Boron-oxygen-related traps in Czochralski grown silicon

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Introduction

Light-induced degradation (LID) of boron (B)-doped Czochralski (Cz)-grown silicon has been studied for several decades [1]–[3]. It has been suggested that in uncompensated wafers, a boron-oxygen (BO) complex in the form of BO_2 is responsible for this phenomenon [3]. The complex causing LID appears to exist in three states: degraded state, annealed state, and stabilized state [4]. The degraded state is induced by injection of charge carriers. In this state, the complex is recombination-active and leads to a reduction of the minority carrier lifetime of the sample. The degraded state is meta-stable. By dark annealing at high temperatures (typically around 200 °C), the complex changes to the “precursor” form of the BO complex and the minority carrier lifetime recovers to the starting lifetime (‘annealed state’). The annealed state is also meta-stable and may revert to the degraded state with further carrier injection. The third state, the ‘stabilized state’, is achieved by carrier injection at temperatures around 200 °C. After the stabilization process, the wafer is no longer prone to degradation at the typical operating condition of solar cells. Like the previous states, this is a meta-stable state and the wafer returns to the annealed state after dark annealing for extended lengths of time [5].

Photoconductance (PC)-based lifetime measurements have been heavily used to investigate the kinetics and extent of the BO complex formation [5]. However, this method is unable to study the evolution of the BO precursor (annealed state), since in this state the recombination activity of the complex is negligible and does not affect the lifetime. Considering this constraint of lifetime measurement, in this study we investigate LID using photoconductance decay (PCD) measurements. Using this method, we observe a trap in the annealed state of B-doped Cz wafers, which is removed after the degradation process. We demonstrate that such a trap is not present in phosphorous (P)-doped Cz wafers and B-doped float-zone (FZ) wafers. Our results suggest that this trap is connected to the LID-related BO complex.

Method

Three sets of wafers are used in this study, B-doped Cz wafers (1.3 Ω.cm), P-doped Cz wafers (7.4 Ω.cm), and B-doped FZ wafers (0.3 Ω.cm). All wafers were phosphorus diffusion gettered, followed by removal of the diffusion layer. The samples were then rapid thermal annealed (peak temperature of 800 °C for 10 seconds) to remove thermal donors. Finally, the wafers were passivated with an aluminum oxide layer capped with silicon nitride.

The degradation process was performed using a 938 nm laser at 120 °C under 96 suns intensity. This choice of temperature and light intensity has the benefit of accelerating the formation kinetics of the defect whilst avoiding stabilization of the defect. For dark annealing, the wafers were annealed at 200 °C for 15 minutes.

PCD measurements were performed at 45 °C using our custom-made PCD lifetime tester. Each measurement was averaged for 500 times to increase the signal-to-noise ratio. Sufficient interval was used between two consecutive excitations to ensure that the traps were empty at the beginning of the next measurement. For excitation, an X5DR flash head (Quantum Instruments) was used in 1/64 mode with a decay time constant of ~35 μs. Lifetime measurements were done at 30 °C before and after each PCD measurement, using the same system.

Results and discussion

Figure 1(a) illustrates the injection dependent effective lifetime curves of a representative B-doped Cz sample after several consecutive cycles of degradation and annealing. As expected, the lifetime cycles between a higher value and a lower value via the dark annealing and degradation processes. Figure 1(b) presents the photoconductance signal as a function of time for the same sample. In these curves, initially, the PC increases due to excitation by the flash. This is followed by a reduction of the PC signal due to carrier recombination. In the degraded state, the initial drop continues until it returns to the dark PC value. On the other hand, in the annealed state, this initial drop is followed by a second, very slow decay. Since we used surface passivation with a negative fixed charge, we can rule out depletion region modulation [6] as the cause of this slow decay. Hence, the measurement appears to be impacted by a minority carrier trap in the annealed state which is removed after the degradation process. The traps cannot be explained by thermal donors as they were removed before the PCD measurements. Considering the direct correlation between the trapping behavior and the annealed/degraded state of the sample, our results suggest that this trap is correlated with the BO complex. It seems our results support the conclusions of a recent study, where the authors suggested that a deep donor defect is acting as the BO defect's precursor [7].

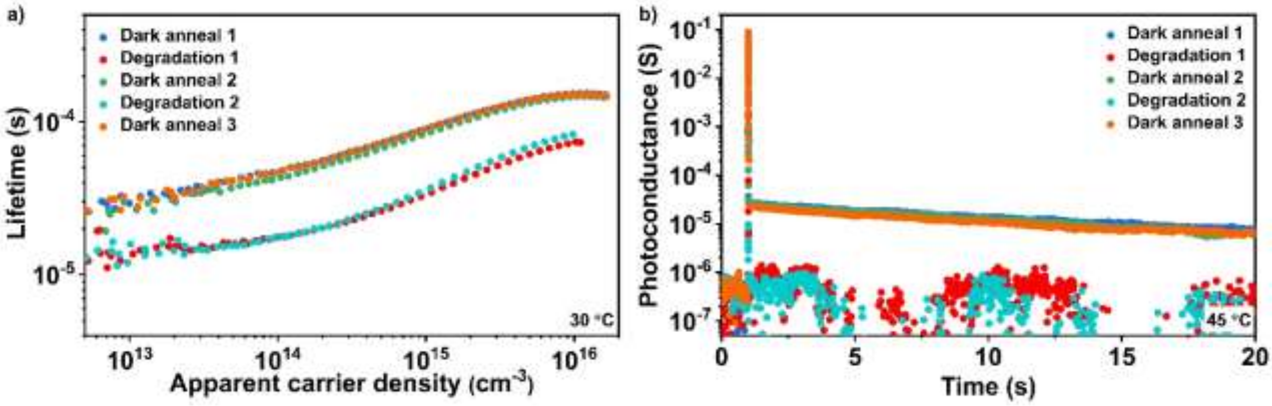

Figure 1 – Lifetime measurements (a) and PCD measurements (b) of a B-doped Cz sample after dark annealing and degradation cycles.

