

---

This is an electronic reprint of the original article.  
This reprint may differ from the original in pagination and typographic detail.

Author(s): Lindroos, Jeanette & Yli-Koski, Marko & Haarahiltunen, Antti & Schubert, Martin C. & Savin, Hele

Title: Light-induced degradation in copper-contaminated gallium-doped silicon

Year: 2013

Version: Post print

**Please cite the original version:**

Lindroos, Jeanette & Yli-Koski, Marko & Haarahiltunen, Antti & Schubert, Martin C. & Savin, Hele. 2013. Light-induced degradation in copper-contaminated gallium-doped silicon. *Physica Status Solidi RRL*. Volume 7, Issue 4. 262-264. DOI: 10.1002/pssr.201307011.

Rights: © 2013 Wiley-Blackwell. This is the post print version of the following article: Lindroos, Jeanette & Yli-Koski, Marko & Haarahiltunen, Antti & Schubert, Martin C. & Savin, Hele. 2013. Light-induced degradation in copper-contaminated gallium-doped silicon. *Physica Status Solidi RRL*. Volume 7, Issue 4. 262-264. DOI: 10.1002/pssr.201307011, which has been published in final form at <http://onlinelibrary.wiley.com/doi/10.1002/pssr.201307011/abstract>.

---

All material supplied via Aaltodoc is protected by copyright and other intellectual property rights, and duplication or sale of all or part of any of the repository collections is not permitted, except that material may be duplicated by you for your research use or educational purposes in electronic or print form. You must obtain permission for any other use. Electronic or print copies may not be offered, whether for sale or otherwise to anyone who is not an authorised user.

# Light-induced degradation in copper-contaminated gallium-doped silicon

Jeanette Lindroos<sup>\*1</sup>, Marko Yli-Koski<sup>1</sup>, Antti Haarahiltunen<sup>1</sup>, Martin C. Schubert<sup>2</sup>, and Hele Savin<sup>1</sup>

<sup>1</sup> Department of Micro and Nanosciences, Aalto University, Tietotie 3, 02150 Espoo, Finland

<sup>2</sup> Fraunhofer Institute for Solar Energy Systems (ISE), Heidenhofstraße 2, 79110 Freiburg, Germany

Received 10 January 2013, revised 20 February 2013, accepted 20 February 2013

Published online 25 February 2013

**Keywords** degradation, lifetime, silicon, gallium, copper

\* Corresponding author: e-mail [jeanette.lindroos@aalto.fi](mailto:jeanette.lindroos@aalto.fi), Phone: +358 9 470 22322, Fax: +358 9 470 25008

To date, gallium-doped Czochralski (Cz) silicon has constituted a solar cell bulk material free of light-induced degradation. However, we measure light-induced degradation in gallium-doped Cz silicon in the presence of copper impurities. The measured degradation depends on the copper concentra-

tion and the material resistivity. Gallium-doped Cz silicon is found to be less sensitive to copper impurities than boron-doped Cz silicon, emphasizing the role of boron in the formation of copper-related light-induced degradation.

**1 Introduction** Light-induced degradation (LID) is a deleterious effect in crystalline silicon causing a significant solar cell efficiency loss during one day of illumination. LID has been found to increase in Czochralski (Cz) silicon with either increasing boron or oxygen concentration, attributing LID to a boron–oxygen defect complex [1–4]. Therefore, traditional methods of minimizing LID consist of choosing either a high-resistivity boron-doped Cz bulk material or oxygen-free silicon, such as Magnetic Czochralski (MCz) and Float Zone (FZ) silicon. Degradation-free solar cells have also been manufactured by replacing boron doping with gallium or by switching to n-type silicon [2–4]. However, all these alternative materials come with tradeoffs either in cell efficiency or cost [5].

Recently, Savin et al. [6] have observed light-induced degradation similar to boron–oxygen LID in both boron- and phosphorous-doped FZ silicon by intentionally contaminating the material with low concentrations of copper. Copper concentrations of  $10^{14} \text{ cm}^{-3}$  did not affect the initial FZ minority carrier lifetime, but degradation was measured during sample illumination. Consequently, light activation was proposed to enable the formation of highly recombination-active copper precipitates [7]. LID was more pronounced in copper-contaminated Cz silicon than in FZ silicon, suggesting that oxygen and its related defects provide nucleation sites for copper precipitation during illumination.

