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Finite- vs. infinite-source emitters in silicon photovoltaics: Effect on transition metal gettering

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Abstract — Control of detrimental metal impurities is crucial to silicon solar cell performance. Traditional silicon solar cell emitters are diffused in an infinite-source regime and are known to cause strong point defect segregation towards the emitter and thus enhance bulk minority carrier diffusion length. With the advent of ion-implantation and chemical vapor deposition (CVD) glasses, finite-source diffused emitters are attracting interest. This contribution aims to increase their adoption by elucidating the dominant gettering mechanisms present in finite-source diffused emitters. Our findings indicate that infinite-source diffusion is critical for effective segregation gettering, but that high enough surface phosphorus concentration can activate segregation gettering *via* finite-source diffusion as well. In the case of ion-implanted emitters, the traditional segregation gettering may be considerably enhanced by impurity precipitation in the implanted layer.

I. INTRODUCTION

The art of gettering, the mitigation of deleterious trace impurities, has garnered attention throughout the history of photovoltaics. While this topic is thoroughly researched for phosphorus emitters operating under infinite-source diffusion, the topic of gettering with finite-source emitters is still in its infancy [1–3]. Finite-source emitters offer benefits, such as, better blue response and no phosphosilicate glass formation [3–5].

This work quantitatively characterizes the gettering efficiency of iron with industrially relevant finite-source emitters facilitated via ion-implantation. We study the extent to which ion-implanted emitters induce segregation of iron point defects and discuss whether their gettering efficiency is enhanced by the formation of iron-silicide precipitates at the implanted layer. We compare the results to an infinite-source diffused POCl_3 emitter. We work with intentionally iron-contaminated high-quality Czochralski-silicon (Cz-Si) wafers processed in IC-grade cleanrooms. Such work on “model” iron-contaminated Cz-Si samples [6] has previously proven to be transferable to other materials and contaminants, such as multicrystalline silicon [7] or chromium [8].

II. EXPERIMENTAL

Single-crystalline, 4-inch, 380 μm thick, p-type, 3–5 $\Omega\text{-cm}$, Cz-Si wafers were intentionally contaminated by immersing them in an iron-spiked RCA solution [9]. The iron was in-diffused by annealing the wafers at i) 940°C for 50 minutes for a high contamination level $[\text{Fe}_0]$ of $9 \times 10^{13} \text{ cm}^{-3}$ or ii) 850°C for 55 minutes for a low contamination level of $8 \times 10^{12} \text{ cm}^{-3}$.

After contamination, the front sides of the wafers were phosphorus implanted with an energy of 10 keV and a dose of $2.5 \times 10^{15} \text{ cm}^{-2}$. The implant was activated by annealing at 850°C for 20 minutes. These implant parameters are typical for silicon solar cells [4, 5]. After the implant activation, the wafers were cooled at 4°C/min to either i) 700°C and pulled out of the furnace to room temperature, or underwent a low temperature anneal (LTA) at ii) 700°C for 5.5 hours or iii) 620°C for 8 hours. These samples are later referred to as the “700°C”, “700°C+LTA” and “620°C+LTA (A)”, respectively. We compare the results to earlier implanted samples [1], which were intentionally iron-contaminated at same in-diffusion temperatures, but whose phosphorus was implanted with a 50-keV energy through a 31-nm-thick screen oxide with a dose of $1 \times 10^{15} \text{ cm}^{-2}$. The implant was activated at 1000°C for 40 minutes, followed by a slow cool to and an anneal at i) 750°C for 3.5 h or ii) 620°C for 8 h. These samples are referred to as “750°C” and “620°C+LTA (B)”, respectively.

For comparison, an industry-standard infinite-source emitter was created by depositing POCl_3 on both sides of the samples at 830°C for 25 minutes, followed by a 4°C/min cool to 700°C, which is later referred to as “ POCl_3 ”. Emitter and gettering parameters of all samples are summarized in Table I.

