Chapter 38
Impact of Phosphorus Diffusion Gettering on HEM Multicrystalline Silicon Wafers Taken from Different Ingot Regions

Nabil Khelifati, Djoudi Bouhafs, Seddik-El-Hak Abaidia, Abd El-Ghani Boucheham, Baya Palahouane and Messaoud Boumaour

Abstract In this present contribution, we investigate the effect of extended phosphorus diffusion (PD) gettering on the electrical quality of p-type HEM mc-Si wafers. The study was made for three sets of wafers taken from top, center and bottom of the same ingot. The gettering process was performed through two annealing plateaus; the first is standard and the second is extended at different temperatures. Wafers characterization was mainly made by quasi-steady state photoconductance (QSSPC) technique. The obtained results indicated that the gettering effectiveness mainly depends on the position of wafers in the ingot and also the temperature of gettering process. Furthermore, appropriate modeling of QSSPC lifetime curves using Hornbeck–Haynes model reveals that the origin of the electrical property improvement is due to the reduction of the density of specific metallic impurities in the bulk.

38.1 Introduction

The multicrystalline silicon (mc-Si) wafers are widely used as precursor elements in solar cells manufacturing, and constitute more than half of the overall industrial market. This is due to their low cost of manufacturing as compared to that of monocrystalline silicon (c-Si) [1].

However, the high contamination level of mc-Si wafers by metallic impurities (Fe, Cr, Mn, Cu, Ni, Co, etc.) during the elaboration process is considered as their major disadvantage. In the case of cast mc-Si grown by Heat Exchanger Method

N. Khelifati (✉) · D. Bouhafs · A. E.-G. Boucheham · B. Palahouane · M. Boumaour
Research Center in Semi-conductors Technology for the Energetic, Bd. 2 Frantz Fanon, les sept merveilles, B.P. 140, Algiers, Algeria
e-mail: n.khelifati@gmail.com

N. Khelifati · S.-E.-H. Abaidia
University of M'hamed Bougara, Faculté des Sciences, Boumerdès 35000, Algeria

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(HEM), the quality of wafer depends on the location in the ingot from where it is sourced. Indeed, the wafers cut out of top, bottom and sides regions of an ingot show an inferior quality compared to those from the center region. The low quality of the bottom region is mainly due to oxygen-related defects [2, 3], high density of dislocations [4, 5], and higher concentration of metals due to the solid-state diffusion from the crucible during and after crystallization [6]. However, the low lifetime in the top region of the ingot, which freezes at the end, is attributed mainly to the segregation of the metallic impurities. It has been shown that the concentrations of transition metals are determined by the segregation from the liquid-to-solid phase in the central regions of the ingots, which produces high concentrations of these metals in the top region of the ingot [6].

The presence of such impurities in different ingot region can provoke a high carrier recombination activity and greatly limiting the efficiency potential of mc-Si based solar cells.

Nevertheless, most metallic impurities dissolved or precipitated can be partially removed from the whole bulk of a Si wafer, using extrinsic gettering method. It refers to a thermal process step that activates the diffusion of interstitial impurities from the bulk of the wafer to less important superficial regions of high solubility. These regions are generally created by phosphorus diffusion (PD) and/or by aluminum-silicon (Al-Si) alloying [7–12].

In this study, we report on the investigation of the response of wafers taken from top, middle and bottom regions of HEM mc-Si ingot to the PD gettering. The process was carried out through two annealing plateaus. Wafers characterization was mainly made by QSSPC techniques and the obtained results were inspected using Hornbeck–Haynes model [13].

38.2 Experimental Details

The wafers investigated in this study were 1.5 Ωcm, p-type mc-Si grown by HEM [14]. Three sets of sister wafers, with thickness of ∼300 μm were chosen from top, middle and bottom of the same ingot. The wafers from the top and bottom regions were adjacent to the discarded region (usually few centimeters between top and bottom) of the ingot.

Before any experimental process, the as-cut wafers were slightly etched in a bath of NaOH:H_2O (30 %) to remove the saw damage. After this step, the wafers have undergone PD on both sides, at 900 °C for 20 min (standard gettering), in a tube furnace using a phosphorus oxychloride ($POCL_3$) liquid source. Subsequently, wafers were subjected to an extended annealing under a nitrogen flow (extended gettering) during 120 min and at temperatures T_L varied between 600 and 900 °C. Some wafers were processed without any PD or annealing, they are considered references. Following to PD and annealing steps, a stripping of ∼10 μm from each side of wafers was made, using NaOH:H_2O solution, to remove the phosphorus-silicate-glass (PSG) layer.

