Room-temperature method for minimizing light-induced degradation in crystalline silicon

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Although light-induced degradation (LID) in crystalline silicon is attributed to the formation of boron-oxygen recombination centers, copper contamination of silicon has recently been observed to result in similar degradation. As positively charged interstitial copper stays mobile at room temperature in silicon, we show that the bulk copper concentration can be reduced by depositing a large negative charge onto the wafer surface. Consequently, light-induced degradation is reduced significantly in both low- and high-resistivity boron-doped Czochralski-grown silicon. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4769809]

Light-induced degradation (LID) is a current topic in silicon solar cell research, since LID causes severe efficiency loss during one day of solar illumination. LID is imputed to the formation of recombination-active boron-oxygen defect complexes[1] in crystalline silicon, rendering low-resistivity boron-doped Czochralski (Cz) silicon particularly sensitive to LID. Recently, LID has also been observed in crystalline silicon with low levels of copper.[2,3] In boron-doped Cz silicon, copper concentrations as low as $10^{-9}\,\mathrm{cm}^{-3}$ can cause degradation.[3] As interstitial copper has both high solubility and diffusivity in silicon,[4] unintentional copper contamination may easily occur during silicon solar cell manufacturing. Moreover, the proposed replacement of expensive silver front contacts with low-cost copper-plated contacts might further increase the probability of copper contamination in the solar cell line.[5] Therefore, copper might well be the culprit behind LID in some solar cell studies.[6]

Recently, much effort has been put into mitigating light-induced degradation. Most solutions rely on avoiding the use of 1-2 Ω-cm boron-doped Cz silicon,[7] but Herguth *et al.*[8] have developed a technique to actually remove LID from silicon. However, the technique is based on illuminating silicon above 90 °C for extended periods. In this paper, we present a room-temperature method to minimize LID in crystalline silicon. This method is based on optimizing the sample surface charge.

The experiments were performed on 100-mm-wide, ⟨100⟩-oriented boron-doped electronic-grade Cz silicon with two different resistivities: 2.7-2.8 Ω-cm (low-res) and 18–24 Ω-cm (high-res). Both wafer types had relatively high oxygen concentrations. The 400-μm-thick low-res wafers had an oxygen concentration of 15.3 ppm, while the 525-μm-thick high-res wafers contained 11–13 ppm of oxygen.

After RCA surface cleanings, all wafers were oxidized for 40 min at 900 °C and annealed in nitrogen for 40 min at 950 °C, producing a 15 nm surface-passivating thermal oxide. Some of the wafers were kept as clean reference wafers, while other wafers were intentionally copper contaminated. The intentional contamination was performed by spin coating 2 or 8 ppm of copper solution onto the front surface of the wafer. The surface copper contamination was then diffused into the wafer bulk during a 20 min anneal at 800 °C in nitrogen atmosphere. After cooling, a positive corona charge was deposited onto both sides the wafers.

Next, the initial minority carrier recombination lifetime (τ_{initial}) was measured at medium injection with microwave photoconductance decay (μ-PCD) by a WT-85XL Semilab lifetime scanner. A small area (1 mm^2) of the sample was then subjected to bias light illumination (>25 $\mathrm{W/cm}^2$, 973.5 nm) at room temperature for up to 94 h to induce LID. During illumination, the bias light intensity was momentarily decreased several times in order to measure lifetime as a function of illumination time at a high injection level with a pulsed 904 nm bias laser (200 ns).[9] Once full degradation had been achieved, bias light illumination was stopped, and the final lifetime (τ_{final}) was measured with μ-PCD at medium injection.

After the degradation measurement was completed with a positive surface charge, a negative surface charge was deposited onto both sides of the wafer. Two days or more after the charge reversal, the degradation measurement procedure detailed above was repeated on the same wafer but in a different spot. The small illumination area (1 mm^2) of the bias light allowed several degradation measurements to be performed on the same wafer with different surface charges without interference from previous measurements.

