Comparison of POCl_3 Diffusion and Phosphorus Ion-implantation Induced Gettering in Crystalline Si Solar Cells

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Abstract

Most p-type Si solar cells involves phosphorus-doped emitter by POCl_3 diffusion or phosphorus ion-implantation. Although the formation of the phosphorus emitter is known to getter impurities like Fe, the difference in the impact of these two gettering techniques on cell performance is not well quantified. Therefore, this paper compares the gettering efficiency of POCl_3 diffusion and phosphorus ion-implantation on Czochralski(Cz) and cast quasi-mono Si wafers. Cz-Si wafers were used to measure bulk lifetime and iron concentration before and after POCl_3 diffusion and phosphorus implantation with different doses. Increase in phosphorus implantation dose improved the gettering efficiency by increasing bulk lifetime and decreasing iron concentration but remained inferior to POCl_3 diffusion partly due to single side gettering as opposed to double side gettering with higher phosphorus surface concentration during POCl_3 diffusion. Moreover, large-area solar cells were fabricated on cast quasi-mono and Cz-Si wafers to quantify the impact of these emitters on cell parameters. POCl_3 diffused cast quasi-mono cells showed ~0.4% higher efficiency due to higher bulk lifetime compared to phosphorus implanted emitter. However, phosphorus implanted Cz cells gave ~0.3% higher efficiency due to lower emitter saturation current, resulting from the benefit of in-situ oxide surface passivation during the implant anneal.

1. Introduction

Crystalline Si accounts for more than 90% of the solar cells produced today and about 95% of those cells are fabricated on p-type Si[1]. This is because of the well-established technology and equipment base for p-type cell fabrication and lower wafer and cell processing cost compared to n-type cells. However, p-type wafers generally have lower bulk lifetime and are more susceptible to metal impurities compared to the n-type wafers [2, 3]. It has been reported that the minority carrier lifetime in p-type Si is frequently limited by iron related defects[2, 4] with larger electron capture cross section compared to hole[5]. Iron is often present in the feedstock material and can be introduced during processing [6]. Therefore, majority of the PV industry currently uses POCl_3 diffusion to remove metal impurities including iron [7-11]. POCl_3 gettering is attributed to the formation of misfit dislocations on the surface which provide the sink for impurity gettering. In addition, higher phosphorus surface concentration enhances gettering because it increases solid solubility and segregation coefficient of metal impurities[7-17]. The phosphorus ion-implanted emitter has recently shown higher performance due to in-situ oxide passivation during the implant annealing process [18, 19]. However, its gettering quality is not fully understood and compared

with POCl_3 diffusion. This paper conducts a systematic and controlled study to compare the impact of phosphorus ion-implantation and POCl_3 diffusion induced gettering on cast quasi-mono and Czochralski(Cz) Si solar cells.

2. Experiment

Commercial grade 200 μm thick 1~2 $\Omega\text{-cm}$ p-type Cz wafers (boron-doped, 239 cm^2) and cast quasi-mono Si wafers (boron-doped, 243.34 cm^2) were used for this research. Two separate experiments were conducted: first study involved determination of the iron concentration and bulk lifetime (Fig. 1), and the second study involved complete cell fabrications (Fig. 2 and 3) with phosphorus ion-implantation and POCl_3 diffusion followed by detailed characterization and PC1D device modeling.

Fig. 1. Procedure and structure for iron concentration and bulk lifetime measurements.

Fig. 2. Procedure for cell fabrications of phosphorus ion-implanted and POCl_3 diffused solar cells.

Fig. 3. Full Al-BSF cell structures of (a) phosphorus ion-implanted and (b) POCl₃ diffused solar cells.