The main characterization technique used in this study is QSSPC measurements. It was performed by *WCT-120* tester. Before any lifetime measurement, the wafers surfaces have been passivated by Iodine-Ethanol (I-E) solution 0.08 mol. These measurements allow determining the injection level dependent minority carrier lifetime. Lifetime values were taken at 1×10^{15} cm^{-3} excess carrier density to exclude the influence of trapping artefacts.

38.3 Results and Discussion

Figure 38.1 shows the results obtained by QSSPC measurements and the performed fits employing Hornbeck–Haynes model (solid lines).

We observe clearly an improvement of carrier lifetime for all wafers of three sets; top, centre and bottom, but with different orders of magnitude. Qualitatively, the more important improvement is observed for the wafers taken from the top of ingot, where the low lifetime is attributed mainly to the segregation of the metallic impurities, indicating an effective PD gettering.

Indeed, for the top region the carrier lifetime measured at $\Delta n = 1 \times 10^{15}$ cm^{-3} (see Fig. 38.2) varies significantly by 3,500 %; from 0.7 μs for the reference to 24.5 μs for the wafers gettered at 900 °C. The improvement is less important in the case of wafers taken from centre and bottom region, where the increment was estimated by 350 and 690 %. However, we note that the higher carrier lifetime observed (47 μs) is referred to wafers of bottom region gettered at 900 °C. This effect is certainly due to an effective PD gettering through the diffusion of undetermined metals impurities towards phosphorus doped region.

Using Hornbeck–Haynes model, a complete modeling of injection-level dependent lifetime curves (see Fig. 38.1) allows to estimate the recombination center density N_r and the electron to hole capture cross-sections ratio so called symmetry parameter ($k = \sigma_n / \sigma_p$), and then to conclude the origin of dominant recombination activities after gettering process. The basic formula used for modeling measured QSSPC data can be found in [15]. More details about the calculation formula and the fitting procedure are reported elsewhere in [16–18].

The variation of estimated N_r (see Fig. 38.3) is in agreement with the evolution of effective lifetime presented in Fig. 38.2, and then confirm the explanation above based on PDG phenomenon. This can be especially observed between the as-cut wafers and those gettered at 900 °C, where the increment of τ_{eff} is accompanied by a significant decrease of N_r from 1×10^{13} cm^{-3} to 9×10^{10} cm^{-3}, from 1.2×10^{12} cm^{-3} to 1.1×10^{11} cm^{-3} and from 2×10^{12} cm^{-3} to 1.2×10^{11} cm^{-3} for top, center and bottom region, respectively.

Figure 38.4 illustrates the variation of symmetry parameter k ratio estimated from modeling as a function of the extended gettering temperature T_L for top, center and bottom wafers. For wafers of top region, it is obviously shown that the k values vary independently between those associated to Fe_i on the one hand, and to FeB, CrB pairs, Co_s (Acceptor) and W_i on the other hand. So, this result indicates

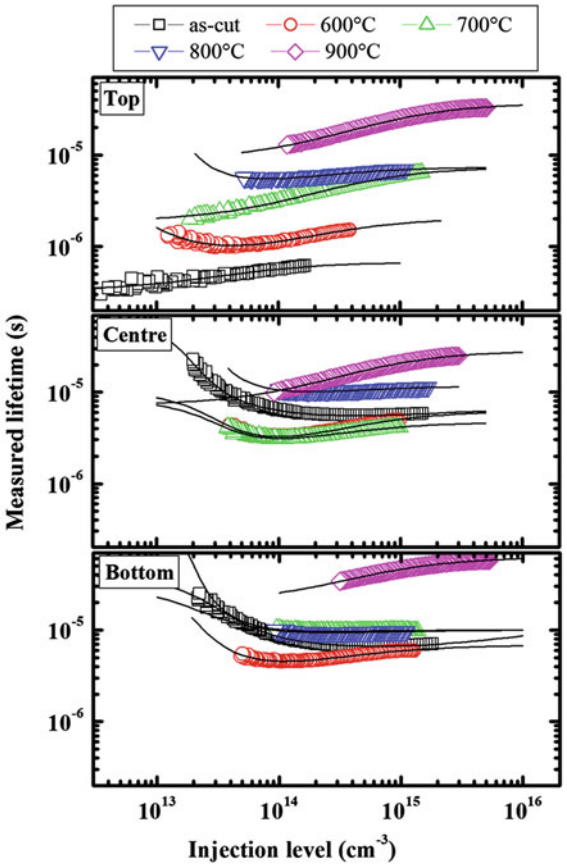

Fig. 38.1 Evolution of apparent minority carrier lifetime versus minority carrier density curves as a function of extended gettering temperature T_L for investigated wafers taken from different ingot regions. The *solid lines* represent the fits obtained by Hornbeck–Haynes model

