

LIFETIME DEGRADATION IN DARK OBSERVED IN MONO CRYSTALLINE CZ-SILICON

Jayaprasad Arumughan¹, Jens Theobald¹, Marshall Wilson², Lejlja Hildebrand¹, Roman Petres¹, Alexandre Savtchouk², Jacek Lagowski², Radovan Kopecek¹

¹International Solar Energy Research Center - ISC Konstanz, Rudolf-Diesel Str.15 , D-78467 Konstanz, Germany; e-mail: jayaprasad.arumughan@isc-konstanz.de

²Semilab SDI LLC Tampa, FL 33612, USA

ABSTRACT: In this work, we report minority charge carrier lifetime degradation in dark of up to 20 μ s at room temperature in air ambient in P-gettered Cz-Si wafers passivated with PECVD SiNx. We have shown that this effect is dominated by the bulk and not effected by the surface or the measurement. The degradation is much slower than the degradation observed during the light induced degradation (LID) process. Furthermore, increase in substrate temperature slows down the degradation in dark (DID) mechanism to large extend. The substrates show very fast LID when exposed to light and the light induced defects can be repaired within a few seconds by an annealing at 200°C. In the degraded states of LID and DID, the characteristic rings of Cz-Si material are visible. It indicates that the DID mechanism is driven by the B-O complexes in the bulk of the material. In order to observe this effect, which was not found yet by other groups, we assume that our material has high oxygen concentration, low Fe_i concentration and high dislocation density.

Keywords: lifetime, diffusion length, degradation, c-Si.

1 INTRODUCTION

Minority charge carrier lifetime degradation in boron doped Czochralski (Cz) grown silicon is topic of discussion for the last few years. The widely studied degradation mechanism in Cz-Si is the boron-oxygen (B-O) related light induced degradation of lifetimes. The degradation mechanism is mainly observed in oxygen rich boron doped Cz-Si materials. There are mainly three lifetime degradation mechanisms identified and reported so far in various literatures [1-5] and the references there in. A well known lifetime degradation mechanism is Light Induced Degradation (LID) that originates when the Cz-Si materials are exposed to light. The mechanism responsible for the LID effect is the formation of B-O complexes whose formation possibilities are much higher in boron doped Cz material and the dissociation of iron-oxygen pairs. In another lifetime degradation mechanism, the minority charge carrier degradation is occurring due to thermal treatment above $\sim 100^\circ\text{C}$ [2]. The third known mechanism causing the minority charge carrier is taking place in dark when minority charge carries are injected into the solar cells (forward bias) The first two degradation mechanisms are photon induced and the third one is carrier induced [1].

In this work, lifetime Degradation In Dark (DID), on Cz-Si material kept at dark, (samples were kept at room temperature, air ambient and protected from light) is reported. The samples found to degrade lifetime exponentially at quite slower rate. Various aspects of this effect are addressed in this work. Our earlier work on Cz-Si gave indications on DID mechanism [6].

2 EXPERIMENTAL DETAILS

The samples used are 125 x 125 mm² pseudo square, p-type, <100> oriented Cz silicon wafers with resistivity of around 1 ohm-cm. In order to getter the impurities from the bulk of the material, P-diffusion is carried out in a POCl₃ tube furnace. As our aim is to study the bulk quality of the material, about 20 μ m of silicon is removed (about 10 μ m from each side). Please note that the

emitter including the impurity gettered P-glass region is just around 0.5 μ m from the surface of the wafer. In the next step, P-gettered layer is stripped-off and the surface passivation is done by depositing PECVD 70 nm of SiNx on both sides of the wafers. To benefit from the hydrogen present in the SiNx, the samples are fired in a belt furnace at 820°C. Spatially resolved bulk lifetime mapping is done using a microwave photo conductance decay (μ W-PCD) tool from Semilab. Another instrument, PV2000 (Semilab) based on surface photo-voltage (SPV) method is used to map B-O complexes, diffusion length and light induced defects concentration. The machine is capable of doing oxygen equivalent Fe_i mapping as well.

3 RESULTS AND DISCUSSION

3.1 DID process and its dependence on temperature

In the DID mechanism the τ_{avg} is mapped using μ W-PCD at around 48 hours interval on samples kept at room temperature (25°C) and τ_{avg} versus time is plotted as illustrated in Figure 2 (green curve). The lifetime-time curve shows an exponential decay. In order to study the dependence of temperature on DID effect, studies are carried out on substrates by keeping them at 50°C and 150°C. In each case the τ_{avg} versus time is plotted and compared. In Figure 2, measured dependencies of τ_{avg} (taken from the lifetime maps) with substrate temperatures are shown. The green curve shows that the DID at 25°C is behaving similar to the sample kept at 50°C (blue curve). The only difference is that the sample at lower temperature (25°C) is degrading slightly faster than the sample kept at 50°C. When the temperature is further increased to 150°C, the rate of lifetime degradation in dark is reducing significantly. The decrease in the rate of lifetime degradation at higher temperatures could be due to the reduction in the formation of B-O complexes as discussed in section 3.3.

