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EFFECTIVE AND PRACTICAL PHOSPHOROUS GETTERING OF MULTICRYSTALLINE SILICON.

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ABSTRACT: Gettering during an emitter diffusion in multicrystalline silicon is improved by adding a low-temperature tail to the standard diffusion. The tail keeps the emitter sheet resistance within the usable range for solar cells. An increase in minority carrier lifetime by a factor ten is obtained. Decrease in recombination activity of grain boundaries and decrease in interstitial iron concentration are mainly responsible for this improved lifetime. The proposed mechanisms for this improvement are: reduction of size of precipitates because of the longer duration and improved thermodynamics and kinetics of the gettering because of the lower temperature.
Keywords: Silicon, Lifetime, Gettering, Iron, Defects

1 INTRODUCTION

Multicrystalline silicon (mc-Si) incorporates many impurities and defects that limit the minority carrier lifetime and thus the solar cell performance. The quality of mc-Si wafers may become worse in the future, for several reasons. First, lower-quality feedstock will probably have to be used, for cost reduction and availability reasons. Second, faster crystallisation, increased recycling of contaminated silicon, lower-cost and lower-quality furnace materials, and ribbon growth techniques may be used which result in more contamination of the wafers. Third, wafers may be cut closer to the contaminated edge zones of ingots to increase the yield of wafers from an ingot.

Therefore, there is a growing need for techniques to improve the quality of mc-Si wafers, i.e., to increase the minority carrier lifetime, during the cell process. The carrier lifetime should preferably be increased by adaptation of existing cell process steps, which in addition should not alter any other process characteristics such as sheet resistance or contact resistance. In this paper, we will investigate the increase of carrier lifetime by an extended phosphorous gettering, an adaptation of the existing emitter diffusion. Several attempts at enhanced gettering by adding a low-temperature tail to phosphorous diffusion have been reported [1]. Our experiment differs in both the total duration of the gettering step and the effectiveness of the gettering. Gettering time has been reduced to one fifth of that previously used; to 2.5 hours. A longer duration does not improve gettering any further. The increase in lifetime by a factor of 10 between normal gettered and improved gettered wafers for commercial material is much better (approximately five times better) than reported previously. A more extensive report of the results of this paper is given in ref [2]. Results related to ours were published recently by Bentzen et al. [3]. Instead of a low-temperature tail, these authors used a slow temperature ramp-down after diffusion of 58 minutes duration, resulting in a factor 2 improvement of lifetime, and nearly 1% improvement of cell efficiency.

2 EXPERIMENT

Phosphorous gettering at variable temperature was studied on commercial multicrystalline silicon wafers. As a boundary condition in all cases the gettering must result in normal emitter sheet resistance. Therefore two different phosphorous gettering methods were performed on the selected wafers. Standard gettering consisted of a standard 50 Ohm emitter diffusion, identical to the ECN 15% scenario of 2003. Improved gettering consisted of the same emitter diffusion followed by a low-temperature tail of varying duration (Fig. 1).

Wafers were analysed from different types of ingots and at different locations within the ingots. This corresponds to a variation in material properties typically encountered in solar cell production. Wafers from two ingots were used, from one ingot at 5% and 15% height, and another ingot at 10 and 50% height (sample code A5, A15, B10, B50, respectively).

The results are evaluated with lifetime and interstitial iron measurements by quasi-steady state photoconductance (QSSPC), and lifetime mapping by modulated free carrier absorption.

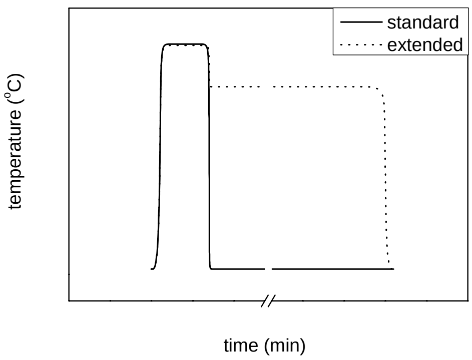

Figure 1: Schematic of the two different temperature profiles used for the phosphorus diffusion/gettering in this experiment; i) the standard gettering at a constant temperature, and ii) the extended gettering consisting of same temperature and duration as i) followed by an extended time at lower temperature. The investigated durations of the low-temperature tail were 45 minutes, 150 minutes, and 480 minutes.

