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Improvement of charge carrier lifetime in heat exchange method multicrystalline silicon wafers by extended phosphorous gettering process

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Abstract- *External phosphorous diffusion gettering were applied using homogenous and extended schemes on multicrystalline silicon (Mc-Si) wafers obtained from solar grade (SOG) silicon feedstock by the heat exchange method (HEM) growth technique. X-ray fluorescence (XRF) characterization shows the presence of transition metals like Chromium (Cr), manganese (Mn) and iron (Fe) in the analyzed as-cut Mc-Si substrates with a predominance of Mn and Fe elements. Before and after gettering process, we have observed that the Cr atoms concentration drop from 4.10^{15} at.cm^{-3} in the as-cut Mc-Si samples to $2.5\ 10^{15}$ at.cm^{-3} with homogeneous gettering and to 3.10^{14} at.cm^{-3} in the wafer undergoes extended gettering. The quasi-steady-state photo conductance (QSSPC) technique is used to characterize the minority charge carrier's lifetime τ_n before and after gettering process. It was found that the response of Mc-Si wafers is better (form point of view of lifetime improvement) to the extended process but in some regions it is less effective and the homogenous process give the best amelioration due probably to the spatial distribution of crystalline defects and metallic precipitates densities. With τ_n initial values before gettering in the range of 2.5-8 µsec, we have measured lifetime values in the range of 15 to 37 µsec with extended process and from 10 to 30 µsec with the homogenous one which ensure cell efficiencies in the range of 15 to 16%.*

Résumé– *Les techniques d'effet Getter externe par diffusion du phosphore ont été appliquées en utilisant des procédés homogènes et étendus sur les plaquettes de silicium multi cristallin 'mc-Si' obtenues à partir des matières premières de silicium de qualité solaire (SOG) par la méthode de l'échangeur de chaleur (HEM) en technique de croissance. La caractérisation par la fluorescence X (XRF) révèle la présence de métaux de transition comme le chrome 'Cr', le manganèse 'Mn' et le fer 'Fe' dans les substrats analysés brutes 'mc-Si' avec une prédominance des éléments 'Mn' et 'Fe'. Avant et après le procédé Getter, nous avons observé que la baisse de la concentration des atomes Cr se fasse à partir de 4×10^{15} at.cm^{-3} dans les échantillons brute 'mc-Si', les échantillons à $2,5\times10^{15}$ at.cm^{-3} avec l'effet Getter homogène et à 3×10^{14} at.cm^{-3} dans la plaquette subissant l'effet Getter prolongé. La technique quasi-stationnaire de la photo conductance (QSSPC) est utilisée pour caractériser la vie du porteur de charge minoritaire τ_n avant et après le procédé Getter. Il a été constaté que la réponse sur les plaquettes de mc-Si est meilleure (sous forme de points de vue de l'amélioration de la durée de vie) pour le procédé étendu, mais dans certaines régions, il est moins efficace. Le procédé homogène peut donne une meilleure amélioration en raison probablement de la distribution spatiale des défauts cristallins et des densités des précipités métalliques.*

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Avec des valeurs initiales τ_n avant le procédé Getter dans la gamme de 2,5 à 8 msec, nous avons mesuré des valeurs de la durée de vie de l'ordre de 15 à 37 msec avec le procédé étendu et de 10 à 30 msec avec le procédé homogène, qui en assurent l'efficacité des cellules dans la gamme des 15 à 16 %.

Keywords: Multicrystalline silicon - Gettering - Metallic impurities - Lifetime carrier.

1. INTRODUCTION

Photovoltaic (PV) industry based on crystalline silicon has a strategy during four decades, the cost reduction of the PV generator through the improvement of the output of the solar cell and the reduction of its fabrication cost. This objective can be achieved by the reduction of the technological step number in the solar cell fabrication process, and also by reducing the cost of the used material [1, 2].

