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Light-induced degradation in multicrystalline silicon: the role of copper

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Abstract

In this contribution, we provide an insight into the light-induced degradation of multicrystalline (mc-) silicon caused by copper contamination. Particularly we analyze the degradation kinetics of intentionally contaminated B- and Ga-doped mc-Si through spatially resolved photoluminescence (PL) imaging. Our results show that even small copper concentrations are capable of causing a strong LID effect in both B- and Ga-doped samples. Furthermore, the light intensity, the dopant and the grain quality were found to strongly impact the degradation kinetics, since faster LID was observed with stronger illumination intensity, B-doping and in the grains featuring low initial lifetime. Interestingly after degradation we also observe the formation of bright denuded zones near the edges of the B-doped grains, which might indicate the possible accumulation of copper impurities at the grain boundaries.

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Keywords: Light-induced degradation, multicrystalline silicon, copper metal impurities

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1. Introduction

Light-induced degradation (LID) in silicon solar-cells has been investigated for nearly four decades, with a special focus on B-doped Czochralski (Cz-) Si, whose degradation mechanisms were explained through the formation of metastable boron-oxygen (BO-) defects. Although multicrystalline silicon has been observed to suffer from weaker LID than classical BO-LID due to its lower oxygen concentration and initial minority carrier lifetime, several reports have recently emerged on slow, yet strong, LID (>10% rel.) in mc-Si PERC and Al-BSF cells with both Ga and B doping. (1) (2) Since interstitial oxygen is unlikely to be directly involved in the degradation of the mc-Si substrates (3), such strong LID cannot be explained by the B-O defect and clearly arises from a different, yet unknown, degradation mechanism. While the degradation kinetics related to the B-O defect are known to follow a double-exponential decay and fully recover at 200°C (4), the observed LID in mc-Si features a strong single-exponential decay that only partially recovers at 200°C (5). Furthermore, more severe LID in mc-Si was observed in presence of crystal defects, such as grain boundaries and dislocations (6). All the aforementioned properties of LID, *i.e.* single exponential decay (7) (8), partial recovery at 200°C (5), and stronger degradation in presence of crystal defects (9) have also been reported for Cu-related LID, making no surprise that copper contamination has been recently found to strengthen LID in mc-Si wafers (8) and Al-BSF cells (10). Therefore, it is worth investigating in more detail the role that copper might play in the LID of mc-Si substrates.

In this contribution, we have investigated the LID effect in intentionally Cu-contaminated B- and Ga-doped mc-Si. The defect density and the degradation rate are studied as a function of Cu contamination level, dopant type, and light intensity. Special attention is devoted to LID occurring at grain boundaries and intra-grains of different initial quality. The use of sister wafers allows the comparison of the degradation kinetics in the same crystal while varying certain parameters, such as copper concentration and light intensity.

2. Experimental

The experiments were performed with solar-grade 156x156 mm² boron- and gallium-doped mc-Si sister wafers, with the resistivity of 2.2 Ω·cm ($N_A=6.5 \cdot 10^{15}$ cm⁻³) and the thickness of ~170 μm. The samples underwent RCA-1 and RCA-2 cleanings followed by an HF dip for 2 minutes. The wafers were then passivated through the growth of a 15 nm thick thermal oxide layer formed during 40 minutes of dry oxidation at 900°C, followed by annealing in nitrogen ambient at the same temperature. Some samples were then kept as clean reference samples, while the rest of the batch was subjected to intentional copper contamination, which was performed by spinning a Cu-sulfate solution with a copper dose ranging from 0.1 and 4 ppm. The samples were then annealed at 800°C for 20 minutes in inert ambient to allow copper to diffuse into the wafer bulk. Next, an external corona charge was deposited on both wafer sides (+0.3 μC/cm²) to prevent Cu out-diffusion and reduce the surface minority carrier recombination through the formation of an inversion layer near the surface.

