Efficiency Improvement Of Crystalline Silicon Solar Cells By Optimizing The Doping Profile Of PoCl$_3$ Diffusion

Hocine Ghembaza, Abdellatif Zerga, Rachid Saïm

Abstract: The emitter formation constitutes a crucial step in the manufacturing of the crystalline silicon solar cells. Several techniques are used in the photovoltaic industry and the most well-known one is based on the POCl$_3$ diffusion in cylindrical quartz tube. Despite the efficiency of this technique to be reproducible, economic and simple, it presents the major inconvenient to have a heavily doped region near the surface which induces a high minority carrier recombination. To limit this effect, an optimisation of diffused phosphorous profiles is required. Our modelling of phosphorus profiles is summarized in the presence of an erfc distribution near to the surface and other Gaussian distribution in the bulk region of the emitter. However, this work is devoted to study the effects of the temperature, diffusion time, surface concentration and doping profile on the crystalline silicon solar cells performances by using the new parameters. The first results of our numerical modelling carried out by the Silvaco Atlas® simulation package show the possibility to improve the efficiency by 2.78%. This result is also confirmed by the IQE calculus which present an obvious enhancement in short wavelength region (380-450nm) about 23%.

Index Terms: Crystalline silicon solar cells, Emitter, Phosphorus, POCl3 diffusion.

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1 INTRODUCTION

During the last decades, the research in crystalline silicon solar cells is mainly focused on improving the cell efficiency and reducing the cost of watt peak. The emitter is the most relevant element of solar cell. It is formed by POCl$_3$ diffusion which is actually the most used technique in silicon solar cells processing. Unfortunately, this technique imposes a high concentration of dopants in surface which limits considerably the passivation of surface. Thus, the design of an efficient emitter must take into account a low surface concentration of dopants without affecting the quality of screen printed contacts. In the literature, the classical phosphorus diffusion profile in crystalline silicon is constituted by a plateau in the region over 10^{20}cm^{-3}, a kink in the 10^{19}cm^{-3} region and a tail in the region below 10^{18}cm^{-3} [1]. Actually, in order to improve solar cells efficiencies, several optimization of emitter have been proposed by many researchers and they are based on varying the design of experiments. However, few theoretical models with analytical solutions have been used to study emitter [2-3]. Dunham [4] and Bracht [5] describe the phosphorus diffusion in silicon with the pair-diffusion model where phosphorus diffuses in association with interstitials (I) and vacancies (V). Fermi level dependencies of various charge states are taken into account to capture the kink and tail of the diffusion profile [6].

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In this work, the principal motivation is to optimize the emitter according the different diffusion parameters by using a new modelling of POCl$_3$ diffusion. In our modelling, the analytical considerations of Dunham and Bracht are taken into account and integrated in the numerical code which it was accomplished by Silvaco-TCAD package [7]. However, an experimental phosphorous diffusion profile was used to validate our numerical simulation results. This experimental profile was obtained with phosphorus diffusion in crystalline silicon at 825°C during 30 minutes. The sheet resistance of emitter was about 40Ω/sq. The phosphorous profile was determinate by the Secondary Ion Mass Spectroscopy (SIMS) [8].

2 MODELING

2.1 Process description

The phosphorus diffusion process was carried out in an industrial diffusion tube furnace under a low-pressure atmosphere of about 200mbar. The wafers are vertically placed into a quartz support for loading 156x156 mm² wafers. Every wafer is placed at a distance of 3 mm next to each other. The support is placed into the quartz tube and is heated up to 800°C. A flow of nitrogen is used to carrier the liquid dopant source POCl$_3$ via a bubble trap. Before POCl$_3$ injection, the O$_2$ gas is introduced into the diffusion tube to ensure the thermal oxidation of silicon. At the higher temperatures, phosphorus diffuses into silicon matrix forming the p-n junction with the p-type substrate doped initially at 10^{16}cm^{-3} (0.1Ω.cm resistivity). All the wafers have a thickness of 200µm. Usually, the diffusion process consists of an active dopant deposition step followed by a drive-in step. During the deposition, a Phospho-Silicate Glass PSG is formed on surface of substrate. The PSG glass is a mixture of phosphorus pentoxide (P$_2$O$_5$) and silicon dioxide (SiO$_2$) [9]. This glass is etched by fluorydric acid 10% during 5 minutes before SIMS and sheet resistance characterizations.