The multicrystalline silicon (Mc-Si) wafers grown by relatively low cost techniques compared to Float Zone and Czochralski ones, such as the Heat Exchanger Method (HEM) and Edge-defined Film-fed Growth and (EFG) [3, 4] are potential alternatives to reach this objective.

Nevertheless, the material obtained by these last present a low optoelectronics qualities compared to those of single-crystal silicon due to the presence of a high grain boundaries density, high density of crystalline defects [5] and an important density of metal impurities and their precipitates or clusters [6]; which results in a strong recombination density of the electric charge carriers and finally a weak lifetime [7, 8].

In order to improve this important parameter, the gettering process is commonly used to reduce the density of the impurities and their precipitates in silicon [9, 10]. This process enhances the photo generated current and give a best electrical performances of Mc-Si wafers.

In this paper we have carrying out an experimental work on homogeneous (with one temperature step) and extended (with two temperature step) gettering on multicrystalline wafers for improving their electrical quality by the diminution of the transition metal density and the neutralization of some active recombination centers.

2. EXPERIMENTAL

In all our experiments the starting material is 10 × 10 cm^2 P-type multicrystalline silicon wafers boron doped with a resistivity 1-2 Ωcm. The wafers are obtained from ingots grown by the directional solidification heat exchanger method (HEM). Our study was focused on the top briquette located in the center of the ingot.

Before introducing the wafers in the quart boat of the diffusion furnace, they are initially cleaned in an ultrasonic bath in deionised water using a special detergent to eliminate all the traces of dust and slurry on surface. After that, they are immersed in a trichloroethylene bath (TCE) at 80°C during 10 minutes, followed by an acetone bath during 2 minutes.

The last step is the remove of the saw damage by chemical etches of a 10 µm on from each side in NaOH: H_2O (80 °C). Homogeneous and extended external phosphorous gettering were performed in an open tube furnace by diffusion phosphorous at a temperature of 900 °C for homogenous gettering during 180 minutes. This temperature is choice to avoid the complete dissolution of the metallic precipitates knowing the segregation coefficient of transition metal in multicrystalline silicon become very significant at high temperature notably at the grain boundaries and the high density defects regions.

This scenario allows us to obtain an effective gettering of undesirable metallic elements from the silicon and accelerates their migration to the wafer extremities. The second scheme the gettering process applied to the same wafers is the extended one.

This process is characterized by two stages: high (T_H) and low (T_L) temperatures. Temperatures used in our experiment are T_H = 930 °C and T_L = 700 °C during 30 minutes and 120 minutes respectively.

X-ray fluorescence spectroscopy technique is used to analyze the metallic contents in the bulk Mc-Si wafer. During the first step the metallic impurities are altered from clusters, oxygen precipitates and crystalline defect regions. In the second step at moderate temperature T_L with prolonged time treatment, the migration of transition metals is favorable because the most of them have a high diffusion coefficient at this temperature.

These elements are electrically active as recombination centers and lead to the degradation of the optoelectronic properties in silicon. X-Ray excitation is a cadmium source 109Cd with two emission spectra: $K\alpha$ at 22.16 keV and $K\alpha$ at 24.92 keV. The spot size is about 0.78 cm^2.

This is a qualitative analysis which allows us to observe the predominant presence of such transition metal element. To evaluate the efficiency of the gettering process we have used the IMS-4f secondary ions mass spectroscopy from CAMECA to measure the concentration of Cr atoms before and after gettering.

Measurements of the carrier lifetime were effected using the Sinton WCT-120 Quasi-Steady-State Photo Conductance technique (QSSPC) on the processed Mc-Si samples. 10×10 cm^2 wafers were cut out in four areas (A, B, C, D) of 5×5 cm^2 of dimension. For a valid QSSPC measurement values and to reduce the surface recombination velocity, the Mc-Si samples was coated with silicon nitride layer SiNx of about 80 nm of thickness by PECVD technique (Plasma Enhanced Chemical Vapor Deposition).