Bulk lifetime and iron concentration were measured in as-grown, POCl₃ diffused, and implanted p-type Cz wafers (~2ohm-cm). The measurements were performed by the quasi-steady-state photoconductance (QSSPC) technique[20] using Sinton lifetime tool (WCT-120). Prior to the measurements, Cz wafers were subjected to saw damage etching in KOH solution followed by alkaline texturing process. Emitters were formed by POCl₃ diffusion on both sides of the wafers or phosphorus implantation (AMAT, Solion) on the front side of the wafer with a dose in the range of 1-3e15 cm⁻². Total diffusion time was kept at 30 minutes for both techniques. POCl₃ emitter was formed by a 850°C for 20 minutes diffusion followed by 10 minutes in-situ anneal in N₂. The implanted Cz wafers were annealed at 850°C for 20 minutes in oxygen to grow a high quality ~250Å thick oxide followed by 10 minutes in-situ anneal in N₂. For bulk lifetime and iron concentration measurements, diffused wafers were first etched 20um from each side in KOH for 15 minutes at 80°C down to bare Si, and then passivated by iodine-methanol solution(I₂/ME) for QSSPC measurements.

In the second part of the experiment, large area screen printed p-type industrial cells with full aluminum back surface field (full Al-BSF) were fabricated on both Cz and cast quasi-mono wafers according to a process sequence shown in the Fig. 2. After the emitter formation, SiNx anti-reflection coating was deposited on the front side of all wafers. Industrial screen printing technology was used to print Ag gridline and busbars on the front and full Al on the back side. Finally, cells were co-fired in a belt furnace to form the Ag contacts through the SiNx film on the front and full area Al-BSF on the back. The final cell structure is the Fig. 3. Symmetric test structures (Fig. 4) were fabricated on high bulk lifetime n-type wafers to measure saturation current density (Joe) to compare the emitter quality and the impact of oxide passivation.

Fig. 4. Test structures for emitter saturation current of (a) phosphorus implantation and (b) POCl₃ diffusion.

3. Results and Discussion

3.1 Bulk lifetime and iron concentration measurements and analysis

The total iron concentration (cm^{-3}) in the wafers was obtained by a method described by Zoth and Bergholz. This method uses Eq. (1) and Macdonald et al's prefactor $C(-3.0\text{e-}14 \text{ cm}^{-3}$ for 2 ohm-cm) to calculate iron concentration from effective lifetime measurements before ($\tau_{\text{eff}0}$) and after ($\tau_{\text{eff}1}$) dissociation of FeB pair by light, assuming all other recombination processes remain unchanged[21, 22].

$$[Fe] = C(1/\tau_{\text{eff}1} - 1/\tau_{\text{eff}0}) \quad \text{Eq. (1)}$$

This technique has been widely used for detecting iron concentration in microelectronics industry when other defects are not affected or dissociated by the light source[23-27]. Effective lifetime was measured by the QSSPC method before and after light exposure using Sinton WCT-120 tool. A strong light source (> 20 suns) in the Sinton tool was used to dissociate the FeB pair to form interstitial iron (Fe_i) which has lower hole capture cross section ($\sigma_{p,\text{Fe}_i}: 7\text{e-}17\text{cm}^{-2}$, $\sigma_{p,\text{FeB}}: 2\text{e-}15\text{cm}^{-2}$). This resulted in higher lifetime after light exposure ($> 1.5\text{e}14\text{cm}^{-3}$ injection level). The crossover point at around $1.5\text{e}14 \text{ cm}^{-3}$ injection level for measured lifetimes before and after light exposure, which serves as the “fingerprint” of iron in silicon[22], was verified. Next, total iron concentration was calculated using Eq. (1) and measured effective lifetime at an excess carrier density of $1\text{e}15\text{cm}^{-3}$, which is close to the open circuit voltage of the cell. Fig. 5 shows that higher phosphorus implanted dose results in lower iron concentration and higher bulk lifetime in the Cz wafer after diffusion. The highest bulk lifetime ($\sim 650\mu\text{s}$) was achieved after POCl_3 diffusion because it provides a sink for impurity gettering on both surfaces due to higher phosphorus surface concentration as opposed to single side gettering in ion implantation ($\sim 500\mu\text{s}$). In addition, segregation of impurities toward POCl_3 diffused surface may be greater because of higher phosphorus surface concentration than ion implanted surface (Fig. 8). These factors lead to higher effective impurity segregation coefficient[11, 16, 28] for POCl_3 diffusion. Notice that the bulk lifetime trend is opposite of the iron concentration, indicating that iron contamination is one of the major sources of bulk lifetime degradation in these p-type samples. Consistent with the literature [11, 16, 28], these results indicate that gettering efficiency increases with the increase in phosphorus surface concentration which was found to be higher for POCl_3 diffusion compared to ion implantation in this study (Fig. 8). Also since phosphorus surface concentration is a function of implantation dose, gettering efficiency was found to increase with the dose (Fig. 5).