The sheet resistances and the electrically active phosphorus surface concentrations $[\text{P}^+]_{\text{surf}}$ of the emitters were measured by four-point probe and electrochemical capacitance-voltage (ECV) measurements, respectively. The phosphosilicate glass layer was etched from the POCl_3 samples before characterizing

TABLE I
EMITTER AND GETTERING PARAMETERS

Sample	Emitter formation	Low temperature anneal
POCl ₃	POCl ₃ , 830°C	-
700°C	10 keV, 850°C	-
700°C+LTA	10 keV, 850°C	5 h at 700°C
620°C+LTA (A)	10 keV, 850°C	8 h at 620°C
750°C+LTA	50 keV, 1000°C	3.5 h 750°C
620°C+LTA (B)	50 keV, 1000°C	8 h at 620°C

the emitter. For the 750°C+LTA and 620°C+LTA (B) samples, $[P^+]_{\text{surf}}$ was estimated based on secondary ion mass spectroscopy (SIMS) and sheet resistance measurements [1].

Iron point defect removal from the bulk of the wafers was quantified by measuring the bulk interstitial iron concentration by the traditional iron-boron pair breaking technique [9]. Interstitial iron concentration was measured by surface photovoltage (SPV) for the implanted samples and by emitter etching and microwave-assisted photoconductance decay (μ -PCD) for the POCl₃ samples. The back surfaces of the implanted samples and both surfaces of the POCl₃ samples were passivated by a 25-nm-thick Al₂O₃ layer which was annealed at 400°C for 30 min.

The distribution of iron-silicide precipitates at or near the emitters was studied via synchrotron-based micro-X-ray fluorescence (μ -XRF) at Advanced Photon Source beamline 2-ID-D [10] with incident photon energy of 10 keV and an effective information depth for iron K α fluorescence of 8.8 μ m. Precipitates were separated from background noise by assuming a statistical noise limit of 3.5 standard deviations above the mean of the Gaussian background noise [11].

III. RESULTS AND DISCUSSION

A. High surface phosphorus concentration and infinite-source diffusion facilitate segregation gettering

Fig. 1 shows that the sheet resistances of most samples were near 100 Ω/\square , which is a typical sheet resistance range for PV emitters [12]. Phosphorus appears to have precipitated during the low temperature anneal [13] in samples 620°C+LTA (A), leading to a higher sheet resistance.

Fig. 2 shows that the trends in gettering behavior of the implanted and POCl₃ samples differ significantly. All the implanted samples exhibit “inversion” of the original contamination levels, where a higher initial contamination level (red bars) results in a lower bulk iron concentration after gettering. This is characteristic of precipitation, where a higher initial supersaturation results in stronger precipitate nucleation and more sinks for iron [1]. On the contrary, the highly and lowly contaminated POCl₃ samples show similar bulk iron concentration ratios before and after gettering, differing by an order of magnitude in both cases. Post-gettering iron concentrations are also over an order of magnitude below the

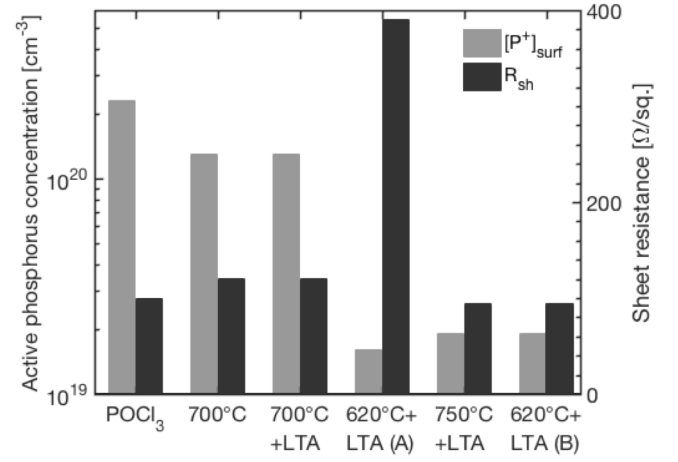


Fig. 1. Emitter properties measured from the studied samples.