3. RESULTS AND DISCUSSION

In the starting Mc-Si material we have detected some metallic elements like Cr, Mn and Fe using X-Ray Fluorescence technique (XRF). The figure 1 show the XRF spectra of some transition metals detected on as-cut Mc-Si wafers which have not undergoes any gettering.

Peaks at channels N°204, 220 and 240 correspond to Chromium (Cr), Manganese (Mn) and iron (Fe). From the same briquette in the ingot, three lots of 10 wafers were studied.

The Lot N°1 without gettering and the Lot N°2 and Lot N°3 with homogeneous and extended phosphorous diffusion gettering processes respectively.

During theses experiment we have take care that all samples were adjacent in the briquette ensuring the same structural growing conditions. To evaluate the efficiency of such gettering process we are firstly measured the concentration of the chromium density in the same region in the three samples which represent Lot N°1, Lot N°2 and Lot N°3 using the SIMS technique.

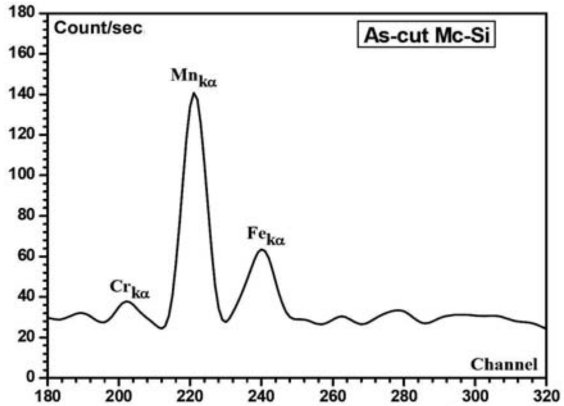


Fig. 1: XRF spectra of transition metals detected in as-cut Mc-Si wafers

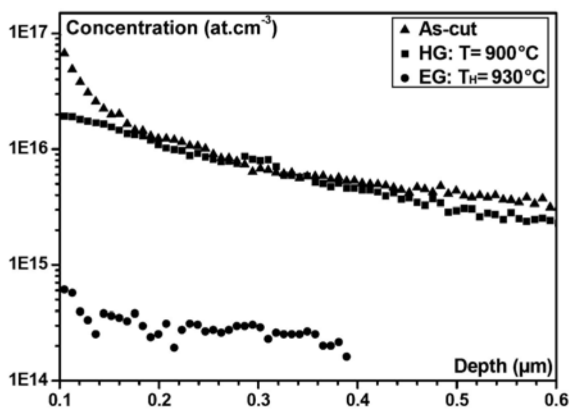


Fig. 2: SIMS spectra of chromium in as-cut Mc-Si wafers with homogenous and extended gettering

Figure 2 show the SIMS spectrum of Cr element measured in the as-cut multicrystalline samples and with homogenous and extended gettering processes. With the extended phosphorous gettering with T_L = 930 °C we can observe that the concentration of Cr were droped from 4×10^{15} at.cm^{-3} in the as-cut Mc-Si samples (Lot N°1) to 3×10^{14} at.cm^{-3} (Lot n°3)

We can show that this diminution have not the same order in the case of the homogenous gettering scheme 2.5×10^{15} at.cm^{-3} (Lot N°2). This higher concentration of Cr is due probably to the dissolution of their precipitates during the prolonged temperature treatment (180 minutes).

This means that the extended scenario is more indicated for multicrystalline silicon material which is characterized by high defect density and inhomogeneous structural regions like grain boundaries and other forms of crystalline defects and metallic clusters very sensible to the nature of heating treatment profile (Time and temperature).

To evaluate the effectiveness of such gettering process it is important to measure electrical properties behavior to each process by measuring the lifetime the electrical charge carriers before and after each step.

In our case this task was carried out using the WCT-120 quasi-steady-state photo conductance technique (QSSPC). This technique is based on the time and the speed of relieving of the photo conductance based on the trapping phenomena via the recombination centers like the transition metal impurities.

