IMPROVEMENT OF DIFFUSION LENGTHS IN MULTICRYSTALLINE SI BY P-AL CO-GETTERING DURING SOLAR CELL PROCESSING

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ABSTRACT: Solar cells based on multicrystalline silicon (mc-Si) from Eurosolare are examined in this study. The influence of various high temperature steps on the diffusion length L_B of bulk minority carriers are investigated, including Al-gettering, P-Al co-gettering and dry thermal oxidations. Al-gettering was compared with P-Al co-gettering for different gettering temperatures. It is shown that co-gettering is most effective at high process temperatures leading to an effective diffusion length of L_{eff}=230 µm at a gettering temperature of 1000°C. Different solar cell processes are investigated in order to find an optimum process sequence leading to a high final diffusion length. The highest value of L_{eff} was found for all applied processes when the oxidation was done as final high temperature step. It was found that the presence of Al on the back during the oxidation is beneficial to prevent a degradation for Al-gettered cells. For co-gettered cells even an improvement of L_{eff} was found during the final oxidation. Highest values of L_B=290 µm were obtained for a process including only two high temperature steps with P-Al co-gettering (simultaneous diffusion of Al and P) and a dry thermal oxidation.
Keywords: Gettering - 1: Multi-Crystalline - 2: Silicon - 3

1. INTRODUCTION

Multicrystalline silicon (mc-Si) is a very attractive material for solar cell processing. At present a large part of the production world-wide is based on cast mc-Si. Due to the poorer material quality as compared to single crystalline Si caused by defects and metallic impurities minority charge carrier diffusion lengths L_B are lower in these materials. In order to reach a good cell performance, additional steps like Al- and/or P-Al co-gettering are effective tools to improve L_B during solar cell processing. Gettering refers to an annealing process where the lifetime reducing metallic impurities are removed from the active region and are captured in regions with a higher solubility. For P-gettering this region is the phosphorus-doped emitter, while in Al-gettering the Al-alloyed region serves as gettering layer. Many authors have described the positive effect of Al-gettering and P-gettering on several mc-Si materials [1-6].

In this study we used cast mc-Si provided from Eurosolare. This material is known to show a positive effect on Al-gettering [3] and P-gettering [4]. P-gettering is often done prior to the solar cell process (pregettering) by a heavy phosphorus diffusion at temperatures around 900°C for longer times. The heavily diffused layer with the captured impurities is removed before starting with the cell process. In this study we rather tried to implement P-gettering in a relative simple process for high efficiency cells. This process includes passivation of the front surface by a dry thermal oxide and passivation of the rear by a full area Al-BSF. Different process sequences are examined in order to determine the best one with the highest value of the diffusion length at the end of the solar cell process which is an important factor for a high cell efficiency. We also tried to simplify the cell process by reducing the number of high temperature steps. This was done by the simultaneous diffusion of P and Al, leading to a P-Al co-gettering step.

2. AL-GETTERING AND P-AL CO-GETTERING

2.1 Experiment

Solar cells have been processed out of neighboring 5x5 cm^2 wafers with the same crystal grain structure and a resistivity of 1 Ωcm. In this section we compared Al-gettering to P-Al co-gettering. The applied process sequences are shown in Figure 1. A planar etch in $HNO_3/HF/CH_3COOH$ was done to remove the saw damage. The thickness after etching was 310 µm. Before the P-diffusion from a liquid $POCl_3$ source all wafers were

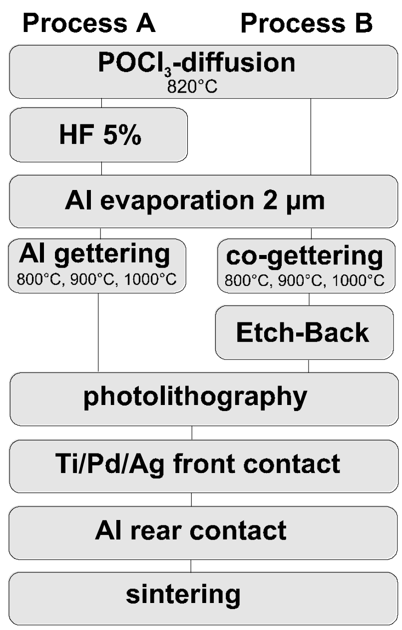

Figure 1*:* Solar cell process for Al-gettering (Process A) and P-Al co-gettering (Process B).