2.2 Phosphorus doping profile simulation

Some authors use the Gaussian [10-12] or the double Gaussian function [13-14] to simulate the phosphorus diffusion profile in silicon. In the present paper, we propose a mathematical model for describe the phosphorus diffusion profile. It can be summarized in a complementary error function for the pre-deposition step and a Gaussian profile for the drive-in redistribution. Our proposed models are in well correlation with [15] and [16]. This result will be used as an input to simulate our solar cells.
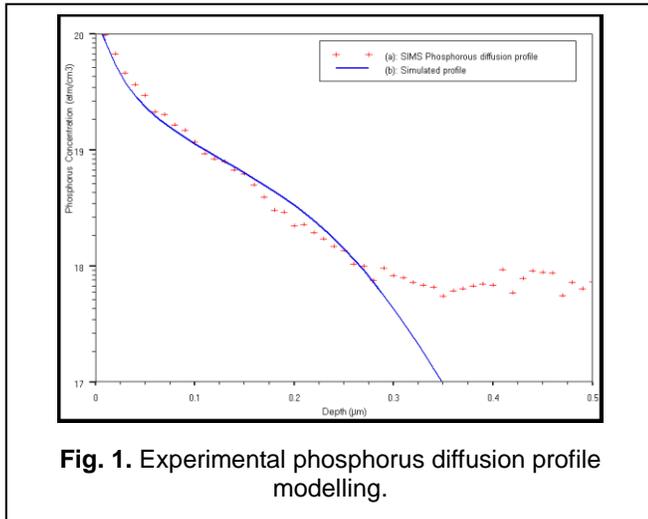

Fig. 1. Experimental phosphorus diffusion profile modelling.

3 RESULTS AND DISCUSSION

3.1 Influence of diffusion temperature

The variation of temperature is the simplest way to control the phosphorous diffusion profile. In figure 2, this variation is showed for a constant diffusion time. As the temperature increases, doping increases, and the formed junctions are deeper. This behavior is explained by the variation of the coefficient diffusion and limit solubility with temperature. For this reason, the process temperature parameter to achieve necessary exact junction depth has proven to be rather delicate.
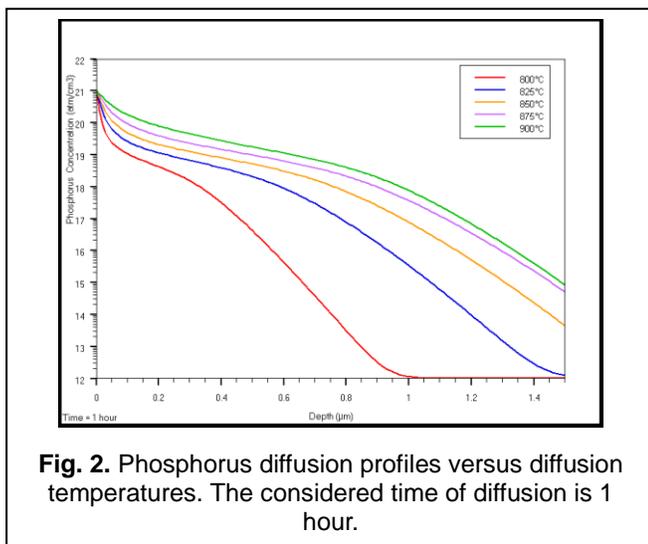

Fig. 2. Phosphorus diffusion profiles versus diffusion temperatures. The considered time of diffusion is 1 hour.

3.2 Influence of diffusion time

For long drive-in time, the junction is deeper. PSG deposited during the pre-deposition step acts as an infinite phosphorus source. This observation is in correlation with the experiment results of [6] which confirms that the PSG layer acts as a constant dopant source in a time frame at constant temperature. All these results confirm that phosphorus profile is highly affected by the tube furnace conditions. Clearly, time and temperature must be considered carefully.
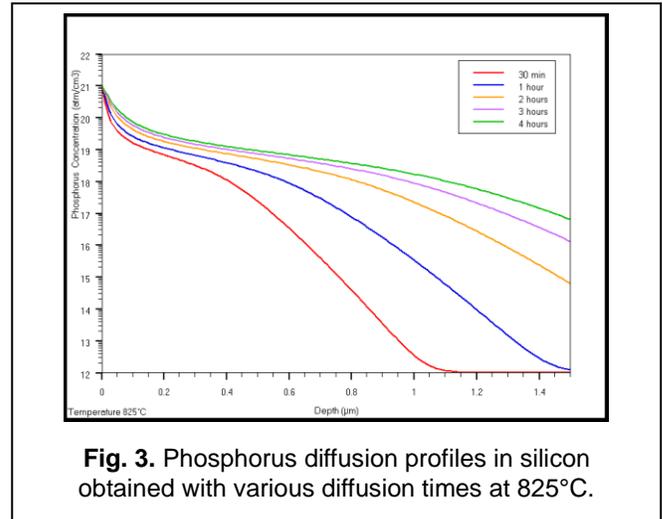