To further investigate the source of this trap, the PCD of P-doped Cz and B-doped FZ samples were measured after the dark annealing process. Figure 2 demonstrates the PCD for these two samples, as well as the B-doped Cz sample. No apparent slow decay can be observed for the P-doped Cz and B-doped FZ samples, in contrast with the B-doped Cz sample. This result further indicates the possibility of a connection between the observed trap and the BO complex responsible for LID.

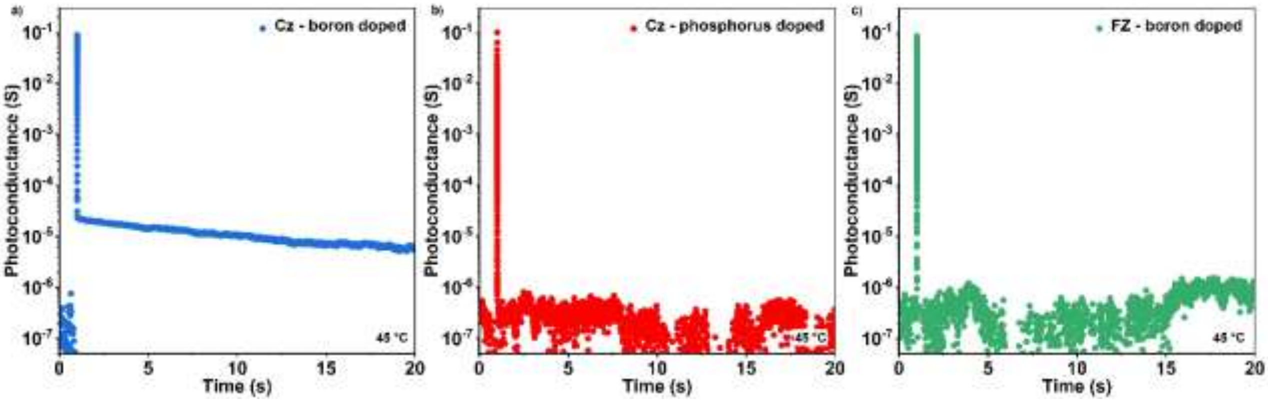

Figure 2 – PCD measurements of B-doped Cz (a), P-doped Cz (b), and B-doped FZ (c) wafers after dark annealing process.

Conclusions

We observed the presence of a trapping center in the annealed state of B-doped Cz wafer, which is removed after degradation. The generation and annihilation of the trap follows a cyclic behavior opposite to the generation and annihilation of the recombination-active BO complex. Measuring PCD of B-doped FZ and P-doped Cz samples, we observed that they do not possess such a trap. Our results suggest that the trap observed in our samples is connected to the BO complex, which is the cause of LID in B-doped Cz wafers. Our study also demonstrates that PCD measurement is a powerful tool to investigate the formation and dissociation of complexes in their non-recombination active form.

References

[1] H. Fischer and W. Pschunder, 1974, 'Investigation of photon and thermal induced changes in silicon solar cells,' *Proc. 10th IEEE Photovol. Spec. Conf.*, pp. 404–411.

[2] J. Schmidt, A. G. Aberle, and R. Hezel, 1997, “Investigation of carrier lifetime instabilities in Cz-grown silicon,” *Proc. 26 th IEEE Photovol. Spec. Conf.*, pp. 13–18.

[3] J. Schmidt and K. Bothe, 2004, “Structure and transformation of the metastable boron- and oxygen-related defect center in crystalline silicon,” *Phys. Rev. B - Condens. Matter Mater. Phys.*, vol. 69, pp. 1–8.

[4] A. Herguth, G. Schubert, M. Kaes, and G. Hahn, 2006, “Avoiding boron-oxygen related degradation in highly boron doped Cz silicon,” *Proc. 21st Eur. Photovolt. Solar Energy Conf.*, pp. 530–537.

[5] T. Niewelt, J. Schon, W. Warta, S. W. Glunz, and M. C. Schubert, 2017, “Degradation of crystalline silicon due to boron-oxygen defects,” *IEEE J. Photovoltaics*, vol. 7, pp. 383–398.

[6] P. J. Cousins, D. H. Neuhaus, and J. E. Cotter, 2004, “Experimental verification of the effect of depletion-region modulation on photoconductance lifetime measurements,” *J. Appl. Phys.*, vol. 95, pp. 1854–1858.

[7] M. Vaqueiro-Contreras et al., 2019, “Identification of the mechanism responsible for the boron oxygen light induced degradation in silicon photovoltaic cells,” *J. Appl. Phys.*, vol. 125, p. 185704.