cleaned in a solution of H_2SO_4/H_2O_2 (IMEC-Clean [7]). The $POCl_3$-diffusion was carried out at 820°C for 15 min (Sheet resistance 70-80 Ω/sq). For half of the wafers the P-glass was removed in 5 %HF (Process A), whereas for the other wafers this glass can serve as a phosphorus source in a following annealing step (Sequence B). An Al layer of 2 µm was evaporated on the back of all wafers and a gettering step was applied for temperatures of 800°C, 900°C and 1000°C. We refer to Al-gettering if the P-glass is removed prior to the Al-alloying (Process A), to P-Al co-gettering (Process B) if it is still present. This might be misleading, because during Al-gettering there is a simultaneous P-gettering in the emitter as well.

The sheet resistances of the emitter for the co-gettered cells were 65-75 Ω/sq (800°C), 30 Ω/sq (900°C) and 17 Ω/sq (1000°C). The obtained sheet resistance indicates that there was a heavy phosphorus diffusion from the deposited P-glass at temperatures of 900°C and 1000°C. These heavily doped emitters will reduce cell performance. Therefore we performed an emitter etch back in a solution of HNO_3:HF:H_2O (1500:2.5:150) to obtain a sheet resistance in the range of 70-80 Ω/sq. Sheet resistances for the Al-gettered cells were 70-80 Ω/sq after the annealing step. The front contact consisted of a photolithographically defined Ti(50nm)/Pd(50nm)/Ag(3µm) layer, the rear contact of a 2 µm thick Al layer. A forming gas anneal was carried out at 380°C for 60min to enhance metal adherence and to remove damage caused by electron-gun x-rays. Processing was completed by cutting the 5x5 cm^2 wafers into four cells (2x2 cm^2) with a conventional dicing saw.

2.2 Results

Finished cells were characterized by their illuminated and dark I-V characteristics, their hemispherical reflectance and their Internal Quantum Efficiencies (IQE) obtained from spectral response measurements. Effective diffusion lengths L_{eff} were extracted by analyzing the IQE in the near infrared as suggested by Basore [8]. A reduced wavelength range from 900 nm to 1000 nm was used in this study. L_{eff} depends on the bulk diffusion length L_B and the effective surface recombination velocity $S_{eff,B}$ at the back of the solar cell. The obtained values of L_{eff} are given in Figure 2 and

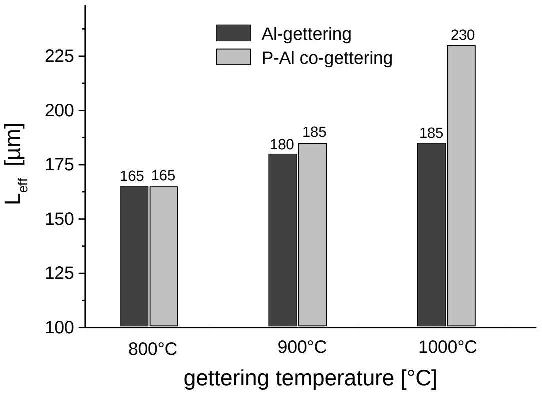

Figure 2: Effective diffusion lengths L_{eff} obtained from a spectral analysis of the IQE in the infrared of Al-gettered (Process A) and P-Al co-gettered (Process B) cells for different gettering temperatures. Given are average values of four cells.

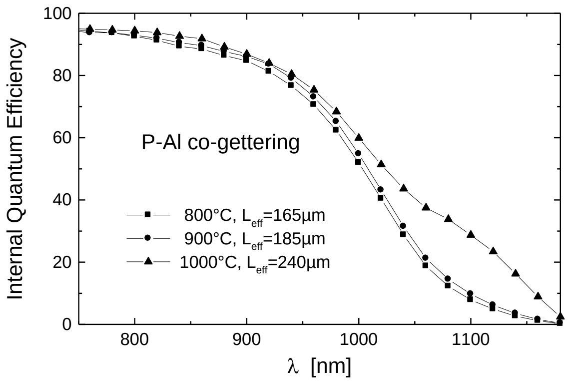

Figure 3: Internal Quantum Efficiency IQE of P-Al co-gettered cells at different gettering temperatures.

are average values of four cells. The measured IQE in the long wavelength range of P-Al co-gettered cells at different gettering temperatures is given in Figure 3.