These metallic elements create the major electric levels in the forbidden band of the semiconductor and their density governs the mechanism of recombination generation following the model established by Shockley-Reed-Hall (SRH).

In the presence of an n+p phosphorus doped emitter, a second mechanism influences the lifetime of the carriers, namely the Auger component due to the phenomenon of heavy doping effect. The effective lifetime in this case is given by the following equation:

$$\frac{1}{\tau_{eff}} = \frac{1}{\tau_{SRH}} + \frac{J_0}{q \times n_i^2 \times W}(N_A + \Delta n) \tag{1}$$

avec,

$$\tau_{SRH} = \tau_{no} + \tau_{po}\frac{\Delta n}{\Delta n + N_A}$$

N_A : Concentration of the doping agent; n_i : Density of the charge carriers at the equilibrium steady state; Δn : Excess of the minority carrier density; τ_{no} and τ_{po} correspond to the lifetime of the charge carriers at the equilibrium state and J_o the saturation current of the transmitter. The presence of high defects and transition metals densities gives the predominance to the SRH mechanism which influences directly the value of τ_{eff} .

The processed Mc-Si samples 10×10 cm^2 wafers were cut out in four areas (A, B, C, D) of 5×5 cm^2 of dimension each one according to the below mc-Si wafer photo as shown in figure 3.

Before measurements A silicon nitride SiN_x were grown on the two surfaces by a pressure enhanced chemical vapour deposition (PECVD) to reduce the surface recombination velocity which affect strongly the QSSPC measured values via the Δn excess carrier and J_o .

The measurements implemented in the region D on the Mc-Si wafer according to the light intensity, shows clearly the effect of the metal contaminants before and after gettering , on the implied open circuit voltage of the substrate as a function of light intensity.

By extrapolation, the value of the implied voltage is lower than 605 mV before gettering and about of 615 mV and 635 mV after homogenous and extended gettering respectively.

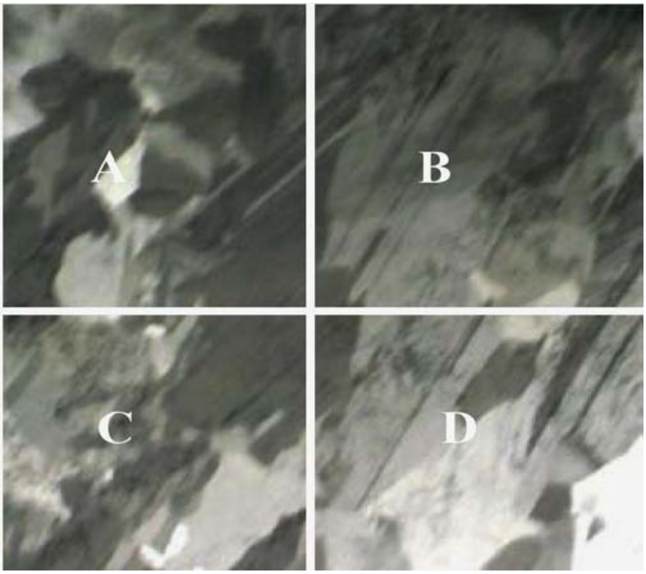


Fig. 3: Image of the A, B C, and D QSSPC studied regions on 10 ×10 MC-Si wafers

These results prove the effectiveness of the used processes as shown in figure 4. Also it correlates between the increase in the lifetime from 8 µsec for as-cut wafers to 14 µsec and 37 µsec at 1-sun illumination and the open circuit voltage increment from about 615 mV to 645 mV respectively.