After intentional contamination, the wafers were then exposed to laser illumination (0.5 and 1 sun) and the photoluminescence (PL) signal was constantly monitored by means of a CCD camera. Finally, the conversion of the raw PL-data into effective minority carrier lifetime maps was achieved through a comparison with spatially averaged QSS-PL lifetime measurements. (11)

3. Results

3.1. Impact of dopant and copper concentration

Figure 1 presents the lifetime decay detected in B-doped and Ga-doped sister wafers that were intentionally contaminated with different copper concentrations. While no significant LID effect is observed in the clean reference wafers, the figure displays a strong correlation between the increasing copper concentration and the lower lifetime saturation value. This behavior was observed in all our samples, irrespective of the dopant or the grain initial lifetime. Note that while LID was detected in Ga-doped Cz-Si only in the presence of rather heavy Cu

contamination, in the case of Ga-doped mc-Si, even low doses of intentional copper contamination (0.1 ppm) are capable of causing a strong LID effect. However, the dependence of the degradation rate on the dopant presented in Figure 2 results in agreement with previous experiments, which showed slower degradation kinetics in intentionally contaminated Ga-doped Cz-Si wafers (12). This phenomenon finds an explanation from the lower diffusivity of copper impurities in Ga-doped material, which is caused by the higher thermal stability of CuGa pairs (13).

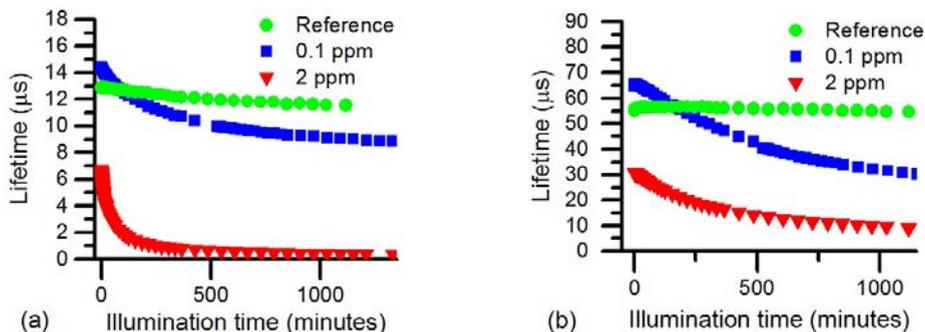


Fig 1. Examples of LID as a function of illumination time in a) B-doped grain with high initial lifetime and b) Ga-doped grain with high initial lifetime. In both cases, the degradation strength results strongly dependent on the copper concentration. The presented lifetime values were averaged over the whole grain area ($\sim 1 \text{ cm}^2$).

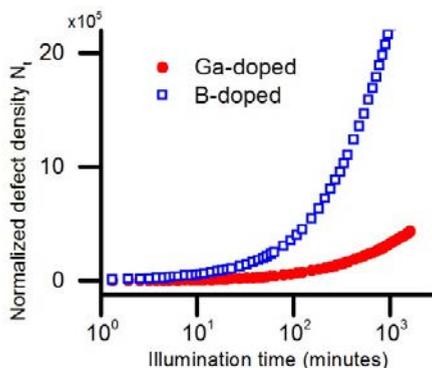


Fig 2. Normalized defect density N_i as a function of illumination time in Ga- and B-doped grains with similar initial lifetime and contaminated with the same copper dose (0.5 ppm). Faster degradation kinetics were observed in B-doped specimens.

3.2. Impact of grain quality

Figure 2 shows the detected lifetime decay as a function of grain quality (a, c) and copper concentration (b). Figure 2a confirms that the grain quality does not impact the final saturated lifetime in Ga-doped mc-Si. Figure 2b displays the degradation time constant in Ga-doped samples calculated by fitting the normalized density of generated defects $N(t) = 1/\tau(t) - 1/\tau(0)$ to a single exponential function, as described in Ref. (8). Faster degradation occurs in the crystals with low initial lifetime, confirming that the grain quality plays a major role on the degradation rate. This result points towards a possible interaction between copper impurities and specific lattice defects, *e.g.*, dislocations that are well-known nucleation sites for highly recombination active copper precipitates. (13) (14) (15) However, the impact of the B-doped grain quality was not as clear as in Ga-doped counterparts. Figure 2c shows that considerably different degradation rates were detected in B-doped grains featuring the same initial lifetime. However, in a large selection of B-doped grains, low initial lifetime resulted in accelerated degradation kinetics, thus showing the same behavior as the Ga-doped mc-Si samples in Fig. 2b.

