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Effect of electrically inactive phosphorus versus electrically active phosphorus on iron gettering

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Abstract

In this study we investigate the efficacy of iron gettering as a function of electrically inactive phosphorus in the emitter in combination with low temperature annealing steps. To achieve different amounts of electrically inactive phosphorus in the emitter a highly doped PSG produced emitter with a large plateau depth of electrical active phosphorus is etched back stepwise by a wet-chemical procedure. Therewith we achieve a gradual reduction in electrically inactive phosphorus with small changes in electrically active phosphorus ($\Delta R_{sh} < 4\ \Omega$/sq). After this step, the wafers with different emitters have been annealed at 700°C for 30 min and the content of Fe_i in the bulk has been measured using QSS-PC. The results show, (i) that for higher amounts of electrically inactive phosphorus a stronger iron gettering effect can be observed and (ii) that an additional annealing step leads to a significant change of Fe_i. This means, (i) that an electrically inactive phosphorus concentration dependence for iron gettering is observed and (ii) additional annealing steps, below the usual diffusion temperature of phosphorus, can be used to reduce interstitial iron in highly contaminated wafers further.

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Keywords: Phosphorus Diffusion Gettering, Electrically Inactive Phosphorus, Gettering, Iron, Low Temperature Annealing

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1. Introduction

The effect of Phosphorus Diffusion Gettering (PDG) of iron using different temperature profiles has been widely studied [1-6]. However, the mechanisms behind phosphorus gettering of iron are still a part of current research. The aim of this work is to better understand the role of the electrically inactive versus electrically active phosphorus in the gettering effect on iron, studying:

- The variation of the content in electrically inactive phosphorus maintaining very small the changes in content of electrically active phosphorus using process at the same temperature, time and gas flow rates.
- The effect on Fe concentration and distribution during annealing as a function of electrically active and inactive P content.
- The gettering effect due to the Phosphosilicate Glass layer (PSG).

2. Experimental approach

For this study, we used p-type Cz-Si wafers with bulk resistivity of about 12 Ωcm and thickness of about 515 μm. The wafers were intentionally contaminated with iron using a SC1 solution with 30 ppb of iron during 10 min. followed by an annealing during 1 hour at 850ºC in nitrogen ambience. After this, they were treated with the same process: an etching in HF:H2O2:H2O solution followed by CP4 etching, a standard chemical cleaning, a P emitter diffusion using liquid POCl3 source in a tube furnace with 60 min of pre-deposition at 875ºC and 30 min of drive-in at the same temperature. Then, we obtained different content of electrically inactive phosphorus by etching-back subsequently the heavily doped phosphorus emitter during 2 min and 4 min (see Fig.1). Finally, all the samples received: an annealing at 700ºC during 30 min in nitrogen ambience, a chemical etching to remove the P emitter, a standard chemical cleaning, and a PECVD deposition of SiNx on both sides with a thickness of approximately 70 nm for dielectric passivation. Then, Fe_i concentration was measured using the QSS-PC technique [7]. Reference wafers with emitter was prepared in parallel for measuring electrically active phosphorus content in emitter using Electrochemical Capacitance-Voltage (ECV) and four point probe. In addition wafers with PSG and without emitter received the same annealing for analyzing the influence of the PSG layer on Fe gettering effect and measuring the dissolution of Fe precipitates, respectively.