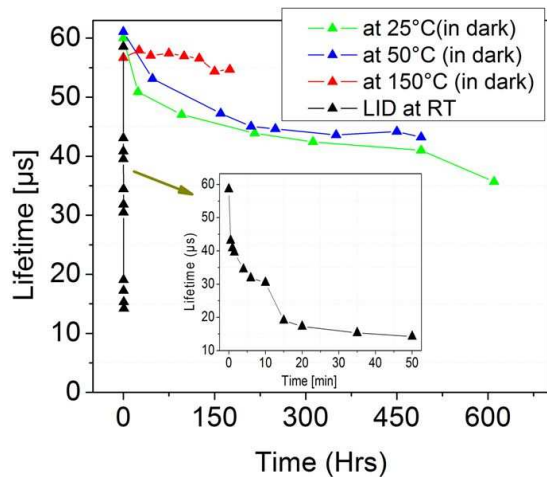


Figure 1: Dependence of DID on temperature. The lifetimes are monitored periodically on samples kept at different temperatures in dark. Figure shows the increase in substrate temperature slows down the DID effect.

3.2 Surface effect or bulk effect?

In order to check the stability of the SiN_x passivation of the lifetime samples, the average bulk lifetime values are compared with SiN_x and with iodine ethanol (IE) passivation (after removing SiN_x in CP4 solution). The average lifetimes in non degraded state with both passivation schemes are compared. Figure 2 shows the comparison of the lifetimes for three different samples. Due to the similar lifetime values obtained in the experiment, it is evident that the DID mechanism is dominated by the bulk as the IE solution was always freshly prepared. In addition, the diffusion length mapping shown in Figure 3 indicates that the characteristic rings of the Cz-Si materials are visible only in the degraded state which is also one of the indication of the assumption that the DID mechanism is dominated by the bulk of the material.

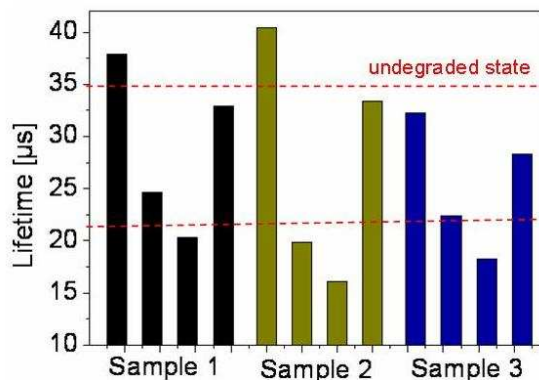


Figure 2: Comparison of lifetimes with SiN_x and iodine-ethanol passivations. The comparable lifetime values indicate that the SiN_x passivation of the lifetime samples is stable.

Slowing down of DID mechanism with increased substrate temperatures could be due to the reduced formation of B-O complexes in higher densities in the vicinity of defects. Therefore at higher temperatures, the probability for the trapping of oxygen in the defects are affecting the formation of B-O complexes and hence the

DID mechanism is slowing down. On the other hand, decrease in substrate temperature allows the oxygen to get trapped in defects in the material to form B-O complexes that acts as effective minority charge carrier traps.

3.3 DID and LID: Similarities between the effects

The characteristic ring-like structures present in Cz-Si material are observed often in μ PCD measurements and diffusion length mapping from (Surface Photo Voltage) SPV. These structures could be formed due to accumulations of Boron and oxygen (in addition to dislocations due to the crystallization process of the mono material) which cause decreased lifetimes due to light induced degradation effects. In order to observe this effect, which was not found yet by other groups, we assume that our material has high oxygen concentration, low Fe_i concentration and high dislocation density.

A comparison of LID with DID is given in Figure 1. It is noted that the LID is very fast and the degradation is taking place in a few seconds to minutes and the complete degradation in a few minutes which is not typical for LID based on B-O complex formation. But the DID is rather slow and takes place in several hundred hours.

The minority charge carrier diffusion length maps are shown in Figure 3. The upper map represents the diffusion length map at the degraded level. The characteristics rings observed in Cz material are visible here. The diffusion length map of samples after annealing at 200°C is given in the lower map.

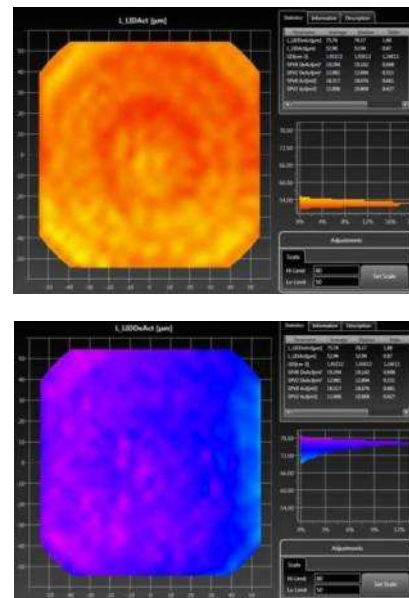


Figure 3: (top) Minority charge carrier diffusion length of wafers in the degraded state. The characteristic rings are visible in the map. (bottom) Minority charge carrier diffusion length mapping after annealing. The disappearance of characteristics rings of appeared in this state are disappeared.