Figure 1 presents the minority carrier recombination lifetime measured at high injection during bias-light illumination in a high-res Cz silicon wafer with 8 ppm of copper solution contamination. The only difference between the two lifetime curves in Figure 1 is the polarity of the wafer surface charge. When a positive corona charge (+3.7 $\mu\mathrm{C/cm}^2$) is deposited on the wafer, a clear lifetime decrease is measured during bias laser illumination. However, when a large negative charge (−11.1 $\mu\mathrm{C/cm}^2$) is deposited on the same wafer, no lifetime change can be detected even after 94 h of illumination.

This is an interesting result as the sample surface charge clearly has a significant impact on light-induced degradation in this high-res copper-contaminated Cz silicon wafer. It is well known that interstitial Cu_i^+ remains mobile at room temperature[4] and that Cu_i^+ will eventually diffuse out of a bare

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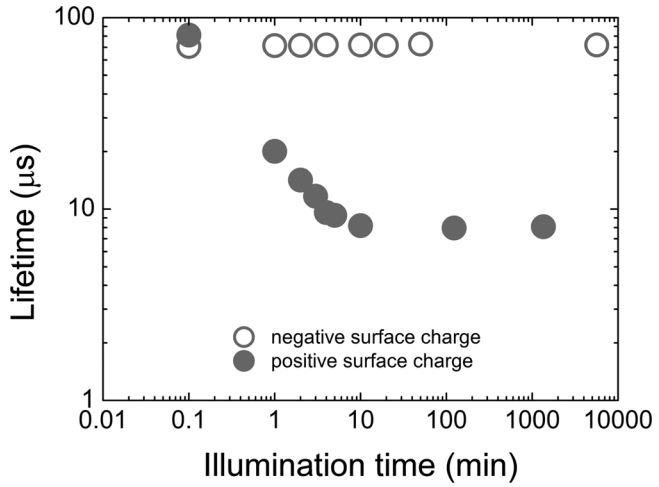

FIG. 1. Lifetime at high injection measured as a function of illumination time with positive and negative surface corona charge in 18–24 Ω-cm boron-doped Cz silicon contaminated with 8 ppm of copper solution.

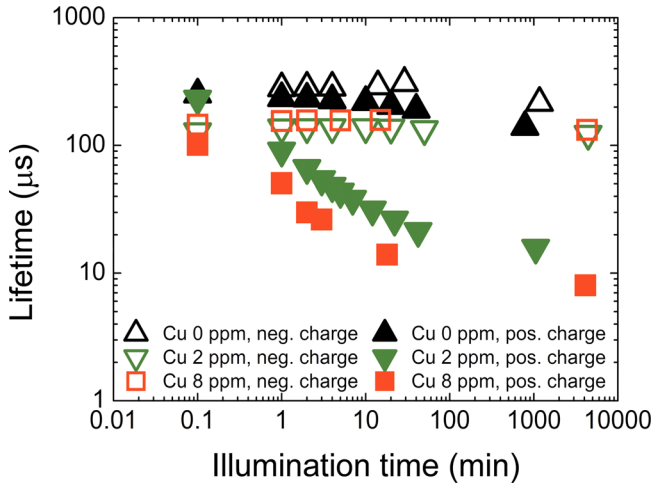

FIG. 3. Lifetime measured at high injection as a function of illumination time with positive and negative surface corona charge in clean 2.7–2.8 Ω-cm boron-doped Cz silicon and with intentional contamination (2 and 8 ppm of copper solution).

silicon sample. Oxidation[10] and the deposition of a positive surface charge[11] can prevent this out-diffusion. Correspondingly, a negative surface charge be can used to actively drive interstitial copper out of the wafer bulk to the silicon and oxide interface, decreasing the bulk copper concentration. As seen in Fig. 1, this results in a reduction in or a complete disappearance of light-induced degradation in crystalline silicon.

Figure 2 shows lifetimes measured at medium injection in the same material before ($\tau_{initial}$) and after (τ_{final}) illumination. A moderate negative corona charge of $-3.7\,\mu C/cm^2$ causes severe degradation in the sample. However, increasing the negative surface charge to $-11.1\,\mu C/cm^2$ removes the degradation almost entirely, maintaining a high initial and final lifetime. Therefore, simply depositing some negative charge onto the sample does not automatically produce the desired result. The negative charge concentration needs to be optimized to efficiently remove Cu_i^+ from the bulk and to minimize light-induced degradation.

