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## Cu gettering by phosphorus-doped emitters in p-type silicon: Effect on light-induced degradation

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The presence of copper (Cu) contamination is known to cause relevant light-induced degradation (Cu-LID) effects in p-type silicon. Due to its high diffusivity, Cu is generally regarded as a relatively benign impurity, which can be readily relocated during device fabrication from the wafer bulk, i.e. the region affected by Cu-LID, to the surface phosphorus-doped emitter. This contribution examines in detail the impact of gettering by industrially relevant phosphorus layers on the strength of Cu-LID effects. We find that phosphorus gettering does not always prevent the occurrence of Cu-LID. Specifically, air-cooling after an isothermal anneal at 800°C results in only weak impurity segregation to the phosphorus-doped layer, which turns out to be insufficient for effectively mitigating Cu-LID effects. Furthermore, we show that the gettering efficiency can be enhanced through the addition of a slow cooling ramp (-4°C/min) between 800°C and 600°C, resulting in the nearly complete disappearance of Cu-LID effects. © 2018 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). <https://doi.org/10.1063/1.5012680>

### I. INTRODUCTION

Copper (Cu) is an abundant and deleterious 3d metal impurity in photovoltaic grade crystalline silicon. Besides being present in significant concentrations in the as-grown feedstock material,<sup>1-4</sup> additional sources of Cu contamination are wafer sawing<sup>5</sup> and the use of cost-effective Cu alloys for contacts and interconnects. The presence of parasitic Cu contamination is known to progressively deteriorate the bulk minority carrier lifetime during exposure to illumination.<sup>6</sup> This phenomenon is referred in literature to as copper-related light-induced degradation (Cu-LID) and recent root-cause investigations have proven that Cu-LID arises from the transformation of interstitial Cu atoms into highly recombination active precipitates in the bulk region of the wafer.<sup>7-10</sup>

Gettering is a well-established technique, by which transition metal impurities are relocated to pre-defined substrate areas where they result less harmful for the device performance. In devices where the wafer bulk represents the region of major relevance for the device performance (e.g. solar cells), the gettering effect is usually achieved by creating a phosphorus-doped surface layer where metal impurities naturally tend to relocate during the high-temperature steps required for device fabrication.

Because of its high diffusivity in silicon,<sup>11</sup> Cu is generally regarded as an easily getterable impurity and, for this reason, little information exists on its actual getterability during device processing. Shabani *et al.* reported a decrement of the bulk Cu concentration by several orders of magnitude after diffusing heavily doped emitters with peak phosphorus concentration up to  $\sim 8 \times 10^{21} \text{ cm}^{-3}$  and subjecting the samples to various gettering anneals.<sup>3,12</sup> However, in state-of-the-art solar cells, it has become desirable to reduce the doping level of the emitter<sup>13</sup> because excessive dopant concentrations lead to the formation of an electrically inactive layer (often called “dead layer”),<sup>14,15</sup> increased

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emitter saturation current and Auger recombination,<sup>16,17</sup> with negative implications on the maximum achievable conversion efficiency. On the other hand, the choice of light emitter doping also weakens the driving force for the segregation of metallic impurities to the phosphorus-doped region, such that the benefits arising from light doping may be counterbalanced by the incomplete gettering of several metallic impurities, including Cu, as indicated by recent observations of Cu-related LID in industrial silicon solar cells.<sup>18,19</sup> It is therefore crucial to investigate the impact of gettering by lightly doped emitters on the strength of Cu-LID effects.

In this contribution, we test the getterability of Cu impurities with an industrially relevant phosphorus emitter and we assess the effectiveness of the gettering treatments by directly monitoring the Cu-LID effects caused by residual bulk Cu contamination after gettering. The aim of this study is (i) to assess whether bulk Cu contamination is controllable by lightly doped emitters to the extent that Cu-LID effects are fully inhibited and (ii) evaluate the impact of different gettering temperature profiles on the resulting Cu-LID effects.