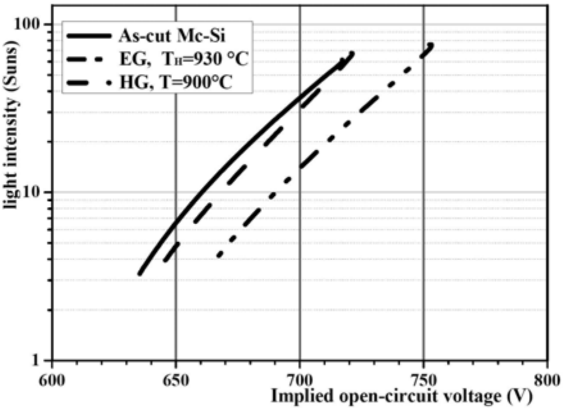


Fig. 4: Implied open-circuit voltage vs. light intensity of Mc-Si wafers before and after phosphorous gettering

The physical meaning of the implied voltage is the electrical potential which can produce each wafer in a finished solar cell and it is related to the diffusion length of the minority carriers in the wafers. A high implied voltage correlate with a longer diffusion length of the charge carriers in the bulk indicating a best amelioration of the electrical quality of the silicon wafer.

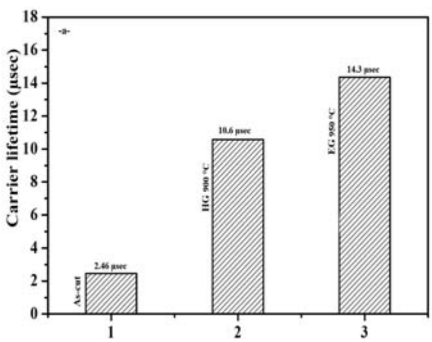
Through all regions in the Mc-Si wafers, we observe a noticeable improvement of the lifetime after the homogeneous and extended gettering processes as showen in

Figure 5. There is an apparent difference between the treated regions, which correlate with the nature of the substrates.

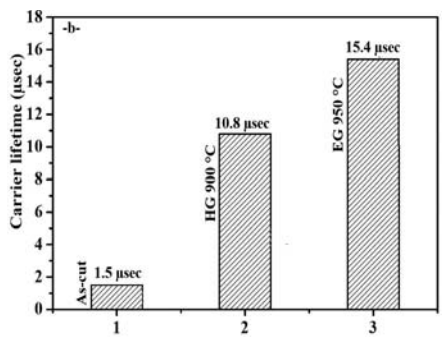
In region A, τ_{eff} is four times higher with the homogeneous gettering and six times with the extended one compared to the initial value measured on as-cut sample with 2.45 microseconds (μsec) as shown in the Figure 5a-.

The same evolution of the measured carrier lifetime is observed in the region B (Fig. 5b-).

The two other regions C and D present acceptable initial values from 7 to 8 μsec from as-cut Mc-Si. After homogeneous and extended gettering treatment, their response to the two processes is different.



5a-



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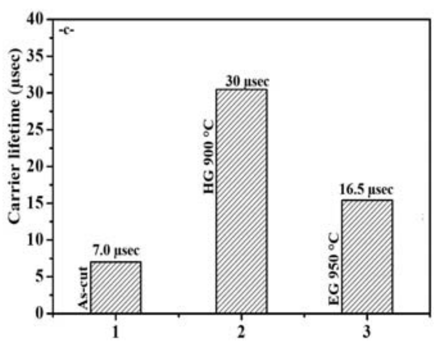
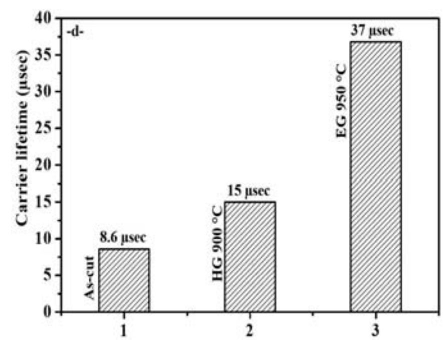


5c-



5d-

Fig. 5: QSSPC effective minority carrier lifetime on different regions of Mc-Si wafer vs. Homogenous and extended phosphorous gettering

In C region, τ_{eff} increases with the homogeneous gettering by four times reaching values of 30 μsec and it is only 16.5 μsec in the same region after extended gettering one at T_L = 930 °C during 30 min. and T_L = 750 °C during 120 min. (Fig. 5b-). This behavior is inversed in the region D and we observe that the extended process is more efficient and give an ameliorated lifetime value τ_{eff} = 37 μsec, practically five times the initial value (Fig. 5d-).

