ANALYSIS OF CELL-PROCESS INDUCED CHANGES IN MULTICRYSTALLINE SILICON

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ABSTRACT

We analyse the effect of individual process steps on the material quality of mc-Si wafers. In addition to the commonly used recombination lifetime, we measure material parameters such as the concentration of interstitial oxygen, and of FeB. We show that such additional variables in the analysis can give much more information and insight into the effect of individual process steps.

We have processed ingots from several manufacturers using a fired-through silicon nitride passivation scheme, and analysed several variations of process steps. Main results include i) the temperature dependence of phosphorus gettering; ii) the absence of a clear synergetic effect of co-firing silicon nitride with an aluminium rear side coating; and iii) influence of phosphorus diffusion on subsequent hydrogen passivation.

1. INTRODUCTION

Impurities and defects determine the minority carrier lifetime in multicrystalline silicon. The average recombination lifetime in multicrystalline ingots is usually quite high, up to about 100 • s, and depends on the position in the ingot. Wafers from the edge regions of the ingot show a strongly reduced lifetime due to a higher concentration of metallic impurities and a high dislocation density. The bottom edge of ingots sometimes has excessive oxygen-related defects. To achieve the highest cell-efficiency, it is essential to maintain the high lifetime of the best wafer regions during cell processing, and to improve that of poor wafer regions.

The effects of process steps on the electronic properties of wafers from different positions of the same ingot are generally different. In this paper, we combine lifetime analysis with the following techniques, which increase the insight in process-induced changes in the material:

i) Measurement of interstitial oxygen by FTIR. This is important because, for example, oxygen can hinder gettering and form lifetime-reducing precipitates.

ii) Measurement of the concentration of dissolved Fe by FeB pair dissociation. This helps to follow quantitatively effects of gettering and passivation.

iii) Comparison of a single-sided versus a double-sided emitter [4], permitting the determination of the effect of gettering versus thermal degradation.

Taking to account the results of this investigation, the response of a wafer to process steps can to some extent be predicted. As the results of processing depend on the origin of the wafer, most of the results in this paper are presented as a function of "vertical" position in the ingot.

2. EXPERIMENTAL

Samples were chosen from different ingot-positions of two manufacturers (A and B). Two columns (A_1 and A_2) of the ingot A were used to investigate the effect of processing steps on wafers coming from the edge (A_1) and from the central position (A_2) of the ingot. The phosphorus was diffused in a belt furnace using a spin-on dopant (SOD), at the following temperatures (745, 830, 920 and 975ºC). The diffusion time was 12 min for all temperatures. Double-sided emitters [1] were diffused in the same (single) thermal step as single sided emitters to ensure the same thermal history.

The plasma-enhanced chemical vapour deposition (PECVD) technique was used for the deposition of silicon nitride, which serves as a source of both surface and bulk passivation [2]. Bulk minority carrier lifetime measurements were performed after removing the emitter(s) and achieving sufficient passivation of the wafer surfaces with silicon nitride coating. Measurements were performed with the quasi-steady-state photo-conductance (QSSPC) technique [3]. The measurement of iron (Fe) concentration before and after phosphorus gettering was based on the lifetime change after dissociation of the FeB pairs by illumination. The model is described in more detail in [4].

3. RESULTS AND DISCUSSION

3.1 Characterisation of ingots

The minority carrier lifetime of wafers -if the same quality of feedstock is used- depends on the growth method of the ingot and on the position of the wafer in the ingot. Fig.1 shows the QSSPC carrier lifetime of the wafers along columns A_1, A_2 and B measured at 5.10^{15} cm^{-3} injection level.

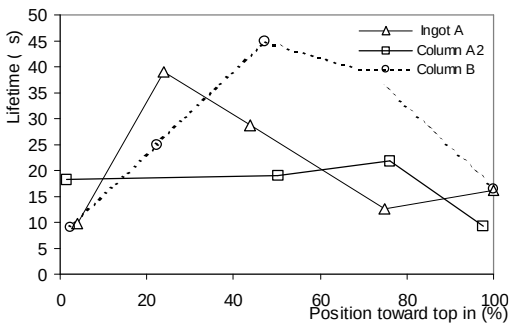

Fig. 1 Minority carrier lifetime in as cut wafers along columns of A and B ingots.