Unintentional copper contamination can easily occur during solar cell processing, due to the high diffusivity and solubility of copper [8]. As expensive screen-printed silver front contacts are replaced with electroplated copper [9], copper contamination will increase in the production line, making copper-related LID a central issue in silicon solar cells. In order to understand the role of the dopant in the copper-related degradation process, we intentionally contaminate Ga-doped Cz silicon with copper and subject the material to illumination. We study the degradation behavior as a function of copper and doping concentrations, comparing the results to boron-doped Cz silicon.

**2 Experimental details** In this experiment, light-induced degradation was studied in 6-inch wide, 300  $\mu\text{m}$  thick gallium-doped Cz silicon and on 4-inch wide, 525  $\mu\text{m}$  thick boron-doped Cz silicon. Table 1 presents the wafer resistivities and oxygen concentrations. The results were also compared to previously published data on similarly processed 17  $\Omega \text{ cm}$  B-doped Cz silicon [6].

All wafers were first subjected to RCA cleanings followed by dry thermal oxide passivation. The boron-doped sample was oxidized for 40 min at 900 °C and annealed in a nitrogen atmosphere for 40 min at 950 °C, producing a 15 nm layer of oxide. A 26 nm passivating thermal oxide was grown on the Ga-doped wafers at 1000 °C. Then, the wafers were intentionally contaminated with copper

**Table 1** Resistivity and oxygen concentration of the studied Cz silicon wafers.

dopant	resistivity ( $\Omega$ cm)	oxygen concentration (ppma)
Ga	0.41	16.1
Ga	10.1	17.7
B	18–24	11–13
B*	17	14.5

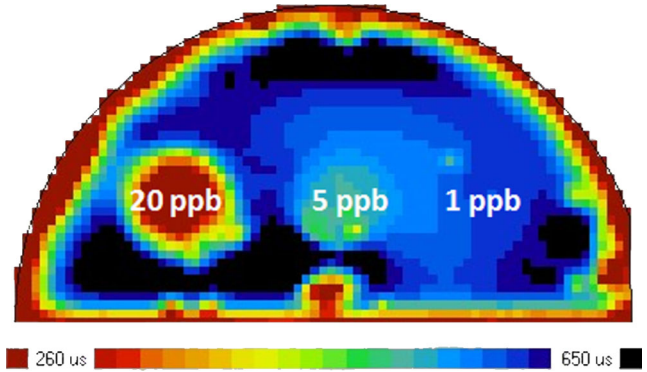
\* Ref. [6].

through the thermal oxide. The lower copper contamination levels in Figs. 1 and 2 were induced through droplets of 1, 5 and 20 ppb% (w/v) copper solution [10]. The higher surface contamination levels were achieved by spin coating the front surface with 8 and 100 ppm% (w/v) of copper solution [11]. The wafers were subsequently annealed for 20 min at 800 °C in a nitrogen atmosphere in order to diffuse the copper contamination into the wafer bulk. Finally, a positive corona charge was deposited on the wafers, in order to keep copper in the wafer bulk [12].

The initial minority carrier lifetime of the wafers was first measured at medium injection level ( $\sim 10^{14}$  cm $^{-3}$ ) with Microwave Photoconductance Decay ( $\mu$ -PCD), after which the wafers were subjected to illumination. On the spin-contaminated wafers, small-area illumination (1 mm $^2$ ) was performed by bias light ( $>25$  W/cm $^2$ , 973.5 nm) at room temperature for up to 117 h [13]. During illumination, the bias light intensity was decreased momentarily to measure the lifetime as a function of illumination time at a high injection level ( $\sim 10^{16}$  cm $^{-3}$ ) with a pulsed 904 nm laser (200 ns). The wafers with droplets of lower copper solution concentration (ppb) were illuminated entirely with a halogen lamp (200 mW/cm $^2$ ) for 20 min at a temperature below 50 °C. After illumination, the final lifetime was again measured at medium injection with  $\mu$ -PCD.