## II. EXPERIMENTAL

The experiments were performed on electronic grade, 4-in., boron-doped, Czochralski-grown silicon with resistivity of 3.4–3.9  $\Omega$  cm, thickness of  $380 \pm 15$   $\mu\text{m}$ , and oxygen concentration  $\geq 14.5$  ppm. A schematic representation of the experimental processing steps is shown in Figure 1. After standard RCA cleanings, the wafers were oxidized in wet ambient at  $1000^\circ\text{C}$  for 84 min, which resulted in the growth of a 440 nm thick oxide layer. Some wafers were then kept as reference samples, while the rest of the batch was subjected to the formation of the phosphorus-doped region. Before dopant diffusion, the thermal oxide at the front side of the wafer was etched off, while the backside oxide layer was kept as a barrier for dopant diffusion. The emitter was then formed by depositing a phosphosilicate glass (PSG) via a phosphorus oxychloride ( $\text{POCl}_3$ ) process and then diffusing the dopant at  $830^\circ\text{C}$  for 20 minutes followed by a 5 min anneal in oxidizing ambient. Next, the PSG was removed in a HF:DIW solution (1:50) and the sheet resistance of the phosphorus layer was measured with a four-point probe to be  $\sim 80 \Omega \text{ sq}^{-1}$ . Electrochemical Capacitance-Voltage (ECV) measurements performed on similarly processed wafers also indicated a peak electrically active phosphorus concentration of  $\sim 2 \times 10^{20} \text{ cm}^{-3}$  and a junction depth of  $\sim 0.4 \mu\text{m}$ .<sup>20</sup>

Next, the processing of all wafers continued with the intentional Cu contamination. This step was executed by thinning the backside oxide layer down to  $45 \pm 10$  nm in buffered HF and subsequently depositing droplets of a 15 ppb% (w/v) Cu sulfate solution on a small area ( $\sim 10\text{-}11 \text{ cm}^2$ ) of the oxidized backside. Cu drive-in and gettering were then simultaneously performed during two different thermal

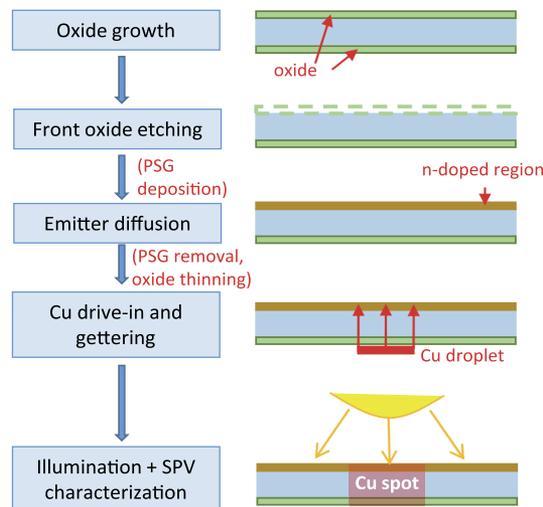


FIG. 1. Schematic representation of the experimental process flow for sample preparation and characterization.

treatments. Samples from Group A experienced an isothermal anneal at 800°C for 20 min followed by a fast air-cooling (*i.e.* direct pullout from the furnace producing a cooling rate of  $\sim 240^\circ\text{C}/\text{min}$ ), whereas specimens from Group B went through an additional temperature tail consisting of a cooling process from 800°C to 600°C at a controlled rate of  $4^\circ\text{C}/\text{min}$  before withdrawal from the furnace.

After the gettering anneals, all specimens were illuminated at room temperature (RT) under a 0.65 Suns LED lamp for up to 120h. The LID caused by the residual bulk Cu contamination was constantly monitored through the surface photovoltage (SPV) technique,<sup>21</sup> which enables the time-resolved monitoring of light-induced variations of the minority carrier diffusion length caused by ungettered Cu impurities without further sample processing.

