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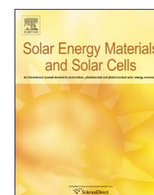

# Influence of the solar cells metallization firing treatment on carrier recombination and trapping in copper contaminated multicrystalline silicon: new insights into the role of the phosphorus-rich layers

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The influence of superficial phosphorus-rich layers during the metallization firing treatment on carrier recombination and trapping in copper contaminated multicrystalline silicon was investigated. Copper contaminated wafers experienced firing steps with and without phosphorus-rich layers. The samples fired without phosphorus emitters feature higher bulk carrier lifetimes, but also a stronger sensitivity to the copper-related light-induced degradation (LID), which was activated by the firing treatment. This last behavior could be used to identify the dominant LID mechanism (boron-oxygen related or copper related) in multicrystalline wafers. In addition, only the samples fired without the phosphorus emitters are subjected to trapping effects, probably involving copper atoms initially precipitated. Copper precipitates are virulent recombination centers whereas the electrical activity of interstitial copper is benign. Therefore these experimental results suggest that on the one hand the wafers fired with the phosphorus-rich layers contain lower interstitial copper concentrations. On the other hand they would feature higher densities of copper precipitates and/or larger copper precipitates.

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## 1. Introduction

Copper (Cu) is one of the most abundant metal impurities in cast multicrystalline (mc) silicon (Si) for solar cells. Cu concentrations ([Cu]) as high as $10^{13}$ cm$^{-3}$ have been found in mc-Si wafers obtained by directional solidifications in crucible [1]. Cu essentially comes from the silica crucible and its Si nitride coating [2]. Furthermore, as a consequence of the wafering process, Cu is the main metal element present at the surfaces of as-cut wafers (with Cu surface concentrations in the range of about $10^{13}$ cm$^{-2}$) [3]. Cu, which is well extracted from the Si bulk by the external gettering effect developed by the phosphorus (P) diffusion, does not significantly affect the initial photovoltaic conversion efficiency of solar cells [4]. However, Cu is responsible for deleterious light-induced degradation (LID) effects [4]. Under illumination the excess charge carriers would reduce the electrostatic repulsion between positively charged interstitial Cu ($Cu_i$) ions (non-recombinant) and positively charged Cu precipitates (highly recombinant), enhancing the Cu precipitation and therefore degrading the charge carrier lifetime ($\tau$) [5]. The last high temperature (T) treatment of the solar cell fabrication process is generally a rapid thermal annealing (RTA), the so-called firing, essentially used for the sintering of the screen-printed metal electrodes. Due to the combined actions of the high T and the fast cooling (enhancing the dissolution of the metal precipitates [6]), this step usually governs the final spatial distribution of metals. Therefore, understanding its effects is crucial to limit the impact of metals on the performances of solar cells. Tan et al. observed that RTA steps conducted on samples without P emitters ($n^+$ layers) degrade the $\tau$ of mc-Si, likely due to the dissolution of metal precipitates (particularly iron precipitates) [7]. On the other hand, when P emitters are present during the annealing, they observed an increase of $\tau$ but could not propose an explanation for such a finding (the $n^+$ emitter during the RTA would neither develop an external gettering effect nor enhance the bulk hydrogenation). In these pioneering works [7], the presence and effects of Cu were not evoked, and the carrier trapping not investigated. Thus, the present study examines the role of the P-rich layer during the firing step on both carrier recombination and trapping in deliberately Cu contaminated mc-Si.