Fig. 5. Measured bulk lifetime and iron concentration in the Cz wafers after POCl_3 and implanted diffusion.

3.2 Effect of phosphorus gettering on the performance of full Al-BSF solar cells on cast quasi-mono and Czochralski-grown Si wafers.

Complete solar cells were fabricated on Cz and cast quasi-mono Si materials with POCl_3 and implanted phosphorus ($3 \times 10^{15} \text{ cm}^{-2}$ dose) emitters. The measured light I-V data and solar cell efficiencies are summarized in the Table 1.

Table 1

Cell results of Quasi-mono and Cz wafers.

Wafer Type	Emitter	Voc (mV)	Jsc (mA/cm ²)	FF (%)	η (%)
Cast Quasi-mono	POCl_3	628	37.4	79.4	18.6 ± 0.10
	Implanted ($3 \times 10^{15} \text{ cm}^{-2}$ dose)	625	37.1	78.5	18.2 ± 0.08
Cz	POCl_3	637	37.8	79.2	19.1 ± 0.13
	Implanted ($3 \times 10^{15} \text{ cm}^{-2}$ dose)	643	37.9	79.5	19.4 ± 0.09

For the cast quasi-mono material, POCl_3 diffused cells showed higher cell efficiency because it has a low starting bulk lifetime which benefits from superior double side POCl_3 gettering. Fig. 6 shows that POCl_3 diffusion increased bulk lifetime from 80us to 330us as opposed to 200us of the phosphorus implanted wafers. Cell Voc, FF and Jsc also showed the same trend (Table 1).

Fig. 6. Measured bulk lifetime on Cz and Cast Quasi-mono wafers on three different conditions by the procedure in Fig. 1.

However, Cz solar cells showed a reverse trend in efficiency where implanted cells showed ~0.3% higher efficiency compared to POCl₃ diffused cells in spite of lower bulk lifetime. In order to explain this, PC1D device modeling was performed as a function of bulk lifetime (Fig. 7) which revealed that efficiency saturates after ~250 us bulk lifetime for our baseline cell design. Fig. 8 shows that the implanted cells had lower Joe (70 fA/cm² vs 210 fA/cm² for POCl₃) compared to POCl₃ diffused cells because of the in-situ oxide passivation. The lower Joe of the implanted emitter contributed to 6mV higher Voc(Table 1) accounting for the observed ~0.3% increase in efficiency.

Fig. 7. PC1D modeling for Full BSF baseline Cz cells.

Fig. 8. Measured emitter saturation current(Joe) (a) on test structures in the Fig. 4 of implanted and POCl₃ diffused emitter and its measured electrochemical capacitance-voltage(ECV) profiles (b).

It is interesting to note that cast quasi-mono cells showed lower Voc and efficiency for ion-implanted cells compared to the POCl₃ diffused cells in spite of superior oxide passivation. This was because the bulk lifetime in the implanted cast quasi-mono cells was much lower compared to the POCl₃ diffused cells(Fig. 6 and Table 2). Therefore, the loss in Voc due to lower bulk lifetime in implanted cast quasi-mono cell was greater than the gain in Voc due to oxide passivation. Photoluminescence(PL)

measurements in the Fig. 9 also support that POCl_3 diffused cast quasi-mono cell has higher effective lifetime than the implanted cast quasi-mono cells due to superior gettering. PL measurements in implanted Cz cells gave higher effective lifetime than the POCl_3 diffused cells in spite of lower bulk lifetime. This is because PL measures effective lifetime including the surface passivation effect which is superior for the implanted cells due to the in-situ oxide passivation.

Fig. 9. Photoluminescence(PL) images (808 nm) on Cz and cast quasi-mono.