### III. RESULTS

An overview of the results that will be hereinafter discussed is presented in Figure 2(a), which reports the diffusion length maps measured after 120 hours of room temperature illumination in reference specimens without phosphorus-doped layer and in the samples with  $n^+$ -emitter that underwent the aforementioned gettering anneals. As indicated by the diffusion length map of the reference specimen, the intentionally Cu contaminated areas appear in the form of a circular low diffusion length region, which stems from stronger LID than the surrounding uncontaminated areas. The more pronounced degradation observable in the middle of the Cu-contaminated region is also an indication of higher local Cu concentrations compared to the peripheral areas.<sup>22</sup>

In the samples from Group A, the Cu-spot remains clearly distinguishable from the neighboring uncontaminated areas. Hence, this result clearly demonstrates that, in these specimens, the gettering treatment did not result in the suppression of Cu-LID effects. In addition, the size of the Cu spot detected in these gettered samples remains comparable to the one observed in the reference samples, indicating that this gettering treatment remains ineffective towards the edge regions of the Cu-spot, where lower Cu densities are expected. Figure 2(a) also reports the SPV maps measured in the specimens from Group B. In this case, the slow cooling process experienced by such specimens appears to considerably enhance the gettering efficiency, as demonstrated by the nearly complete disappearance of Cu-LID effects after such treatment.

For the moment, we turn our attention onto the central region of each Cu spot marked by the white rectangles in Figure 2(a) and we analyze the average diffusion lengths measured within this region-of-interest before and after light soaking. As can be seen from Figure 2(b), a high initial diffusion length ( $\geq 600 \mu\text{m}$ ) was detected before illumination in both contaminated and uncontaminated areas of all samples. After light soaking, the diffusion length in the reference sample diminished to the value of  $155 \pm 15 \mu\text{m}$ , whereas it resulted in the range of  $220 \pm 10 \mu\text{m}$  and  $380 \pm 7 \mu\text{m}$  in the specimens from Groups A and B, respectively. Outside the intentionally contaminated regions, the average diffusion length was also found to decrease from  $\sim 600 \mu\text{m}$  up to  $\sim 425 \mu\text{m}$ , probably due to the light-activation of the so-called boron-oxygen complex.<sup>6</sup>

In order to quantitatively estimate the bulk Cu concentrations before and after gettering, it is possible to leverage earlier studies where the strength of the Cu-LID process (*i.e.* the lifetime/diffusion length variation before and after light soaking) has been correlated to quantitative measurements of the interstitial Cu concentrations involved in the degradation process.<sup>23,24</sup> After transforming the measured diffusion lengths into the corresponding lifetimes and inserting the obtained lifetime values into the empirical formula proposed in Ref. 24, we find an average Cu concentration of  $\sim 7 \times 10^{13} \text{ cm}^{-3}$  in the reference samples with no emitter, which approximately corresponds to the Cu contamination levels reported by several authors in as-cut solar-grade wafers.<sup>1,12,25</sup> In Group A, the residual Cu concentration after gettering is estimated to be  $\sim 3.8 \times 10^{13} \text{ cm}^{-3}$  (*i.e.* a gettering efficiency  $< 50\%$ ). On the other hand, the nearly complete disappearance of Cu-LID in the group B indicates residual Cu concentrations below  $5 \times 10^{12} \text{ cm}^{-3}$  (gettering efficiency  $> 90\%$ ). Hence, the results reported in Figure 2(b) indicate that in Group A the gettering treatment led to partial removal of the bulk Cu contamination, which was however insufficient for effectively suppressing the associated Cu-LID effects.

In order to evaluate the impact of gettering on the Cu-related degradation kinetics, the decay of the diffusion length was constantly monitored during light soaking and the density of Cu-related