**3 Results and discussion** Figure 1 shows the lifetime map of half a high-resistivity Ga-doped Cz silicon wafer with three circular copper solution contamination areas (1, 5 and 20 ppb) measured after 20 min of halogen illumination. Figure 2 presents the average lifetime values measured before ( $\tau_{\text{initial}}$ ) and after ( $\tau_{\text{final}}$ ) halogen illumination in the three contamination spots in the same wafer (orange bars). Figure 2 also depicts the average lifetime values in correspondingly copper-contaminated low-resistivity Ga-doped Cz silicon (gray bars) and high-resistivity B-doped Cz silicon (green bars, values from [6]). Assuming identical copper diffusion conditions in Ga-doped Cz silicon as in B-doped Cz silicon at 800 °C [13, 14], the copper solution concentrations in Figs. 1 and 2 are estimated as  $1.6 \times 10^{10}$  cm $^{-2}$  in the 1 ppb spot,  $4.2 \times 10^{10}$  cm $^{-2}$  in the 5 ppb spot and  $6.3 \times 10^{10}$  cm $^{-2}$  in the 20 ppb contamination area [6].

In Fig. 2, the contamination level 0 ppb refers to the sample reference area located above the contamination spots in Fig. 1. Although this reference area has no inten-

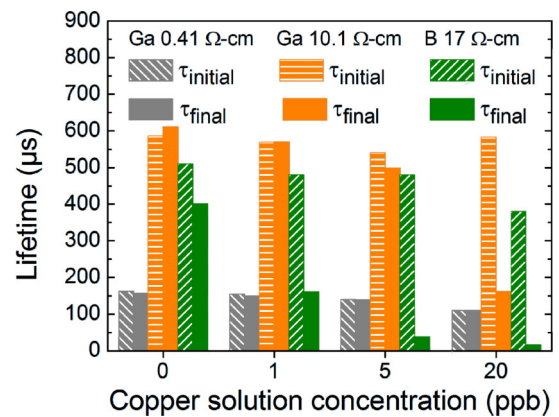


**Figure 1** Lifetime map of half a 10.1  $\Omega$  cm Ga-doped Cz silicon wafer with three contamination spots (1, 5 and 20 ppb of copper solution) measured after 20 min of halogen illumination.

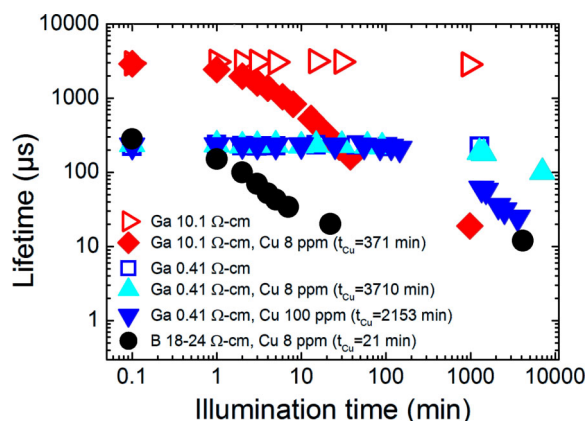
tional contamination, it may still contain some copper as a result of unintentional contamination from the furnace during the 800 °C anneal. Therefore, the small degradation measured in the B-doped Si reference area is most likely due to unintentional contamination.

In the two Ga-doped samples, no lifetime change is observed in the reference area or in the 1 and 5 ppb spots of copper solution. These results are in agreement with the previously reported LID-free behaviour of Ga-doped Cz silicon [2–4]. However, significant degradation is measured in the 20 ppb copper solution spot in the high-resistivity Ga-doped sample in both Figs. 1 and 2. This is an interesting result, as copper contamination appears to cause light-induced degradation also in Ga-doped Cz silicon.

In the high-resistivity B-doped sample, LID is detected in all three contamination spots as discussed in Ref. [6]. As LID is observed only in the 20 ppb spot in the high-resistivity Ga-doped Cz wafer, the dopant has a clear effect on copper-related LID in Cz silicon. Gallium doping appears to make Cz silicon less sensitive to copper contamination than boron doping.



**Figure 2** Average lifetime measured before ( $\tau_{\text{initial}}$ ) and after ( $\tau_{\text{final}}$ ) illumination in a reference area and in three contamination spots (1, 5 and 20 ppb of copper solution) in Ga-doped Cz and B-doped Cz silicon.



**Figure 3** High-injection lifetime as a function of illumination time in Ga-doped and B-doped Cz silicon with varying copper solution concentrations.

As the low-resistivity Ga-doped Cz silicon wafer does not show any degradation in Fig. 2, the copper concentrations were increased in the second experiment. Figure 3 presents the time dependence of the degradation process at these higher copper concentrations. As expected, no degradation is observed in the clean Ga-doped wafers, but clear degradation is measured in all copper-contaminated wafers, including the low-resistivity Ga-doped sample.