Because in this case the internal structures such as clusters, metallic and oxygen precipitates are weakly altered avoiding their complete dissolution which generally generate degradation of the optoelectronic properties of silicon and especially the multicrystalline one [11].

In the same region D, the homogenous process give an amelioration of τ_{eff} = 15 µsec due to the dissolution of metallic precipitates and other clusters under the prolonged (180 minutes) temperature treatment (900 °C in this case).

This phenomenon (inhomogeneous response to the gettering process) is due mainly to the spatial distribution of the crystalline defects density and the transitions metal precipitates density through the all regions of the Mc-Si wafer [12].

Carrier lifetime analysis indicates that the region D contain a higher amount of defect density and transition metals precipitates which dissolve during a long time process (180 mn) at 900°C [13].

The same process gives the best improvement of τ_{eff} in the region C attesting that it contains a relatively low metallic precipitates and crystalline defect densities. These results are in accordance with observation showed by Buonassisi *et al.* [14] on the behavior of transition metallic species in their different forms in Mc-Silicon and especially the irons precipitates and iron point defects which can dissolve at temperatures greater than 500 °C [15].

Despite that the iron point defects can be a major cause of lifetime degradation in Mc-Si solar cells; it is difficult to optimize the gettering process for each transition metal species.

As conclusion of this study we can say that the extended process produce lifetime amelioration on the majority of the silicon wafer region and it is more efficient than the homogenous one as shown in figure 5.

4. CONCLUSION

The effect of external phosphorous diffusion gettering on multicrystalline silicon wafers using both homogenous and extended schemes where examined. Our study suggests that the effectiveness of the gettering is more pronounced in the case of extended process with a significant diminution of Cr atoms concentration before and after gettering and a noticeable minority carrier lifetime improvement.

Also, the implied voltage values measured on Mc-Si wafers indicate that the extended phosphorous gettering process is better than the homogenous one with corresponding values of about 645 mV and 615 mV respectively.

This implies an efficient gettering of the transition metals impurities and a high neutralization of the recombination centers in the bulk of the Mc-Si wafers. An inhomogeneous response to the gettering process is showed on the different regions of the same wafer. This phenomenon is due mainly to the spatial distribution of the crystalline defects and the transitions metal precipitates densities through the surface of the wafer.

The extended process produce lifetime amelioration on the major regions of the silicon wafer and it is more efficient than the homogenous one as observed during the QSSPC measurements. We think that an optimized extended gettering process with TH around 920 °C for a few minutes and with a second temperature stage between 600 and

650°C, permit to have a costly effective thermal budget contribution to lowering the final cost of the high efficiency multicrystalline photovoltaic panels.

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REFERENCES

[1] D.H. Macdonald, '*Recombination and Trapping in Multicrystalline Silicon Solar Cells*', PhD Thesis, Australian National University, 2001

[2] I. Witting, J. Bharathan and G. Rozgonyi, '*Impurity Significance and Sources in Multicrystalline Cast Silicon*', Proceedings of the18th Workshop on Crystalline Silicon Solar Cells and Modules: Materials and Processes, Colorado, pp. 159 – 162, August 3–6, 2008.

[3] T. Saitoh and I. Yamaga, '*Application of Numerical Simulation of Directional Solidification Processes for Improving Crystal Quality*', Proceedings of the 15th Workshop on Crystalline Silicon Solar Cells and Modules: Materials and Processes, Colorado, pp. 38 – 47, August 7–10, 2005.