As low-resistivity p-type Cz silicon is the most common bulk material for silicon solar cells, the method for minimizing LID with a negative surface charge was also studied in such a material. Figure 3 depicts the lifetime measured at high injection during bias-light illumination in clean (0 ppm) and copper-contaminated (2 and 8 ppm solution) low-res Cz silicon as a function of surface charge. Figure 4 also presents the lifetime measured before ($\tau_{initial}$) and after (τ_{final}) illumination in the same samples at medium injection level. In Figures 3 and 4, the notation 0 ppm refers to the clean reference sample with no intentional copper contamination. As the reference sample was annealed for 15 min at 200 °C and copper-contaminated samples were in-diffused at high temperature, all low-res wafers were in a non-degraded state before the first illumination. This is also confirmed by the consistency of the initial lifetime $\tau_{initial}$ values measured with a positive charge in Fig. 4.

With a positive charge (filled markers), LID is observed in all low-res samples in Fig. 3. LID is more severe and appears to form faster in the copper-contaminated wafers than in the clean sample both at high and medium injection levels. However, after the deposition of a large negative charge ($-11.1\,\mu C/cm^2$), the lifetime at high injection remains at its

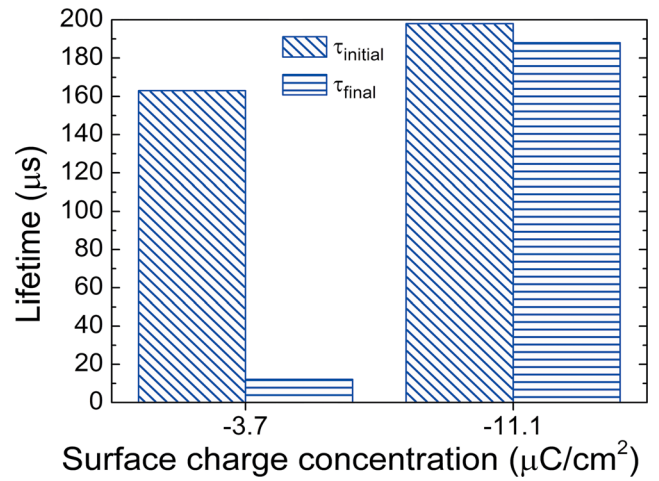

FIG. 2. Lifetime measured at medium injection before ($\tau_{initial}$) and after (τ_{final}) illumination as a function of negative surface charge concentration in 18–24 Ω-cm Cz silicon contaminated with 8 ppm of copper solution.

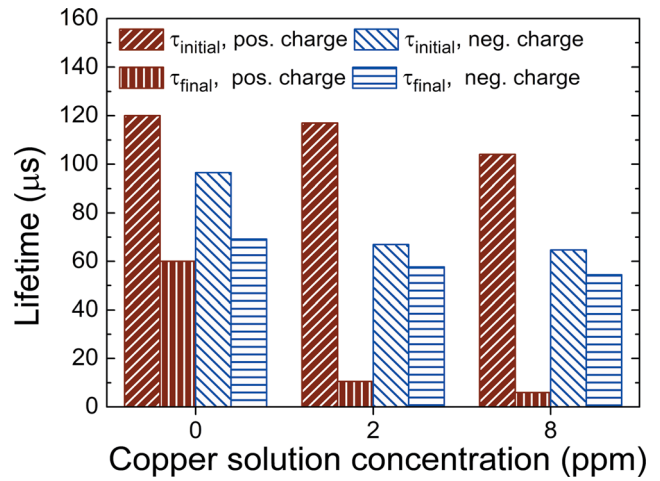

FIG. 4. Lifetime measured at medium injection before ($\tau_{initial}$) and after (τ_{final}) illumination with positive and negative surface charge as a function of copper solution concentration in clean and contaminated 2.7–2.8 Ω-cm Cz silicon.

starting value in copper-contaminated samples throughout three days of illumination. Therefore, reversing the surface charge appears to significantly reduce LID in these samples. The effect is not as clear in the clean low-res sample. Hence, the lifetime values at medium injection should be examined more closely in Fig. 4.