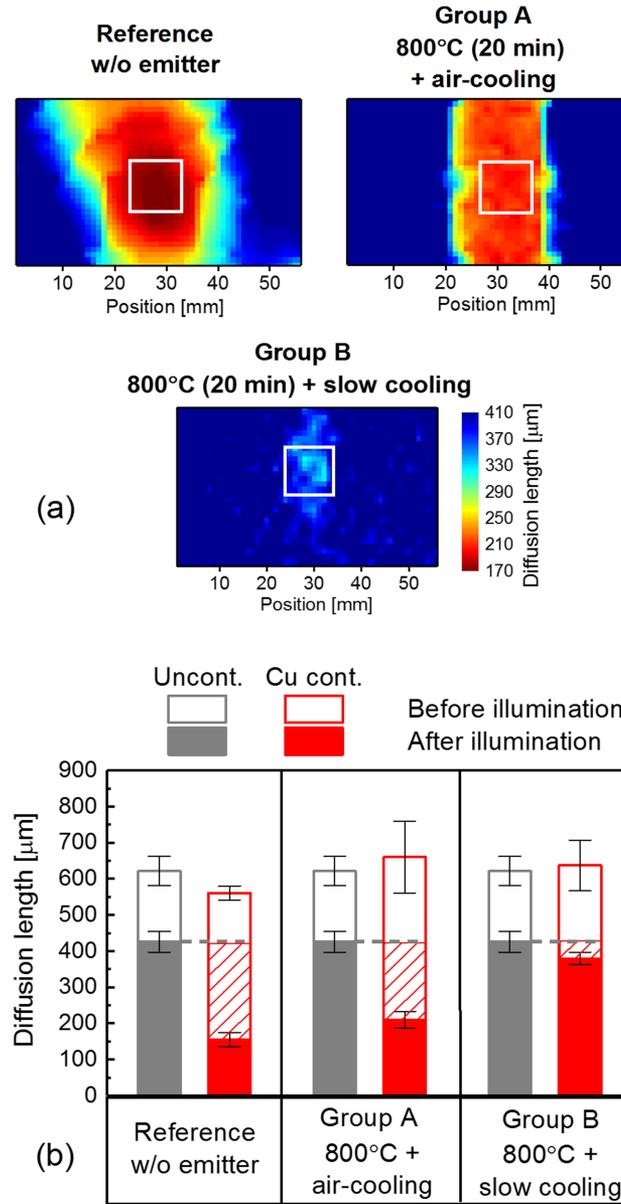


FIG. 2. (a) Diffusion length maps measured after 120 hours of RT illumination in reference specimens without phosphorus layer and in the samples from groups A and B with a  $\text{POCl}_3$ -diffused emitter. The white rectangles mark the region-of-interest (ROI) from which the values were averaged and plotted in figures (b). Figure (b) reports the average diffusion length measured in the reference uncontaminated and within the ROIs displayed in figure (a). The shaded areas highlight the diffusion length decay caused by Cu-LID and the error bars refer to the standard deviation of the measured diffusion length within the ROI.

recombination sites was calculated as

$$N_{Cu}(t) = \frac{1}{L(t)^2} - \frac{1}{L(t=0)^2} - \frac{1}{L_{ref}(t)^2}, \quad (1)$$

where the term  $L_{ref}(t)$  accounts for the aforementioned background degradation in the uncontaminated regions. Figure 3 plots the normalized value  $N_{Cu}(t)/N(t \rightarrow \infty)$  as a function of illumination time.

It is possible to observe that the gettering treatment considerably slows down the Cu-related degradation, as in the specimens from Group A the saturation of the degradation kinetics is reached after several thousands of minutes, whereas in reference samples without emitter the same extent of degradation is reached within few tens of minutes. As the Cu-related degradation rate is proportional

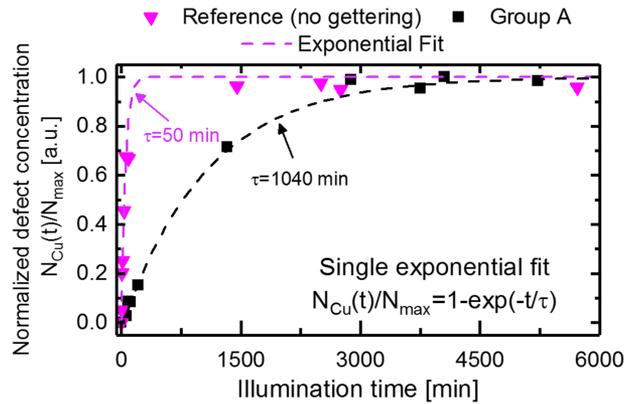


FIG. 3. Normalized Cu-related defect concentration as a function of illumination time for reference samples and gettered sample from Group A. The dashed lines represent the least-mean-square fits according to a single exponential function. The data reported in the figure have been calculated from the average diffusion length measured within the ROIs previously shown in Figure 2.

to the Cu concentration involved in the LID process,<sup>6,26</sup> Figure 3 further supports the conclusion drawn from the results presented above, i.e. the gettering anneal followed by air-cooling resulted in partial, yet incomplete removal of bulk Cu impurities.