[4] M. Dhamrin, R. Ozaki and T. Saitoh, '*Quality Evaluation and Improvement of Iron-Doped Electromagnetic Multicrystalline Silicon Wafers*', Solar Energy Materials and Solar Cells, Vol. 74, N°1-4, pp. 203 – 211, 2002.

[5] A. Peeva, R. Koegler, G. Brauer, P. Werner and W. Skorupa, '*Metallic Impurity Gettering to Defects Remaining in the $R_P/2$ Region of Mev-Ion Implanted and Annealed Silicon*', Material Science in Semiconductor Processing Vol., 3, N°4, pp. 297 – 301, 2010.

[6] T. Buonassisi, M. Heuer, A.A. Istratov, M.D. Pickett, M.A. Marcus, B. Lai, Z. Cai, S.M. Heald and E.R. Weber, '*Transition Metal Co-precipitation Mechanisms in Silicon*', Acta Materialia, Vol. 55, N°18, pp. 6119 – 6126, 2007.

[7] M. Sheoran, A. Upadhyaya and A. Rahatgi, '*Bulk Lifetime and Efficiency Enhancement Due to Gettering and Hydrogenation of Defects During Cast Multicrystalline Silicon Solar Cell Fabrication*', Solid State Electronics, Vol. 52, N°5, pp. 612 – 617, 2008.

[8] S. Pizzini, M. Acciarri, S. Binetti, A. LeDonne, S. Marchionna and M. Bollani, '*Defect Studies on Silicon and Silicon Germanium for PV and Optoelectronic Applications*', Materials Science in Semiconductor Processing, Vol. 9, N°1-3, pp. 66 – 73, 2006.

[9] O. Schultz, S.W. Glunz, S. Riepe and G.P. Willeke, '*Gettering of Multicrystalline Silicon for High-Efficiency Solar Cells*', Proceedings of the 21st European Photovoltaic Solar Energy Conference, pp. 788 – 791, Dresden, Germany, September 4-8, 2006.

[10] R. Schindler and W. Warta, '*Improvement and Limits of the Open-Circuit Voltage of MC-Silicon Solar Cells*', Physica Status Solidi (b), Vol. 222, N°1, pp. 389 – 404, 2000.

[11] S. Cadeo, S. Pizzini, M. Acciarri and A. Cavallini, '*Oxygen Precipitate Precursors and Low Temperature Gettering Processes. I- Segregation of Oxygen and Thermal Donor Generation in the 600 – 850 °C Range*', Materials Science in Semiconductor Processing, Vol. 2, N°1, pp. 57 – 68, 1999.

[12] S. Martinuzzi, O. Palais and S. Ostapenko, '*Scanning Techniques Applied to the Characterisation of P and N Type Multicrystalline Silicon*', Materials Science in Semiconductor Processing, Vol. 9, N°1-3, pp. 230 – 235, 2006.

[13] M. Rinio, C. Ballif, T. Buonassisi and D. Borchert, '*Defects in the Deteriorated Border Layer of Block-Cast Multicrystalline Silicon Ingots*', Proceedings of the 19th European Photovoltaic Solar Energy Conference, pp. 762 – 765, Paris, 7-11 June, 2004.

[14] T. Buonassisi, A.A. Istratov, M. Heuer, M.D. Pickett, M.A. Marcus, B. Lai, S.M. Heald and E.R. Weber, '*From Understanding Towards Engineering Metal Impurities in Multicrystalline Silicon*', Proceedings in the 21st European Photovoltaic Solar Energy Conference and Exhibition, pp. 696 – 699, Dresden, Germany, Sept. 4-8, 2006.

[15] T. Buonassisi, M.D. Pikett, R. Sweeney, '*Reducing the Concentration of Interstitial Iron in Crystalline Silicon Solar Cells via Low (≤ 500°C) Temperature Annealing*', NREL Workshop on Crystalline Silicon PV, 2007.