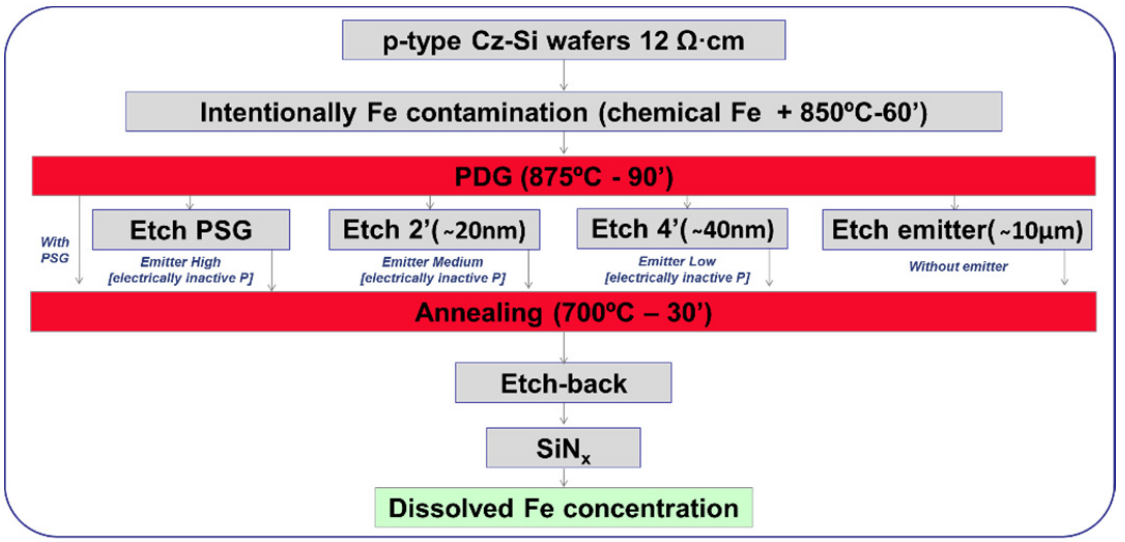

Fig. 1. Processing sequence

3. Results and discussion

Electrically active phosphorus measured by Electrochemical Capacitance-Voltage (ECV) of the emitter with high electrically inactive P concentration is showed in Fig. 2. Etching the emitter subsequently from 18 Ω/sq to 20.1 and 20.9 Ω/sq produces a gradual reduction in electrically inactive phosphorus with small changes in electrically active P ($\Delta R_{sh} < 4$ Ω/sq).

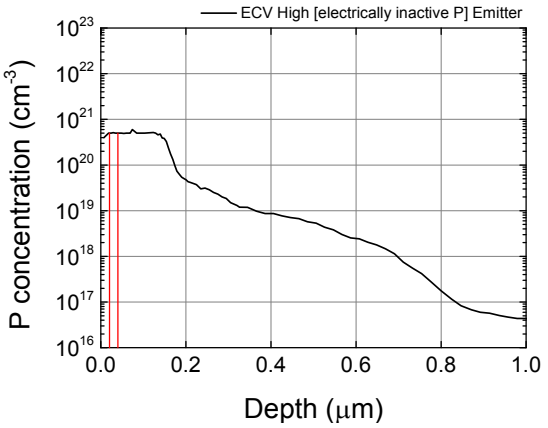

Fig. 2. Electrically active phosphorus measured by Electrochemical Capacitance-Voltage (ECV) of the sample with high content of electrically inactive phosphorus emitter. Red lines represent the approximated subsequent etched-off emitter ECV profile after 2 and 4 min for obtaining the emitter with medium and low content of electrically inactive phosphorus, respectively.

We observe in Fig. 3 that sheet resistance (R_{sh}) measurement after an annealing is slightly higher in all the cases. This means that active phosphorus concentration is reduced during annealing. The reason could be that solid solubility of phosphorus in silicon at the annealing temperature is lower than during the emitter formation. As the active phosphorus as a direct relationship with segregation of iron [1], then we could expect than the iron segregation effect due to active phosphorus is lower than during PDG due to its slight reduced value. This electrically active phosphorus is supposed to form bonds with other compounds converted in a type of electrically inactive phosphorus (and then contributing to its gettering effect of iron) during the annealing at a temperature lower than PDG.

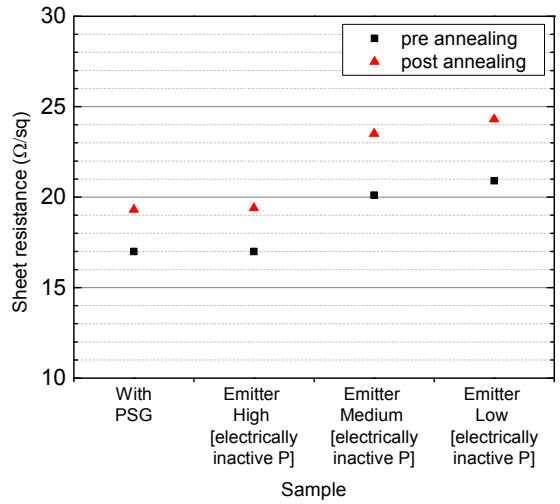

Fig. 3. Sheet resistance measurements by four point probe before and after annealing for the different emitter.