Even though the degradation is visible in all contaminated samples, the degradation time constants  $t_{Cu}$  vary notably [13]. At the lower contamination solution level (8 ppm), the lifetime decreases rapidly in the high-resistivity Ga-doped wafer. In the low-resistivity Ga-doped wafer, the same copper solution concentration does not cause degradation until 100 min in illumination, resulting in a degradation time constant of 3710 min. The slower degradation rate in the low-resistivity material may be caused by the higher gallium concentration, due to the resistivity dependency of the minority carrier injection level at constant bias light intensity. The slightly lower oxygen concentration might also reduce the degradation rate.

Although the degradation rate is much slower in the low-resistivity material, both the degradation rate and the relative degradation increased after increasing the copper solution concentration to 100 ppm. Thus, LID appears to increase in both low- and high-resistivity Ga-doped Cz silicon with increasing copper concentration. However, compared to boron-doped silicon, Ga-doped Cz silicon requires higher copper concentrations and longer illumination times for copper-related LID to occur.

**4 Conclusion** Gallium-doped Cz silicon wafers were intentionally contaminated with copper and subjected to illumination. Light-induced degradation was clearly observed in the contaminated material and found to increase with increasing copper concentration or with increasing resistivity. Higher copper concentrations and longer illumination times were required to induce LID in Ga-doped Cz silicon than in B-doped Cz silicon. Therefore, boron doping renders Cz silicon more sensitive to copper contamination. Previously, oxygen has also been shown to increase copper-related LID [6]. Hence, silicon with both high boron and high oxygen concentration appears to have the lowest tolerance to copper contamination.

**Acknowledgements** This research was undertaken at the Micronova Nanofabrication Centre of Aalto University. The authors acknowledge the financial support of the Academy of Finland, Okmetic Oyj and the Finnish Funding Agency for Technology and Innovation.

## References

- [1] J. Schmidt, A. G. Aberle, and R. Hezel, in: Proceedings 26th IEEE PVSC, Anaheim, CA, USA (IEEE, New York, 1997), p. 15.
- [2] S. W. Glunz, S. Rein, W. Warta, J. Knobloch, and W. Wettling, *Sol. Energy Mater. Sol. Cells* **65**, 223 (2001).
- [3] J. Schmidt and K. Bothe, *Phys. Rev. B* **69**, 024107 (2004).
- [4] S. W. Glunz, S. Rein, J. Knobloch, W. Wettling, and T. Abe, *Prog. Photovolt.* **7**, 466 (1999).
- [5] A. Goetzberger, C. Hebling, and H. W. Schock, *Mater. Sci. Eng. R* **40**, 1 (2003).
- [6] H. Savin, M. Yli-Koski, and A. Haarahiltunen, *Appl. Phys. Lett.* **95**, 152111 (2009).
- [7] R. Sachdeva, A. A. Istratov, and E. R. Weber, *Appl. Phys. Lett.* **79**, 2937 (2001).
- [8] A. A. Istratov, C. Flink, H. Heislmaier, E. R. Weber, and T. Heiser, *Mater. Sci. Eng. B* **72**, 99 (2000).
- [9] J. Bartsch, A. Mondon, K. Bayer, C. Schetter, M. Hörteis, and S. W. Glunz, *J. Electrochem. Soc.* **157**(10), H942 (2010).
- [10] W. B. Henley, D. A. Ramappa, and L. Jastrezbski, *Appl. Phys. Lett.* **74**, 278 (1999).
- [11] M. Hourai, T. Naridomi, Y. Oka, K. Murakami, S. Sumita, N. Fujino, and T. Shiraiwa, *Jpn. J. Appl. Phys.* **27**, L2361 (1988).
- [12] J. Lindroos, M. Yli-Koski, A. Haarahiltunen, and H. Savin, *Appl. Phys. Lett.* **101**, 232108 (2012).
- [13] H. Väinölä, M. Yli-Koski, A. Haarahiltunen, and J. Sinkkonen, *J. Electrochem. Soc.* **150**(12), G790 (2003).
- [14] A. A. Istratov, C. Flink, H. Heislmaier, E. R. Weber, and T. Heiser, *Phys. Rev. Lett.* **81**(6), 1244 (1998).