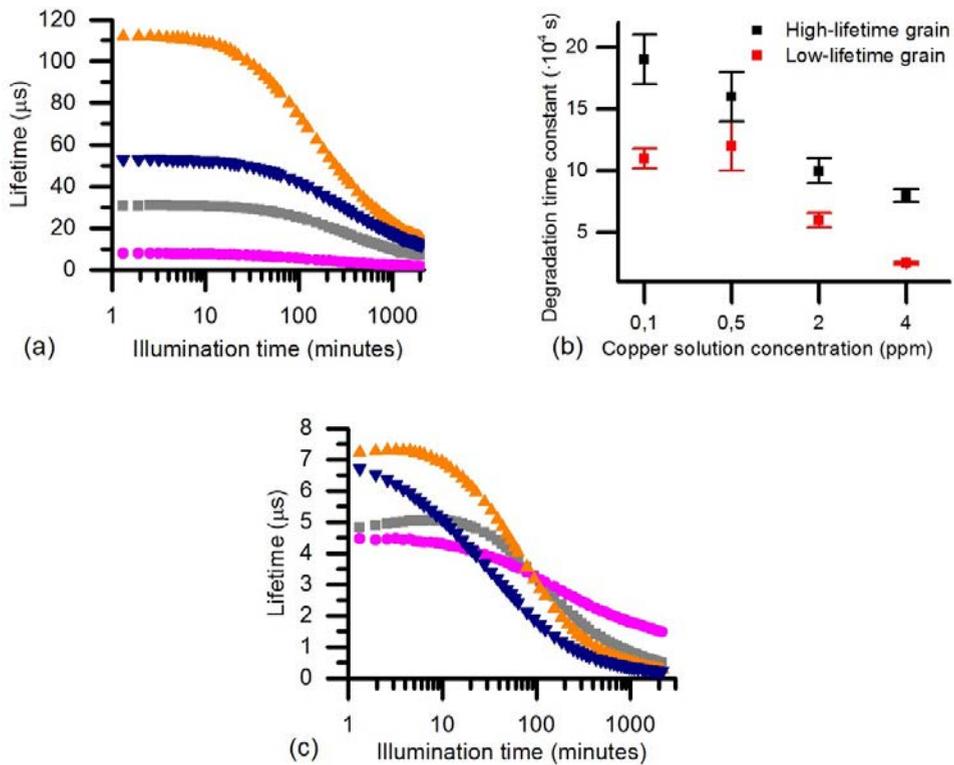


Fig 3. a) LID in different grains of Ga-doped mc-Si with fixed Cu contamination level (0.5 ppm). b) Degradation time constants as a function of the copper solution concentration in Ga-doped mc-Si grains with high initial lifetime (black) and low initial lifetime (red). c) Lifetime degradation in B-doped grains with constant Cu concentration (0.5 ppm). Different degradation rates can be observed in grains featuring similar initial lifetime.

3.3. Degradation near the grain boundaries

In all samples, low lifetime values were initially detected at grain boundaries. Interestingly, in presence of sufficiently high copper doses, bright denuded zones were observed after illumination in the proximity of the B-doped grain boundaries (Fig. 4b). This result suggests that the cooling ramp from 800°C to RT after Cu in-diffusion resulted in the accumulation of interstitial copper atoms at the grain boundaries, thus leaving copper-free areas that featured milder degradation than in the rest of the crystal. The same phenomenon was not observed in any of the Ga-doped wafers (Fig. 4c), probably because of the slower copper diffusivity in Ga-doped material (16). Analytical techniques for microscale chemical and elemental analysis of materials, such as μ -XRF, might provide further information on the concentration of copper atoms segregated at grain boundaries.