3 RESULTS

The recombination lifetime values obtained with the quasi steady state photoconductance technique are shown in Fig. 2. We used vertically adjacent wafers for all comparisons of different gettering profiles. Per sample code we obtained multiple values for a gettering profile by using horizontally adjacent wafers. The grain boundaries and dislocation patterns are not identical for those horizontally adjacent wafers, but impurity contents (including that in precipitates) may be expected to be approximately equal.

All depicted wafers show an increase in lifetime after an improved gettering, relative to normal gettering. An increase in lifetime by an order of magnitude is possible for very low lifetime wafers.

A calculation of the interstitial iron contents from lifetime spectra (before and after light soak) reveals that the increase of lifetime is partially caused by a decrease of the interstitial iron contents (see Fig. 3). Calculating the lifetime in the absence of interstitial iron shows that other defects are also reduced: the effects seen in these wafers can not be solely attributed to the decrease in interstitial iron contents.

Floatzone wafers with in-diffused interstitial iron have been studied on gettering of iron. Results are given in Fig. 4. These results show that with the *standard* gettering iron can gettered much more effectively in these FZ wafers than in the multicrystalline wafers.

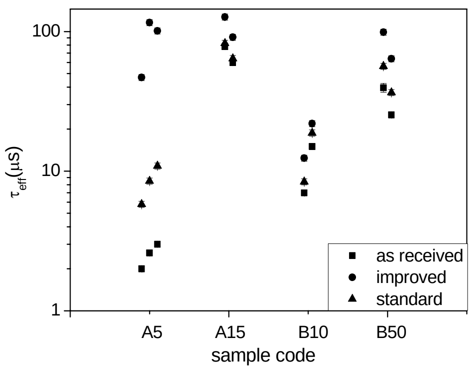

Figure 2: Effective recombination lifetime of as-received, standard gettered, and improved gettered wafers. Lifetime measured with the QSSPC technique at 10^{15} cm^{-3} injection level. Per sample code two or three horizontally adjacent wafers are shown. Tail duration is 150 minutes.

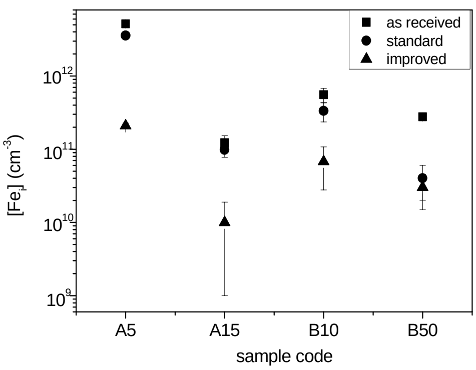

Figure 3: Interstitial iron concentration for the right-side wafers of Fig. 2.

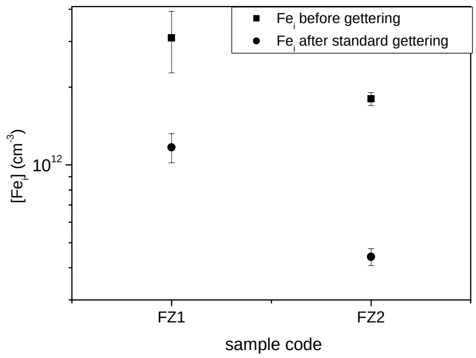

Figure 4: Interstitial iron concentration in two floatzone wafers with artificially in-diffused iron, after standard gettering and extended gettering.

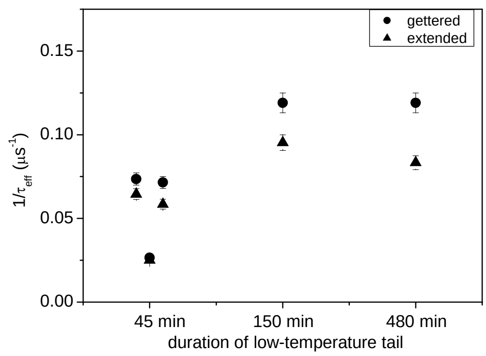

Figure 5: Effective recombination lifetime of standard gettered, and extended gettered wafers, for different duration of the low temperature tail in the extended gettering.

The results given in Fig. 2-4 are for a gettering tail duration of 150 minutes. Fig. 5 shows the lifetime improvement compared to standard gettering, after an extended gettering of 45, 150, and 480 minutes for sample B10. An extended gettering of 480 minutes does not result in a significant additional lifetime improvement compared to 150 minutes. For the 45 minutes extended gettering, exact sister wafers were not available. Wafers from a different brick of the same ingot, at the same height, were used. These show for the 45 minutes low-temperature tail generally a small effect. Also, the variation among different samples in the effect of the extended emitter with a 45 minutes tail is larger than for the longer tails.