For Al-gettering and P-Al co-gettering the highest value of L_{eff} was obtained for the highest gettering temperature of 1000°C. P-Al co-gettering is more effective at higher gettering temperatures leading to the best value of L_{eff}=230 µm at a gettering temperature of 1000°C.

3. PROCESS OPTIMIZATION

The purpose of this section was the development of an optimal fabrication process. To study this four different processes were examined in order to find the process with the highest final diffusion length. The obtained solar cell design for all processes was identical and consisted of a passivated front surface by a thermally grown oxide, an emitter with sheet resistance of 70-80 Ω/sq, and a full area back surface field (BSF). Since the diffusion length can change during any high temperature step when the impurities get mobile, special care has to be taken in order to preserve or even enhance the diffusion length.

3.1 Experiment

The applied different processes are described in Table I. In Processes 1 and 2 a thermal oxidation for surface passivation was included in the process as compared to Process A and B in the previous section. The effect of oxidations for Al-gettered (Process 1) and P-Al co-gettered cells (Process 2) on the diffusion length is examined. Therefore oxidations were carried out at different stages of the process. Processes 3 and 4 were designed with a reduced number of high temperature steps. In those processes the simultaneous emitter diffusion and Al-alloy lead to this reduction and to P-Al co-gettering.

The $POCl_3$ emitter diffusion for Processes 1, 3 and 4 was done at 820°C and included a drive-in step to deepen the emitter. Obtained sheet resistance was 70-80 Ω/sq. The P-glass deposition for the P-Al co-gettered cells was again done at 820°C for 15 min. The heavily doped emitters of the co-gettered cells of Process 2 were etched to obtain a sheet resistance of 70-80 Ω/sq. All thermal oxidations were performed at 900°C to grow a thin thermal oxide of about 12 nm thickness. An Al layer of 2 µm thickness was evaporated before the gettering step on all wafers.

Table I: Applied process sequences for the optimisation of the cell process. Process 1 investigates Al-gettering, Process 2 P-Al co-gettering. For both processes the influence of a dry thermal oxidation on the diffusion length is investigated. In Processes 3 and 4 the simultaneous diffusion of P and Al in one thermal cycle is examined. In Process 4 an additional Al-alloy at 950°C was done as compared to cells of Process 3. L_{eff}, extracted from a spectral analysis of the IQE, V_{oc} and J_{sc} are averaged values. Cells are untextured and have no ARC (AntiReflection Coating). Due to a different IQE in the short wavelength range caused by different temperature loads, not always a direct correlation between L_{eff} and J_{sc} can be observed.

	$POCl_3$-diffusion	Gettering	Oxidation	L_{eff} [µm]	V_{oc} [mV]	J_{sc} [mA/cm^2]
Process 1a	820°C+ drive-in	Al, 950°C	no	210	600	22.8
Process 1b	,,	Al, 950°C	before Al-gettering	185	601	22.8
Process 1c	,,	Al, 950°C	after Al-gettering	205	602	22.8
Process 2a	P-depos. at 820°C	P-Al, 950°C	no	205	588	20.1
Process 2b	,,	P-Al, 950°C	after co-gettering	215	603	23.2
Process 3	$POCl_3$+Al-alloy at 820°C		after co-gettering	170	600	23.0
Process 4	Al-alloy 950°C, $POCl_3$ 820°C after cool.		after co-gettering	230	604	23.5

Gettering for Processes 1 and 2 was done at 950°C (optimum Al-gettering temperature for this specific material [3]) for 30 min under pure N_2-flow. In Process 4 the wafers were subjected to an additional Al-alloy at 950°C for 30 min under N_2 as compared to wafers of Process 3. For wafers of Process 4 the $POCl_3$ flow started after cooling down to 820°C. The cell process was completed (metallization, forming gas anneal, separation into four 2x2 cm^2 cells) as already mentioned in the previous section

3.2 Results

The cells were characterised by their illuminated I-V characteristics, their hemispherical reflectance and their Internal Quantum Efficiency obtained from spectral response measurements. Effective diffusion lengths L_{eff}, extracted from a spectral analysis in the range from 900 to 1000 nm, are given in Table I together with measured values of V_{oc} and J_{sc}. These values represent average values.