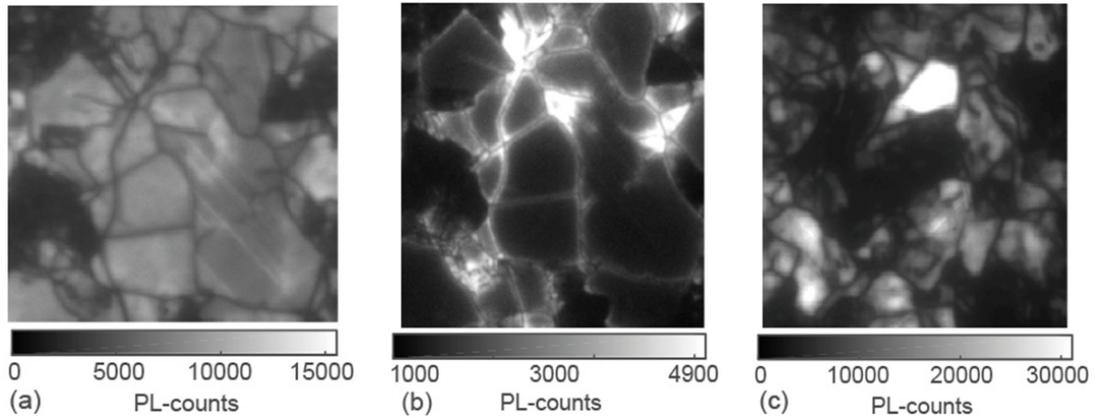


Fig. 4. Photoluminescence images of a B-doped wafer before (a) and after (b) degradation. Figure (c) displays the PL-map of a Ga-doped sample measured after 30 hours of illumination. All wafers were contaminated with a 2 ppm Cu solution. After degradation bright denuded zones appear near the grain boundaries of B-doped wafers. Note that in each picture different scales were used to highlight the appearance of bright denuded zones near the grain boundaries.

3.4. Light-intensity dependence

In order to investigate the light intensity dependence of Cu-LID, we divided a sample in two separate halves that were exposed to different illumination intensities (0.5 and 1 Sun). This procedure allows to ensure exactly the same level of copper contamination (2 ppm) in both specimens and compare the degradation kinetics in grains with similar initial lifetime. In contrast to BO-LID, whose dependence on light intensity was found to be proportional to either the equilibrium majority carrier concentration p_0 (17) or the excess hole density (18), our results in Fig.5 reveal that in both B- and Ga-doped wafers the degradation kinetics of Cu-LID are solely dependent on the illumination intensity, regardless of the total or equilibrium hole concentration. This conclusion is supported by the fact that the excess carrier density generated under illumination was estimated to be between $1 \cdot 10^{13}$ and $5 \cdot 10^{14} \text{ cm}^{-3}$, thus resulting considerably lower than the doping concentration. The observed light dependence of Cu-LID degradation kinetics agrees with earlier results obtained with Cz-Si substrates (18) (9).

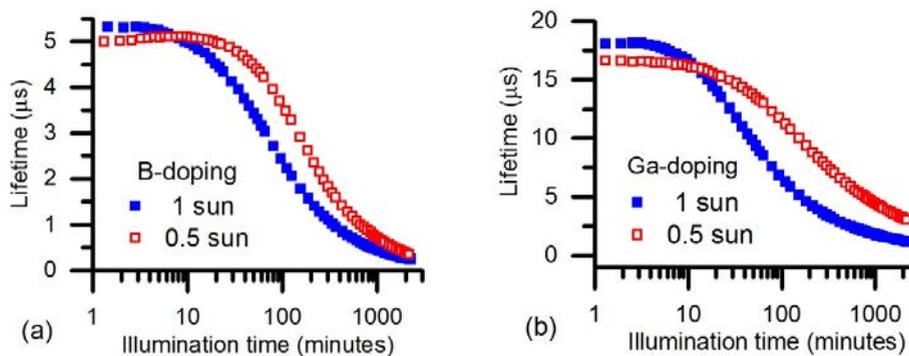


Fig. 5. LID detected in B-doped (a) and Ga-doped (b) samples under different illumination intensities (0.5 and 1 Sun). Faster degradation kinetics are observed at higher illumination intensity in both B- and Ga-doped samples.

4. Conclusion

In this paper copper-related LID has been investigated in both B- and Ga-doped mc-Si wafers as a function of the dopant, Cu contamination level, initial grain quality and light intensity. The saturated lifetime was found to decrease with increasing copper concentration, regardless of the initial grain quality. On the other hand, the degradation rate was observed to depend not only on the copper concentration, but also on dopant material, light intensity, and the grain quality. The correlation between the degradation rate and the grain initial lifetime indicates a possible interaction between copper impurities and the crystal lattice defects. In contrast to Ga-doped Cz-Si, our results also showed that in mc-Si even small copper concentrations can cause severe LID. Thus, it is concluded that copper cannot be ignored as a source of LID in multicrystalline silicon and it might play a role in the observed degradation of solar cells fabricated from mc-Si substrates. However, in order to correlate the observed degradation of mc-Si solar cells with Cu-related LID, further understanding must be achieved on the mechanisms involved in the observed phenomena and the effectiveness of gettering techniques for the removal of unintentional bulk copper contamination.

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