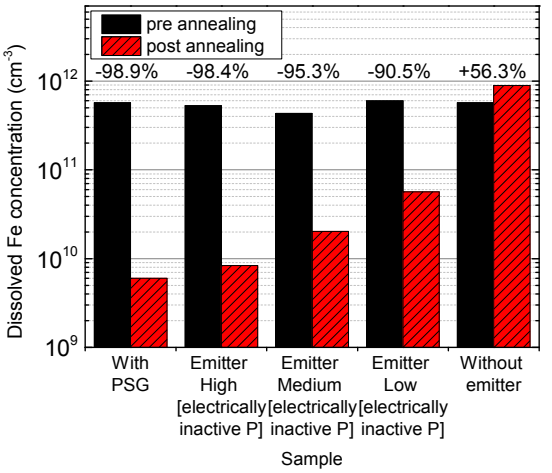

Fig. 4. Interstitial iron concentration QSSPC measurements of samples with emitters that contain different concentrations of electrically inactive phosphorus and similar electrically active phosphorus concentrations ($\Delta R_{sh} < 4$ Ω/sq). The samples are measured before and after an annealing at 700ºC during 30 min. Percentages are the relative [Fe_i] variation calculated as: $\Delta[Fe_i]/[Fe_{i\ pre}]$

Fig. 4 shows Fe_i concentration measurements before and after an annealing at 700ºC during 30 min. First group shows the Fe_i concentration variation due to the annealing of a wafer with an emitter with high content in electrically inactive P and with PSG present. We observe a reduction of dissolved Fe_i from $6{\cdot}10^{12}$ cm^{-3} to $6{\cdot}10^{9}$ cm^{-3} (relative variation of -98.9%). Dissolved Fe measurements of a wafer with the same emitter but without PSG layer varies from $5{\cdot}10^{12}$ cm^{-3} to $8{\cdot}10^{9}$ cm^{-3} (relative variation of -98.4%). The reduction is slightly higher when PSG layer is present. The following two groups in Fig. 4 show the variation of Fe_i concentration before and after the annealing in samples with gradually less content in electrically inactive phosphorus and similar electrically active phosphorus. We observe than in the case of wafer with medium electrically inactive phosphorus content the Fe_i concentration varies from $4{\cdot}10^{12}$ cm^{-3} to $2{\cdot}10^{10}$ cm^{-3} (relative variation of -95.3%) and in the case of low electrically inactive phosphorus concentration Fe_i concentration measurements range from 6·1012 cm^{-3} to $6{\cdot}10^{10}$ cm^{-3} (relative variation of -90.5%). We observe that being the pre-annealing values similar in the three type of emitter, the post-annealing Fe_i concentration are respectively higher when content in electrically inactive phosphorus decreases. Finally, we present the measurements pre and post annealing of a wafer that received the annealing without the presence of phosphorus emitter. We observe an increase of final Fe_i concentration from $6{\cdot}10^{12}$ cm^{-3} to $9{\cdot}10^{12}$ cm^{-3} (relative variation of +56.3%). The annealing step causes dissolution of iron precipitates and when the emitter is present this dissolution is compensated by external gettering into the P emitter layer. Regarding the Fe_i reduction, we observe a better Fe_i gettering in the case of an emitter with high electrically inactive phosphorus content. In all the cases, the dissolution of Fe precipitates is the same, as temperature and time of the process are the same. This result could be attributed to the presence of electrically inactive P bonds that are supposed to increase the segregation of Fe from bulk to emitter.

4. Conclusion

The effect on Fe concentration and distribution during annealing as a function of electrically active and inactive P content has been measured. The variation of the content in electrically inactive P has been approach with process at the same temperature, time and gas flow rates. We have observed that the higher the content in electrically inactive phosphorus, the stronger the iron gettering effect. Extra gettering effect has been measured after the annealing with the presence of the PSG layer.

Acknowledgements

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