The modulated free carrier absorption (MFCA) measurements do not show as strong a difference between improved gettering and normal gettering as the QSSPC measurements do. This is due to the higher injection level of 5 suns. Nevertheless, the MFCA lifetime maps show an increase in lifetime after improved gettering specifically for bad quality regions (see Fig. 6a, b and c). In the figure both the central area of a bad quality grain is improved, and also grain boundaries are positively affected.

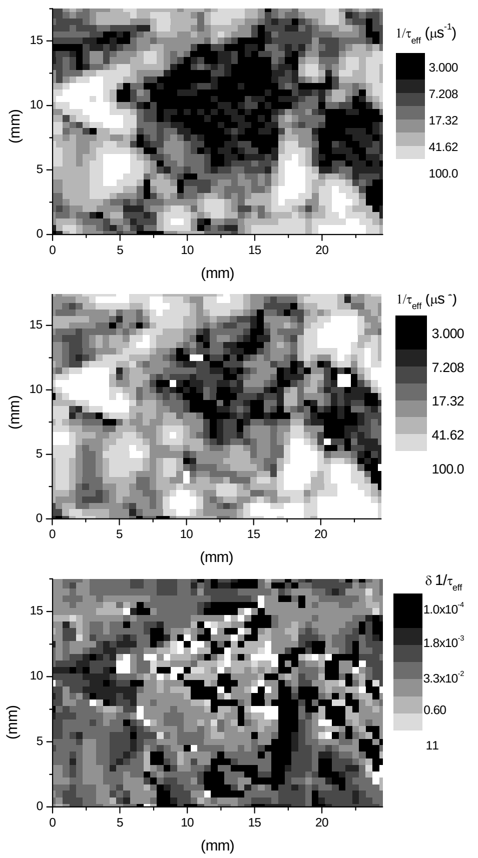

Figure 6: MFCA lifetime maps of sample B10 a) after standard gettering, b) after improved gettering, c) difference in $1/\tau$ of a and b.

4 DISCUSSION

Since metal impurities have a higher solubility in the phosphorous-rich layer at the wafer surface, they will diffuse (segregate) towards this layer. A segregation coefficient describes the ratio of the equilibrium solubility of impurities in the silicon matrix and the phosphorous-rich layer. Since the solubility of metal point defects in silicon decreases at low temperatures, more than it decreases in the phosphorous-rich layer, the segregation coefficient becomes better for decreasing temperature. Therefore using a low temperature tail enhances the gettering. This segregation effect, and its temperature dependence, has received considerable attention in literature [4]. However, our results show a wide variation of gettering efficiency for the same gettering temperature, depending on the sample. Therefore, it seems that the segregation coefficient is not a limiting factor.

The comparison with floatzone wafers with in-diffused interstitial iron shows that in the multicrystalline wafers interstitial iron is not reduced as much by the standard phosphorous diffusion (Fig. 4 compared to Fig. 3). This can be explained by the existence of an iron source within the multicrystalline material; probably iron precipitates. Therefore gettering can be improved by [5]:

- depletion of precipitates,
- reduction of the dissolution rate of precipitates, and
- improved segregation.

The effect of the low-temperature tail is expected to differ according to the type (composition, thermal history, concentration, size) of precipitates because the kinetics of the dissolution of precipitates depend on the precipitate. This can be expected to be rather constant in a horizontal plane in an ingot, but vary significantly vertically through an ingot. The comparability of results between horizontally adjacent wafers support this view.

An extended single high temperature gettering step as a method to reach improved gettering results would suffer from several drawbacks. While it would also succeed in dissolving the precipitates, the segregation would remain at standard level and a higher interstitial iron content would be expected to result. The resulting emitter would be of very low sheet resistivity (generally in the order of 10 Ohm/sq), and would have to be removed.

4 CONCLUSIONS

An increase in minority carrier lifetime of up to a factor of 10 is achieved by extending a phosphorous emitter diffusion with a low-temperature tail, compared to the standard emitter diffusion. This is achieved on commercial multicrystalline silicon wafers. This factor of 10 improvement over standard gettering is three to four times better, and the optimal gettering time of 2.5 hours is five times shorter, than previously reported. A maximum bulk minority carrier lifetime after improved gettering of 100 μs has been achieved on material with an initial lifetime of 2 μs. This is almost the same as the highest lifetimes achieved on any wafer from this ingot.

ACKNOWLEDGMENTS

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