#### IV. DISCUSSION

On the base of the results presented above, it is possible to deduce that the cooling phases after high-temperature anneals are a critical stage for efficient Cu gettering. This is explainable with the hypothesis of impurity segregation<sup>27</sup> in the phosphorus layer driven by the enhancement of the Cu solubility gradient between the emitter and the wafer bulk during the cooling ramps. Figure 4 plots the variation of the Cu diffusivity<sup>28</sup> and the equilibrium segregation coefficient  $k_{seg} = \frac{S_{em}}{S_{bulk}}$  calculated from the average Cu solubility in the bulk ( $S_{bulk}$ ) and in the emitter ( $S_{em}$ ) predicted by the model

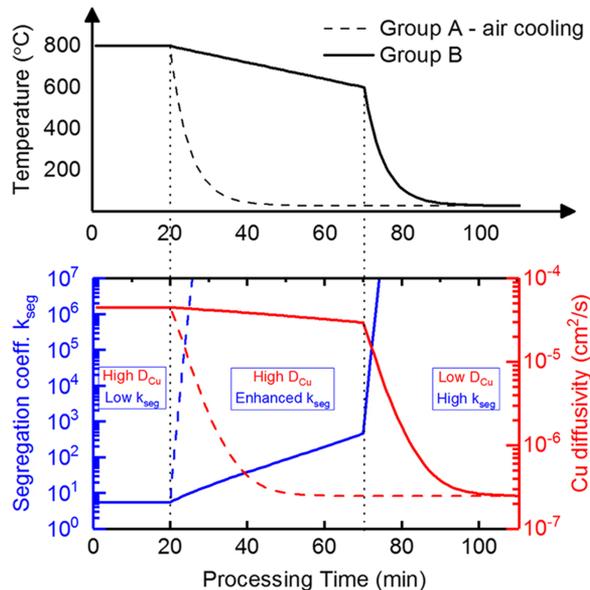


FIG. 4. Cu segregation coefficient and diffusivity during the thermal treatments for Cu drive-in and gettering calculated from the models described in Refs. 29 and 28, respectively. Temperature variation during air-cooling has been approximated through an exponential function with a time constant that reproduces the measured cooling rate (240°C/min).

proposed by Hoezl *et al.*<sup>29</sup> In the temperature range between 700°C and 800°C, the Cu diffusivity is maximum but  $k_{seg} \approx 4$ , indicating that weak impurity segregation takes place during the isothermal anneal at 800°C and the initial phase of the cooling ramp. When temperature approaches 600°C, the Cu diffusivity remains close to its maximum value, while  $k_{seg} \approx 400$  due to the drastic decrease in bulk Cu solubility.

While these considerations are consistent with the experimental observations from Group B, such calculations do not fully explain the persistence of Cu impurities in Group A, which experienced the same temperature variation during the cooling phase (hence the same change in Cu solubility gradient), although on a considerably shorter timescale. Indeed, after integrating the Cu diffusivity during the different cooling transients of Groups A and B, we find that in both cases the theoretical diffusion length of Cu species exceeds the wafer thickness. Hence, the ineffectiveness of the gettering treatment in Group A does not seem to be attributable to the incomplete diffusion of Cu species during air-cooling, but presumably to other competing effects that ultimately reduce the mobility of Cu impurities. Possible competing phenomena might include impurity trapping at bulk microdefects (e.g. oxygen precipitates) or electrostatic interactions of interstitial Cu ions with the electric fields at the interface between p- and n-doped regions. In order to gain deeper insights, future work will focus on the accurate modelling of the gettering process and the in-depth analysis of the effect of precipitated oxygen on the efficiency of phosphorus gettering.

## V. CONCLUSION

In this contribution, we have tested the getterability of Cu impurities in presence of a lightly doped phosphorus-emitter diffused from a  $\text{POCl}_3$  source. The effectiveness of several gettering treatments has been evaluated in relation to their effective capability of mitigating LID effects caused by intentionally added Cu contamination. The results presented in this manuscript have shown that Cu is not necessarily a benign impurity, whose detrimental LID effects can be fully controlled by relocation to the phosphorus-doped layer. Indeed, complete mitigation of Cu-related LID effects was only achievable through the addition of a slow cooling tail after the gettering anneal, which kept the samples at intermediate temperatures (600-700°C) for several tens of minutes.

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