The variation in the minority carrier lifetime is due in large part to the distribution in the ingots of the metallic impurities like Fe, as shown in Fig. 2, and oxygen, as shown in Fig. 3.. For multicrystalline ingots the bottoms have a higher oxygen contamination than the rest of the ingot, this is especially prominent in ingot B.

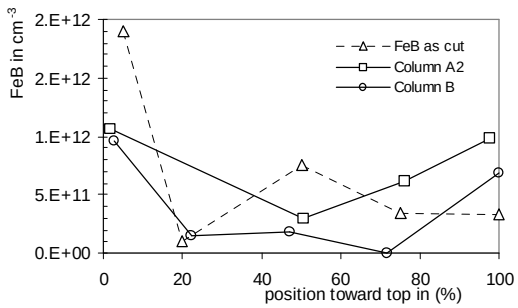

Fig.2 Distribution of FeB in as cut wafers along columns of ingots A and B.

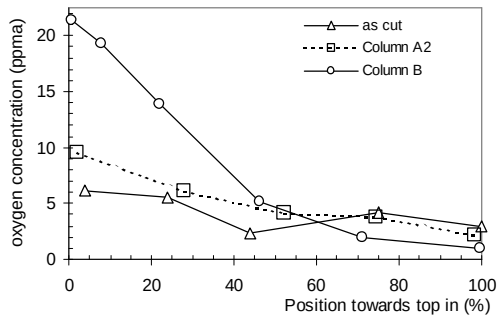

Fig. 3 Distribution of oxygen in as cut wafers along the column of ingots A and B.

3.2 Phosphorus gettering

- Gettering along the ingot

Fig. 4 shows the variation of the bulk minority carrier lifetime along the ingots of the material A_2 and B. The response of the wafer to gettering depends on the position of the wafers. In the ingot B, the minority carrier lifetime decreases at almost all positions. From about 20% to 80% of the ingot, the decrease of the minority carrier lifetime due to the phosphorus diffusion step is slight, much less than the first (0-20%) part. At the top of this ingot (above about 80%), the minority carrier lifetime increases. In contrast, in the column A_2 the minority carrier lifetime increases both in the bottom (to about 35%) and in the top (above 75%).

The dissolved Fe concentrations in these wafers are shown in Fig.5. Although the phosphorus gettering of the Fe impurities seems to be very effective in the bottom of the column B, the minority carrier lifetime decreases. The bottom of this column contains a high amount of oxygen (20ppma), as shown in Fig. 3. We think that after a gettering or pure annealing step, the formation of oxygen-related complexes leads to the decrease of the lifetime in this case. A high oxygen concentration could be the major limiting factor for the efficiency of the phosphorus gettering as also reported in [5]. In low oxygen contaminated samples there is little formation of oxygen precipitates competing with phosphorus gettering [6]. That is the case for the top of ingot B that has a low concentration of oxygen and higher concentration of Fe. After phosphorus gettering, a clear increase of the lifetime is observed.

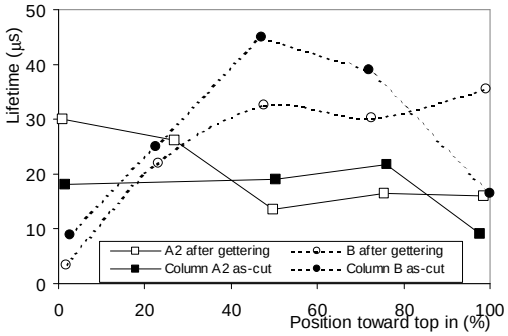

Fig.4 Minority carrier lifetime before and after phosphorus gettering at 890•C for 12 min in wafers along the ingots A_2 and B.