3.4 Progressive annealing in dark

Progressive annealing with out LID is done to study the behaviour of diffusion length and change of the B-O characteristic rings in Cz-Si samples. First of all the

sample has undergone LID (because LID helps to reach the lowest level very fast). The first step is without a 200°C anneal step (0 min, degraded level) followed by 0.17 min, 0,5 min, 1 min to 20 min annealing steps. From 1 min onwards annealing is done in 1 min steps.

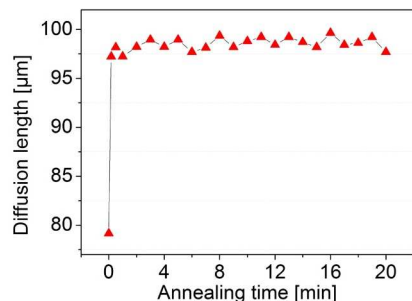


Figure 4: Dependence of diffusion length on annealing temperature. The diffusion length is recovers within a few seconds of annealing.

The first 200°C anneal time is only 10 sec (0.17min) and we already have practically complete recovery of diffusion length (disassociation of BO_2). With 1 minute increments of 200°C annealing times the diffusion length does not increase, indicating that only short anneal times at 200°C are needed to nearly completely annihilate the light induced defect complexes in these samples.

In a progressive annealing experiment with LID, higher 200°C anneal times with light induced defect degradation in between each step 200°C anneal (x time). The annealing steps were chosen exactly as in the last experiment. Fe recovery annealing at 90°C for 3 min is done. Then Diffusion length after LID deactivation is measured (initial). LID at 120°C and 1 sun for 5 min is done. The diffusion length measured after LID. From the SPV method diffusion lengths and the light induced defect density can be calculated [7].

As already seen from Figure 2, it is verified that the SiN_x used in our study can provide good surface passivation for the silicon wafer surfaces and the lifetime measured are in order with the lifetimes measured using IE passivation. It indicates that the DID mechanism is dominated by the bulk. The possible candidates for such degradation effect could be B-O complexes, FeB pairs or CrB pairs. The role of FeB and CrB pairs in our experiment is not dominant as the lifetime never returned to the original value at dark. Therefore the only candidate involved in the DID mechanism is B-O complexes. Please note that the DID effect is on the Cz-Si lifetime samples whose minority charge carrier lifetimes are increased significantly after P-gettering, and firing the PECVD SiN_x coated samples in belt furnace. The samples underwent no gettering step always in the lowest level where no further degradation is taking place.

4 CONCLUSIONS

We report a degrading mechanism, DID, where lifetimes degrade exponentially at a slower rate than standard LID process. Minority charge carrier lifetimes degradation in dark at air ambient is observed in phosphorus gettered Czochralsky c-Si homogeneous lifetime samples passivated with SiN_x . The observed lifetime degradation was found to slow down at higher temperatures. The DID samples are found to exhibit very fast degradation of lifetime under illumination and

characteristic rings of Cz materials are observed at the degraded state like in the degraded state of DID. As the lifetimes never recovered in dark, the later mentioned rings gives an indication of the involvement of B-O complexes in involved in the mechanism. The B-O defects found in the samples were recovered by an annealing at 200°C in a few seconds

5 ACKNOWLEDGES

We would like to thank Daniel Macdonald, Australian National University for helpful discussions.

6 REFERENCES

- [1] S. Glunz, S. Rein, J.Y. Lee and W. Warta J. Appl. Phy. 90 (5), 2001 p.2397M.
- [2] J. Schmidt, K. Bothe, D. Macdonald, J. Adey, R. Jones and D.W. palmer JSPS Si Symposium, Nov. 22 - 26, 2004, Kona, Hawaii, USA
- [3] Karsten Bothe and Jan Schmidt J. Appl. Phy. 99, 013701, 2006
- [4] Jan Schmidt and Rudolf Hezel 12th Workshop on Crystalline Silicon Solar Cell Materials and Processes, Breckenridge, Colorado, August 2002
- [5] Marshall Wilson, Piotr Edelman, Alexandre Savtchouk, John D'Amico, Andrew Findlay and Jacek Lagowski, J. Elec. Mater. DOI: 10.1007/s11664-010-1183-7 April 2010.
- [6] J. Arumughan, R. Kopecek, W. Tulloch, E. Good, G. Bausch, D. Wood, G. Beaucarne, 25th EUPVSEC, Valencia. 2010.
- [7] J. Lagowski, A. Aleynikov, A. Savtchouk, and P. Edelman. Eur. Phys. J. Appl. 27, 503 – 506 (2004)