By analysing the results of cells produced by Processes 1 and 2 the influence of thermal oxidations on diffusion lengths can be investigated. For Process 1 (Al-gettering), a degradation of L_{eff} was found, when the oxidation was performed directly after the $POCl_3$ diffusion (Process 1b,

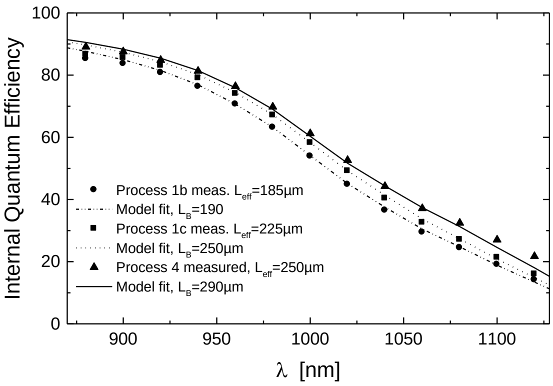

Figure 4: Model data (lines) calculated with PC1D and measured data (points) for best cells of Process 1b, 1c and 4. L_{eff} was obtained from a spectral analysis of the measured curve, L_B was used in PC1D for the model calculation.

L_{eff}=185 µm) as compared to cells without the additional oxidation step (Process 1a, L_{eff}=210 µm). The effect of a degradation due to oxidation after emitter diffusion was already observed by Stocks et al. [6] on mc-Si and by Gee et al. [9]. Stocks et al. did not find this degradation for P-pregettered cells or if there was Al present on the back during the oxidation. They attributed this degradation to the release of impurities already gettered during the emitter formation. In our experiments this degradation was still present even if an Al-gettering step was applied after the oxidation. Almost no degradation was observed if the oxidation was performed after the Al-gettering (Process 1c, L_{eff}=205 µm). In this case Al was present during the oxidation, leading to an Al-gettering action.

For co-gettered cells the opposite effect was observed. Cells with an oxidation (Process 2b, L_{eff}=215 µm) showed a slightly higher value of L_{eff} as compared to cells without oxidation (Process 2a, L_{eff}=205 µm). In the co-gettering sequence, impurities captured in the near surface region are etched during the emitter etch back and hence removed from the wafer (this is similar to P-pregettering where the impurities captured in the gettering layer are etched prior to the cell process). Again there is Al present during the oxidation leading to an additional gettering action during the oxidation. This can account for the observed improvement of L_{eff}.

Cells produced by Process 3 lead to the lowest value of L_{eff}=170 µm. This can be explained by the rather low process temperature of 820°C which was not sufficient for effective gettering. Highest values of L_{eff}=230 µm were obtained for cells of Process 4, which again show the effectiveness of P-Al co-gettering. This result is remarkable since only two high temperature steps were applied as compared to cells of Processes 1 and 2. The highest value of L_{eff} also lead to the best parameters of V_{oc} and J_{sc}. These values are satisfactory since the cells are untextured and no ARC (AntiReflection Coating) was applied.

For three cells (best cells of Process 1b, 1c and 4) model calculations were performed using PC1D [10] to obtain the bulk diffusion length L_B. Measured and fitted data are given in Figure 4. Calculations were performed to best fit the measured data. For the effective recombination velocity at the back of the cell $S_{eff,B}$ a value of $S_{eff,B}$=4000 cm/s was taken. For the cell of Process 1a, L_B=190 µm best fitted the measured curve (L_{eff}=185 µm from the spectral analysis of the measured curve), for

Process 1b L_B=250 µm (L_{eff}=225 µm), for Process 4 L_B=290 µm (L_{eff}=250 µm). This high value of L_B for the cell of Process 4 clearly shows the effectiveness of P-Al co-gettering to improve the diffusion length during solar cell processing.

4. CONCLUSION

In this study we have shown the effectiveness of P-Al co-gettering to improve the diffusion length of mc-Si from Eurosolare during solar cell processing. We compared P-Al co-gettering to Al-gettering and found that co-gettering was more effective at higher temperatures leading to a value of L_{eff}=230 µm at a gettering temperature of 1000°C. A thermal oxidation was implemented in the solar cell process and a process optimisation was carried out. It was shown that a careful design of the used high temperature steps is necessary to get a high diffusion length at the end of the process. The obtained results indicate that it is beneficial to perform the oxidation as final high temperature step and to have Al present on the back as a gettering agent in order to prevent a degradation of L_B. Even an improvement of L_B was found for P-Al co-gettered cells during the final oxidation. The highest value of L_B=290 µm was obtained for cells with a simultaneous diffusion of Al and P in one thermal cycle.

5. ACKNOWLEDGEMENTS

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