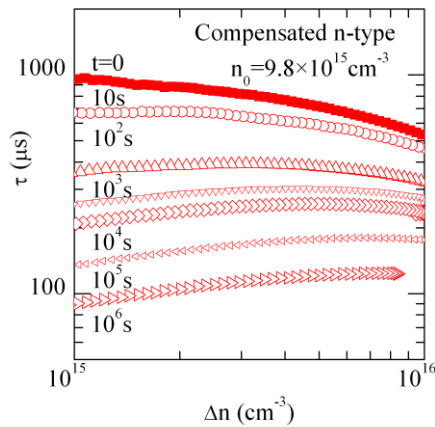


Fig. 3 Measured injection dependence of the minority carrier lifetime after different lengths of time under illumination in compensated n-type silicon.

6. CONCLUSIONS

Our early results suggest the potential formation of iron-boron pairs in lightly doped compensated n-type silicon. However further measurements on a wider set of samples are needed in order to validate this result. Additionally study of the formation kinetics of the defect could be undertaken. Due to the precipitation at the surfaces of implanted chromium during annealing we were not able to prove the existence of chromium-boron pairs in low doped compensated n-type silicon. Except for very highly contaminated samples, the BO defect is likely to be the dominant defect limiting the efficiencies of compensated n-type silicon solar cells. The successful use of compensated solar-grade silicon as a substrate for high efficiency solar cells therefore relies heavily on managing the BO defect in the cell process or during material fabrication.

REFERENCES

[1] D. Macdonald and L. J. Geerligs, "Recombination activity of interstitial iron and other transition metal

point defects in p- and n-type crystalline silicon" *Applied Physics Letters* **85**, 4061-4063, (2004).

[2] M. Forster, E. Fourmond, R. Einhaus, H. Lauvray, J. Kraiem and M. Lemiti, "Ga co-doping in Cz-grown silicon ingots to overcome limitations of B and P compensated silicon feedstock for PV applications" *Physica Status Solidi (c)* **8**, 678-681, (2011).

[3] F. E. Rougieux, B. Lim, J. Schmidt, M. Forster, D. Macdonald and A. Cuevas, "Influence of net doping, excess carrier density and annealing on the boron oxygen related defect density in compensated n-type silicon" *Journal of Applied Physics* **110**, 063708, (2011).

[4] A. A. Istratov, H. Hieslmaier and E. R. Weber, "Iron and its complexes in silicon" *Applied Physics A: Materials Science & Processing* **69**, 13-44, (1999).

[5] H. Lemke, "Dotierungseigenschaften von Eisen in Silizium" *physica status solidi (a)* **64**, 215-224, (1981).

[6] L. C. Kimerling and J. L. Benton, "Electronically controlled reactions of interstitial iron in silicon" *Physica B+C* **116**, 297 - 300, (1983).

[7] H. Conzelmann, K. Graff and E. R. Weber, "Chromium and chromium-boron pairs in silicon" *Applied Physics A: Materials Science & Processing* **30**, 169-175, (1983).

[8] J. Schmidt, R. Krain, K. Bothe, G. Pensl and S. Beljakowa, "Recombination activity of interstitial chromium and chromium-boron pairs in silicon" *Journal of Applied Physics* **102**, 123701, (2007).

[9] G. W. Ludwig and H. H. Woodbury, "Electron Spin Resonance in Semiconductors" *Solid State Physics*, **13**, (1962).

[10] H. Habenicht, M. C. Schubert and W. Warta, "Imaging of chromium point defects in p-type silicon" *Journal of Applied Physics* **108**, 034909, (2010).

[11] P. Zhang, F. Stevie, R. Vanfleet, R. Neelakantan, M. Klimov, D. Zhou and L. Chow, "Diffusion profiles of high dosage Cr and V ions implanted into silicon" *Journal of Applied Physics* **96**, 1053-1058, (2004).

[12] T. Schutz-Kuchly, J. Veirman, S. Dubois and D. R. Heslinga, "Light-Induced-Degradation effects in boron-phosphorus compensated n-type Czochralski silicon" *Applied Physics Letters* **96**, 093505, (2010).

- [13] B. Lim, F. Rougieux, D. Macdonald, K. Bothe and J. Schmidt, "Generation and annihilation of boron--oxygen-related recombination centers in compensated p- and n-type silicon" *Journal of Applied Physics* **108**, 103722, (2010).
- [14] V. V. Voronkov, R. Falster, K. Bothe, B. Lim and J. Schmidt, "Lifetime-degrading boron-oxygen centres in p-article and n-article compensated silicon" *Journal of Applied Physics* **110**, 063515, (2011).
- [15] V. V. Voronkov and R. Falster, "Latent complexes of interstitial boron and oxygen dimers as a reason for degradation of silicon-based solar cells" *Journal of Applied Physics* **107**, 053509, (2010).
- [16] D. Macdonald and A. Cuevas, "Recombination in compensated crystalline silicon for solar cells" *Journal of Applied Physics* **109**, 043704, (2011).