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## 2. Experimental details

A mc-Si ingot was grown by directional solidification from ultra-pure electronic-grade Si (EG-Si) deliberately contaminated with 90 ppm wt of Cu. The ingot was boron (B)-doped in order to obtain *p*-type wafers with standard resistivity (ρ), around 1 Ω cm. On a vertical cut, the interstitial oxygen concentrations ($[O_i]$) and the substitutional carbon concentrations ($[C_s]$) were determined by Fourier transform infrared spectroscopy. The following calibration coefficients were used for the $[O_i]$ and $[C_s]$ determinations: $3.14 \times 10^{17}\ cm^{-2}$ and $1.0 \times 10^{17}\ cm^{-2}$, respectively. The ingot was cut in $156 \times 156\ mm^2$ square wafers with a thickness of about 200 μm. Adjacent sister wafers were then taken at an ingot's height of about 41%. For these wafers, the corresponding $[O_i]$ and $[C_s]$ (determined on the vertical cut, but for an identical height) were equal to $6.9 \times 10^{16}\ cm^{-3}$ and $3.0 \times 10^{17}\ cm^{-3}$, respectively. Reference mc-Si wafers (ρ around 1 Ω cm), grown without intentional Cu contamination, were also used as references. These wafers were taken at an ingot's height of about 39%. The corresponding $[O_i]$ and $[C_s]$ were equal to $1.9 \times 10^{17}\ cm^{-3}$ and $3.4 \times 10^{17}\ cm^{-3}$, respectively. Furthermore, single-crystalline Czochralski (Cz) EG-Si wafers (thickness of about 200 μm), B-doped to about $10^{16}\ cm^{-3}$, were used as references for the determination of the recombination characteristics of surfaces/emitters (see below). All the wafers (mc and Cz) were acid etched and RCA cleaned before a double sided $POCl_3$ diffusion resulting in a sheet resistance of 70.6 Ω/sq. The P-diffusion treatment is composed of two main steps. First the wafers were annealed at 850 °C for about 45 min, before the temperature was lowered to 800 °C for about 20 min. Notice that we confirmed that this P-diffusion treatment develops strong external gettering effects for fast diffusing metal impurities. For instance we showed that the effective carrier lifetime of *n*-type mono-like wafers could be improved from 150 μs to 1.0 ms using this treatment [8]. Some wafers were then stripped of their $n^+$ emitters by acid etch. All samples received a double sided plasma enhanced chemical vapor deposition (PECVD) hydrogenated Si nitride ($SiN_x$:H) coating. The $SiN_x$:H film is a high mass density SiN layer with a refractive index equal to 2.0 (for a corresponding wavelength of 605 nm). This $SiN_x$:H coating layer features moderate passivation properties, but the corresponding surface passivation is perfectly stable under illumination. This point was checked experimentally in our institute in the frame of a study on FZ samples [9]. Then the samples were fired in an infrared lamps conventional belt furnace. The annealing consists in two steps: a first step between 100 °C and 500 °C with a duration of 20 s, and a second step at about 750 °C during 3 s. Samples were characterized before and after the firing at 5 locations across each sample, by inductively-coupled quasi-steady-state photoconductance decay (IC-QssPC) measurements, giving the variation of the apparent effective τ ($\tau_{app}$) with the apparent excess carrier density ($\Delta n_{app}$) [10]. For $\Delta n_{app}$ higher than $7 \times 10^{14}\ cm^{-3}$, the IC-QssPC data were not affected by minority carrier trapping. Therefore for such $\Delta n_{app}$, $\tau_{app}$ could be assumed to be equal to the effective τ ($\tau_{eff}$) and $\Delta n_{app}$ to the excess carrier density (Δn). Just after the firing, before any prolonged illuminations, the wafers were kept in the dark at 20 °C and IC-QssPC measurements were done at various time intervals. Furthermore, the evolutions at 50 °C of $\tau_{eff}$ under illumination (halogen lamp, intensity of $0.04\ Wcm^{-2}$) were monitored before and after the firing. For a Cu-contaminated mc sample fired without the $n^+$ layer, the procedure for determining the dissolved iron (Fe) concentration ($[Fe_d]$) based on $\tau_{eff}$ measurements before and after the dissociation via light soaking of the iron-boron (FeB) pairs, was applied [11,12]. Notice that this procedure was applied after a prolonged illumination for stabilizing $\tau_{eff,}$ followed by a 24 h storage of the wafers in the dark, to ensure a complete re-association of the FeB pairs. Also, as a microwave-based technique was used for determining $\tau_{eff}$, this $[Fe_d]$ determination was limited to the samples without the $n^+$ layers.