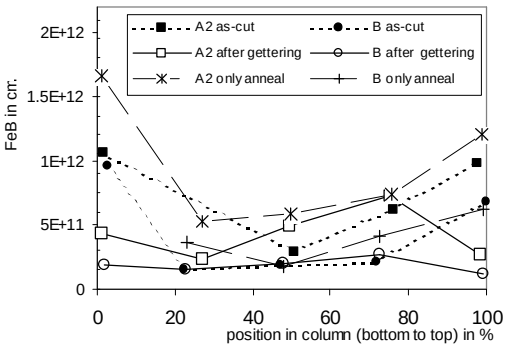

Fig. 5 Distribution of FeB in wafers along the ingots A_2 and B before and after phosphorus gettering at 890•C for 12 min.

The increase of the Fe concentration in Fig. 5 after a pure anneal step must be due to the dissociation of iron-rich precipitates. The gettering shows clear effectiveness only in highly-contaminated positions of the ingot, namely around 5.10^{11} to 5.10^{12} cm^{-3}.

- Variations of gettering parameters

Fig. 6 shows the bulk minority carrier lifetime of neighbouring wafers after single and double-sided gettering [1] at different temperatures. The wafers were chosen from the middle of column A_2 in order to minimise the effect of the high concentrations of metallic impurities and oxygen at the edges. The minority carrier lifetime decreases when the diffusion temperature increases. The phosphorus gettering of metallic impurities results in the best lifetimes at temperatures around 830ºC. Double-sided emitter diffusion leads to higher lifetimes than single side diffusion for low temperatures. For higher temperatures, there is no significant difference.

The Fe diffusion distances (L_{Fe}) for the diffusion temperatures and durations used are shown in Fig.6. When L_{Fe} is greater than the thickness of the wafer the

minority carrier lifetime for double sided and single-sided emitter diffusion are the same.

Fig.7 shows the dissolved iron concentration after gettering, measured on the same wafers as shown in Fig.6. At higher temperatures, the concentration of interstitial iron atoms becomes higher and leads to a decrease in the minority carrier lifetime. It is likely that the higher temperature leads to a higher rate of dissociation of precipitates [7]. With the exception of the double-sided emitter diffusion at 745 ºC, the measured Fe concentration is consistent with the lifetime in Fig. 6. i.e , a higher Fe concentration correlates with lower lifetime.

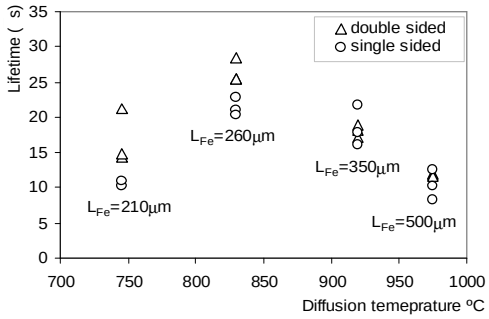

Fig. 6 Minority carrier lifetime after single-sided versus double-sided emitter diffusion (column A_1) at different temperatures.

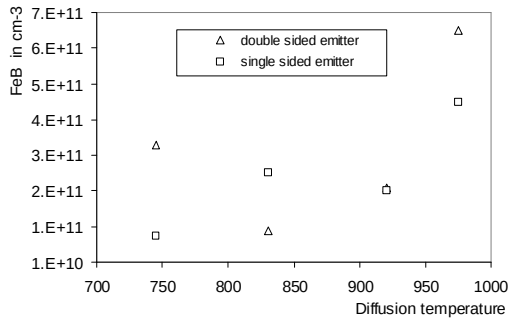

Fig. 7 Dissolved FeB concentration in wafers from column A after single-sided versus double-sided emitter diffusion (column A_1) at different temperatures.

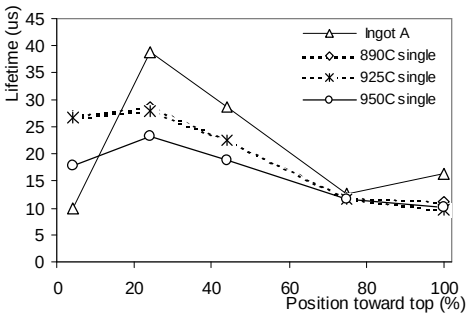

Fig. 8 Lifetime after emitter diffusion (12 minutes at varying temperatures), as a function of position in the column for ingot A.