PC1D device simulation and internal quantum efficiency(IQE) measurements were performed on both Cz and cast quasi-mono cells with POCl_3 and implanted emitters (Table 2 and Fig. 9) to validate the above conclusions. Note that compared to the bulk lifetime measured at $1\text{e}15\text{cm}^{-3}$ injection level (Fig. 6) in wafers after diffusion, a lower bulk lifetime was used in PC1D modeling of the finished cells(Fig. 10) to obtain the best fit to the experimental data. This is partly because injection level dependence in these materials showed lower bulk lifetime at maximum power point which corresponds to an injection level of $\sim 3\text{e}13\text{cm}^{-3}$ [29].

Table 2

PC1D Simulation on Cz and cast quasi-mono cells.

Cell Parameters	Cz		Cast Quasi-mono	
	Implanted ($3\text{e}15\text{ cm}^{-2}$ dose)	POCl_3 diffusion	Implanted ($3\text{e}15\text{ cm}^{-2}$ dose)	POCl_3 diffusion
Wafer thickness (um)	190	190	190	190
Base Resistivity ($\Omega\text{-cm}$)	1.5	1.5	1.5	1.5
R_{series} ($\Omega\text{-cm}^2$)	0.60	0.71	0.50	0.53
R_{shunt} ($\Omega\text{-cm}^2$)	4950	3007	5640	7842
Cell τ_{bulk} (us)	250	500	40	250
BSRV (cm/s)	200	200	200	200
FSRV (cm/s)	10000	25000	15000	35000
R_{back} (%)	65	65	65	65
$J_{\text{o}2}$ (fA/cm 2)	20	20	42	42
n_2	2.25	2.25	2.1	2.1
Modeled Voc (mV)	643	637	624	630
Modeled Jsc (mA/cm^2)	37.9	37.8	37.4	37.7
Modeled FF (%)	79.6	78.9	78.5	78.5
Modeled Efficiency (%)	19.4	19.0	18.3	18.6

Fig. 10. Measured and PC1D fitted IQE data of Cz(a) and cast quasi-mono(b) full Al-BSF solar cells.

PC1D modeling (Table 2) gave a very good match between the calculated and measured light I-V data and IQE response (Fig. 10). As expected, POCl₃ diffused cast quasi-mono cells showed higher IQE response in the long wavelength (800nm~1100nm) due to superior bulk lifetime compared to the implanted cells. This accounts for ~0.4 % higher efficiency compared to implanted cells. However, in the case of Cz cells, very little difference was observed in the long wavelength response of POCl₃ diffused and implanted cells because bulk lifetime is so high that the long wavelength response is limited by the back surface recombination velocity (BSRV). On the contrary, implanted Cz cells showed higher response in the short wavelength (350nm~500nm) due to lower front surface recombination velocity (FSRV) and Joe due to in-situ oxide passivation. This explains ~0.3% higher efficiency compared to POCl₃ diffused cells.

4. Conclusion

Both POCl₃ diffused and implanted emitters show gettering effect but the gettering efficiency of POCl₃ diffusion was superior to implantation because of higher phosphorus concentration near the surface (Fig. 8b) and double side gettering. This was confirmed by iron concentration and the bulk lifetime measurements of the wafers gettered with POCl₃ diffusion and with phosphorus implantation with varying dose ($\sim 1e15$, $\sim 2e15$, $\sim 3e15$ cm⁻²) for the same gettering time and temperature. Commercially available large area Cz and cast quasi-mono wafers were used to fabricate baseline cells with full Al-BSF structure to quantify the impact of POCl₃ and implanted emitter formation on the cell efficiency. In the case of cast quasi-mono solar cells, the POCl₃ emitter gave ~0.4% higher cell efficiency compared to the implanted emitter due to lower iron concentration and higher bulk lifetime. In contrast, implanted Cz solar cells gave ~0.3% higher absolute efficiency due to lower Joe, resulting from in-situ oxide surface passivation, in spite of lower bulk lifetime. This is because lifetime above 250us has no effect of efficiency for this cell structure.

5. ACKNOWLEDGEMENTS

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