The total Cu concentrations ([Cu]) were determined on sacrificial samples by inductively-coupled plasma mass spectrometry (ICP-MS) before and after the P-diffusion (after the emitter etch). The ICP-MS analyses were conducted on adjacent samples to the studied wafers. They were systematically performed after a surface etching step, to remove about 20 μm of Si (from each side of the wafer). For the as-cut samples this etching step removed the contaminations due to the sawing step, and for the P-diffused wafer, it removed the $n^+$ layer and the large amounts of Cu accumulated in this region of the wafer. Then, the etched samples experienced a digestion procedure by acidic solutions, before the quasi total evaporation of the solution and the analysis by ICP-MS of the remaining droplet. Therefore the results are representative of the total (dissolved and precipitated) Cu bulk concentration within the wafer. For the as-received Cu-contaminated and reference mc-Si samples, [Cu] were equal to $7.7 \times 10^{14}\ cm^{-3}$ and $8.7 \times 10^{12}\ cm^{-3}$, respectively. For the P-diffused Cu-contaminated sample, [Cu] was below the measurement detection limit (around $7 \times 10^{11}\ cm^{-3}$), which confirms the fact that Cu atoms, due to their high diffusivity, are well extracted from the Si bulk by the external gettering effect developed by the P-diffusion [4].

## 3. Results and discussion

### 3.1. Effect of the metallization firing on the charge carrier lifetime

Fig. 1 displays the $\tau_{eff}$ (for $\Delta n = 10^{15}\ cm^{-3}$) of P-diffused Cu-contaminated mc wafers, before and just after the firing. $\tau_{eff}$ are improved by the firing, with and without $n^+$ layers. These results are *a priori* contradictory with those of Tan et al. [7], who highlighted increases of $\tau_{eff}$ after the firing for the samples with the $n^+$ layer only. Notice that in Tan's study, after the RTP treatment, the $SiN_x$:H layers and the $n^+$ emitter were removed before the redeposition of new $SiN_x$:H layers. Therefore all their samples featured identical surface recombination velocities (S). However for our study, we decided to determine $\tau_{eff}$ directly after the firing treatment. Indeed, as Cu is a very fast diffuser in Si, the PECVD step

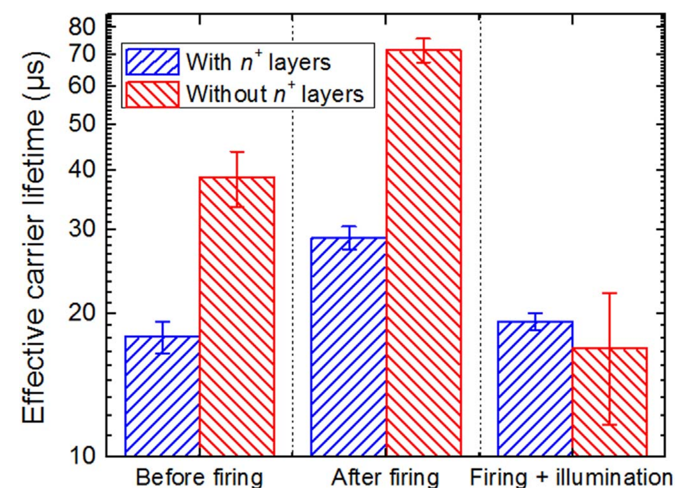


**Fig. 1.** Effective carrier lifetime of Cu-contaminated mc-Si wafers with and without the P-rich layers ($n^+$ layers). The values were extracted for an excess carrier density of $10^{15}\ cm^{-3}$. The samples experienced a P-diffusion step. The measurements were done after the P-diffusion step (before firing), after the firing step before illuminating the samples (after firing), and after 30 h at 50 °C under permanent illumination (firing+illumination). The error bars represent the standard deviation of results.

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