Fig.8 shows the minority carrier lifetime of the wafers along a central column of ingot A (A_1) after phosphorus gettering at different temperatures. The gettering time was about 12min. The highest temperature (950ºC) leads to the lowest minority carrier lifetime along the ingot. Because of the low concentration of the oxygen, in the bottom of this ingot, the gettering of metallic impurities increases the minority lifetime.

3.3 Hydrogen passivation

Minority carrier lifetime due to the hydrogen passivation is different depending on the material quality and on the combined process steps. Fig. 9 shows the effect of hydrogen passivation on the minority carrier lifetime along the ingot B. Similar effects were observed in ingot A. The minority carrier lifetime increases after the hydrogen passivation and reduces the amount of FeB measured to a very low level as shown in Fig.10. This is the case even in the absence of aluminium on the rear surface during firing, We do not see a clear synergetic effect of aluminium alloying with hydrogen diffusion from the nitride. This is not in agreement with the results in [8]. We observe a similar effectiveness of passivation, whether the emitter is stripped after phosphorous diffusion (before nitride deposition and firing) or not. Surprisingly, wafers which had an anneal without SOD instead of phosphorus diffusion, resulted in a similar amount of dissolved Fe as the phosphorous-diffused wafers, and were not at all improved by nitride deposition and firing. The reason for this is unknown.

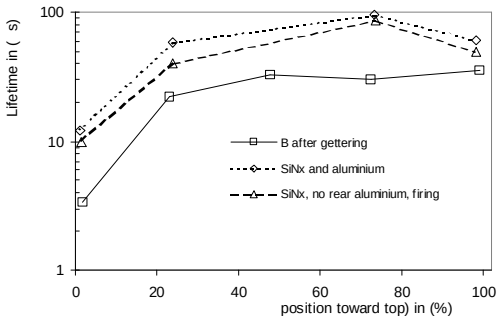

Fig. 9 Minority carrier lifetime along the ingot B: effect of phosphorus gettering and Al rear side on the hydrogen passivation. Diamonds: co-firing of SiNx with Al rear side metallisation. Triangles: firing of SiNx without Al rear side.

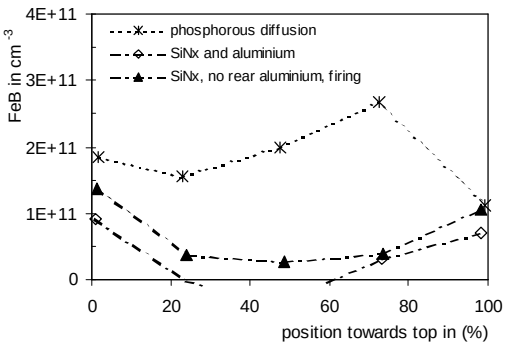

Fig. 10 Change of FeB concentration along the ingot B after passivation. Same wafers as in Fig. 9.

4. SUMMARY AND CONCLUSIONS

Gettering during phosphorus diffusion is effective and useful for highly contaminated (edge) wafers, but the remaining FeB concentration levels off at a high level. For relatively clean wafers (most of the ingot), lifetime and FeB concentration do not improve. Common diffusion temperatures of around 900 °C for 12min are not effective for gettering of Fe to levels below a few times 10^{11} cm^{-3} [9]. Often, good quality wafers already have such a low FeB concentration to start with.

The gettering is limited by process parameters such as gettering temperature, and material parameters such as oxygen concentration. The characterisation of ingots (measuring [O] and [Fe]) can help to predict and optimise the effectiveness of the gettering step. Moreover, the changes induced by processing in the cell process can be interpreted.

Hydrogen passivation reduces the recombination activity of FeB. A synergetic effect of co-firing a SiNx coating with Al rear side metallisation was not observed.

ACKNOWLEDGMENTS:

This work has been carried out with financial support of NOVEM (The Netherlands Agency for Energy and the Environment) under contract numbers: 146.110-010.1, 146.110-020.1 and 2020.01.13.11.2002. We acknowledge the manufacturers of mc-Si wafers who supplied test material. We acknowledge valuable discussions and assistance from the group members of ECN-solar.

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