In the reference sample in Fig. 4, the lifetime after degradation τ_{final} is 60 μs with the positive charge, while the negative charge results in 70 μs. However, these two values cannot be directly compared, as the initial lifetime with the negative charge is unexpectedly low in comparison to $\tau_{initial}$ with the positive charge. The initial lifetime decrease after the negative charge deposition indicates a change in the surface recombination rate. As the effect is more pronounced in the copper-contaminated wafers, the surface recombination might increase due to the collection and consequently precipitation of copper at the silicon and oxide interface. The lower initial lifetime might also be caused by oxide interface deterioration due to the large surface charge. Nevertheless, both $\tau_{initial}$ and τ_{final} measured with the negative charge are significantly larger than τ_{final} with the positive charge, assuring that the lifetimes measured in Fig. 4 still reflect the bulk lifetime in the samples. Therefore, the medium-injection lifetime measurements also support the above conclusion that an optimized negative surface charge reduces significantly light-induced degradation in crystalline silicon, particularly in copper-contaminated wafers.

We have presented a room-temperature method for minimizing light-induced degradation in crystalline silicon. The method is based on optimizing the surface charge of a silicon wafer. Depositing a large negative surface charge prompts the diffusion of interstitial Cu_i^+ from the sample bulk to the wafer and oxide interface, reducing the interstitial bulk copper concentration. As a result, less copper is able to react in the bulk during illumination, and light-induced degradation is decreased. We have demonstrated that a large negative surface charge (-11.1 $\mu C/cm^2$) prevents degradation entirely in copper-contaminated 18–24 Ω-cm boron-doped Cz silicon. The negative charge also reduces LID efficiently in copper-contaminated 2.7–2.8 Ω-cm boron-doped Cz silicon with high oxygen concentration. As this is the dominating resistivity range in the photovoltaic industry and the silicon material suffering most from LID, optimizing the surface charge could lead to significant improvement in the final solar cell efficiency. Most importantly, the implementation of this method could decrease cleanliness requirements for both the silicon material and the cell process line, reducing the cost of silicon solar cells.

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[1]J. Schmidt, A. G. Aberle, and R. Hezel, in *Proceedings of the 26th IEEE PVSC, Anaheim, CA, USA, 1997* (IEEE, New York, 1997), p. 15.
[2]D. A. Ramappa, Appl. Phys. Lett. **76**(25), 3756 (2000).
[3]H. Savin, M. Yli-Koski, and A. Haarahiltunen, Appl. Phys. Lett. **95**, 152111 (2009).
[4]A. A. Istratov, C. Flink, H. Hieslmair, S. A. McHugo, and E. R. Weber, Mater. Sci. Eng., B **72**, 99 (2000).
[5]J. Bartsch, A. Mondon, C. Schetter, M. Hörteis, and S. W. Glunz, in *Proceeding of the 35th IEEE PVSC, Honolulu, HI, USA, 2010* (IEEE, New York, 2010), p. 1299.
[6]K. Ramspeck, S. Zimmermann, H. Nagel, A. Metz, Y. Gassenbauer, B. Birkmann, and A. Seidl, in Proceedings of the 27th EU PVSEC, Frankfurt, Germany, 24–28 September 2012.
[7]S. W. Glunz, S. Rein, W. Warta, J. Knobloch, and W. Wettling, Sol. Energ. Mater. Sol. Cells **65**, 219 (2001).
[8]A. Herguth, G. Schubert, K. Kaes, and G. Hahn, Prog. Photovoltaics **16**(2), 135 (2008).
[9]H. Väinölä, M. Yli-Koski, A. Haarahiltunen, and J. Sinkkonen, J. Electrochem. Soc. **150**(12), G790 (2003).
[10]C. Flink, F. Henning, S. A. McHugo, W. Seifert, H. Heislmair, T. Heiser, A. A. Istratov, and E. R. Weber, Phys. Rev. Lett. **85**(23), 4900 (2000).
[11]M. B. Shabani, T. Yoshimi, and H. Abe, J. Electrochem. Soc. **143**, 2025 (1996).