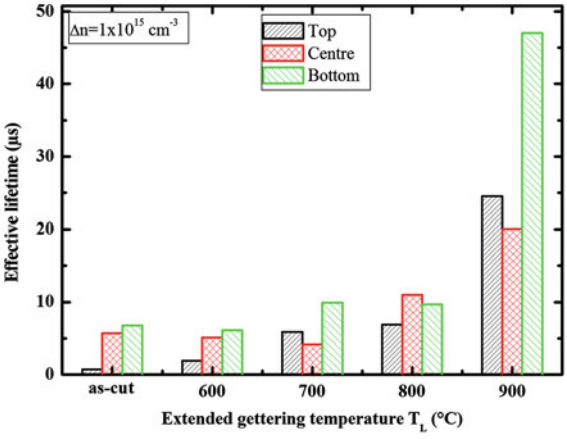

Fig. 38.2 Variation of the effective lifetime measured at $\Delta n = 1 \times 10^{15}$ cm^{-3} as a function of gettering temperature T_L, for wafers taken from *top*, *centre* and *bottom* of the ingot

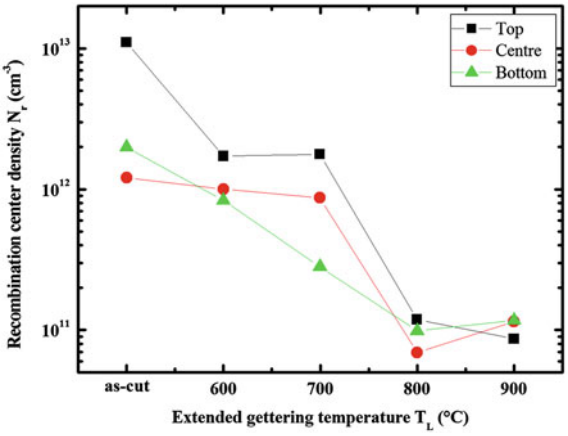

Fig. 38.3 Variation of the recombination center density N_r estimated by fitting, as a function of gettering temperature T_L

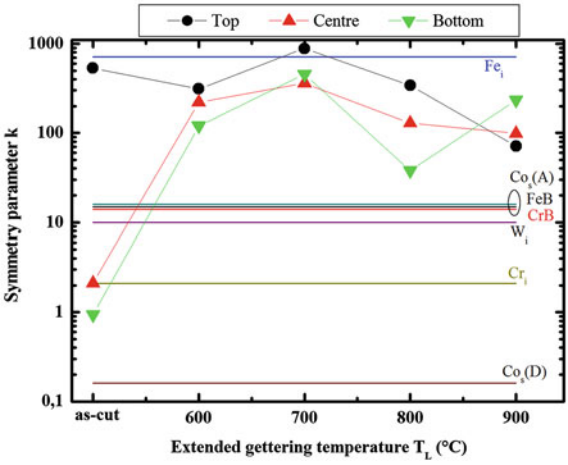

Fig. 38.4 Variation of the electron to hole capture cross-sections ratio as called symmetry parameter ($k = \sigma_n / \sigma_p$) versus extended gettering temperature T_L

that in spite of the reduction of its density, the type the dominate recombination center remain practically unchanged.

For the wafers of middle and bottom, the same result can be observed, with the exception of the important shift of k from the value associated to Cr_i towards those of Fe_i and this is just after the gettering processed at 600 °C. These results indicate the quasi-dominance of Fe_i, FeB, CrB pairs, Co_s (Acceptor) and W_i recombination activities and probably an effective PD gettering of Cr_i atoms.

38.4 Conclusion

In summary, we have studied the effect of extended PDG on recombination activity of minority charge carrier in p-type HEM mc-Si wafers taken from top, middle and bottom of the ingot.

The QSSPC measurement results showed an improvement of lifetime in high injection level indicating an effective extended gettering. This effect was especially noticed for the wafers of the top region strongly contaminated by metallic impurities, where the effective minority carrier lifetime was improved by more than 3,500 %. But the higher value of carrier lifetime (47 μs for $\Delta n = 1 \times 10^{15}$ cm^{-3}) has been found for the wafers of bottom treated at 900 °C. Hornbeck–Haynes model fitting of QSSPC curves showed that this improvement is accompanied by a decrease of the recombination center density and that probably FeB, CrB pairs, Co_s (Acceptor) and W_i impurities are the dominant sources of these centers after each gettering temperature.

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