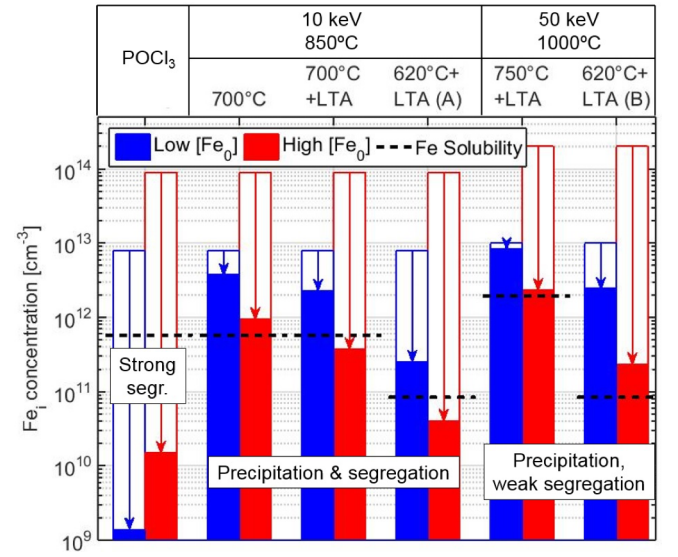


Fig. 2. Gettering efficiencies of the performed anneals. Solid solubility of iron at the lowest furnace temperature of each anneal is shown as a dashed line. Dominance of segregation and precipitation gettering is highlighted.

solid solubility limit at the lowest furnace temperatures. These observations suggest that segregation gettering, caused by enhanced iron solubility in the emitter, is the dominant gettering mechanism.

The high gettering efficiency of the POCl₃ samples is striking: their bulk iron concentration decreases by almost four orders of magnitude. The difference compared to the implanted emitters is notable, given that the thermal budget of the POCl₃ samples is the smallest of all samples, underscoring the importance of infinite-source diffusion for segregation.

The implanted wafers of this study were activated at 850°C, whereas in the previous study [1], 1000°C was used, resulting in a deeper junction and lower $[P^+]_{\text{surf}}$ of around 2×10^{19} cm⁻³. We thus hypothesize, that the increased gettering efficiency

observed in the lowly contaminated samples with an 850°C activation versus the samples activated at 1000°C, is due to segregation gettering due to a higher $[P^+]_{\text{surf}}$ of around $1 \times 10^{20} \text{ cm}^{-3}$. The apparent segregation gettering of the 620°C+LTA (A) sample, on the other hand, is likely due to a high concentration of electrically inactive phosphorus in the emitter [14].

B. Precipitation-enhanced gettering at highly contaminated implanted samples

The higher relative iron reduction in the highly-contaminated implanted samples was confirmed to be precipitation by detecting precipitates by μ -XRF in all the highly contaminated implanted samples from all samples with both 10 keV and 50 keV [2] P-implants. Precipitates above the detection limit (6×10^4 atoms, or 8-nm-radius sphere) were not found from comparable areas of the lowly-contaminated 700°C+LTA or the 620°C+LTA (A) samples, or from the highly contaminated POCl_3 sample. Thus, iron precipitation at the implanted layer is indeed a significant gettering mechanism, even in the 700°C sample, whose thermal budget and emitter profile is well-suited for industrial, high-performance solar cells. Further analysis of the μ -XRF findings will be presented elsewhere [15].

IV. CONCLUSIONS

Our results indicate that infinite-source diffused phosphorus emitters can induce orders of magnitude stronger segregation gettering of iron than finite-source emitters with comparable sheet resistances. Finite-source diffusion can also result in segregation gettering, given a sufficiently high ($\sim 1 \times 10^{20} \text{ cm}^{-3}$) surface phosphorus concentration. Ion-implanted emitters, a specific kind of a finite-source diffused emitter, appear to gain additional gettering benefit from iron precipitation at the implanted layer, possibly at residual implantation damage, including resulting surface defects.

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