Fig. 3. Phosphorus diffusion profiles in silicon obtained with various diffusion times at 825°C.

3.3 Emitter optimization by reducing the dead layer

In the preceding sections, we showed the effect of temperature and time on the diffusion profiles. In this part, we will see the effect of another so important parameter: the oxygen flux. During emitter formation and at high phosphorus concentrations, precipitates are formed on silicon surface and promote the existence of electrically inactive phosphorus which forms a dead layer at the silicon surface. This behaviour is characterized by a kink shape on the experimental profiles. This kink has a great impact on the solar cell performance since it results in low collection efficiency near the front surface [17]. The high phosphorus concentration causes an important degradation in the Internal Quantum Efficiency (IQE) especially at the short wavelength region [15]. Many manufacturers tried to reduce the heavy inactive phosphorus concentration and the thickness of the dead zone by an additional step in the industrial process, i.e.: chemical etching of PSG layer after the phosphorus diffusion [15-19]. So this solution increase the duration of industrial process and it appears expensive. We propose another low cost method to reduce the dead layer based on the work of Cuevas et al. [20] and reported by [21-23]. They demonstrate a strong influence between the kink shape of diffusion profile and emitter sheet resistance. This supposes that the inactive phosphorus atoms are present on the top of surface [24]. Our approach is based on the criteria that oxidation enhance phosphorus diffusion [25-26]. This method has an objective to decrease inactive phosphorus by an additional oxidation step before phosphorus diffusion. Graphically this implies the reduction of the plateau width which appears on the top of diffusion profiles near the high phosphorus concentration zone. Bentzen and Holt demonstrate that the sheet resistance is determined directly by the depth of the flat plateau near the surface in profiles of

electrically active phosphorus [21]. Figure 4 shows the emitter sheet resistances as a function of surface concentration at 825°C during 1 hour. The sheet resistances decreased with increasing phosphorus concentration. This behaviour is confirmed by [27] at 875°C for 30min.
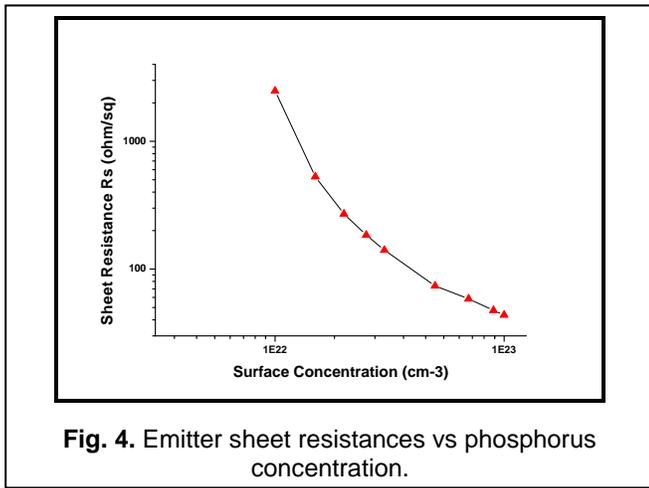

Fig. 4. Emitter sheet resistances vs phosphorus concentration.

By introducing the SiO2 barrier, the surface phosphorus concentration has decreased for a standard emitter with 40Ω/sq sheet resistance. This result shows also a reduction in profile plateau width. Then, by superposing our surface concentration with the silicon oxide thickness we found a value of about 83.3nm. This value is the optimum for reducing the dead layer. Some authors obtained a depth of 75nm for 40Ω/sq [21-22], this value was also found for 50Ω/sq [28]. Finally, it appears that the control of physical and technological diffusion parameters is a low cost alternative method to reduce the non-desired inactive phosphorus [28-30].
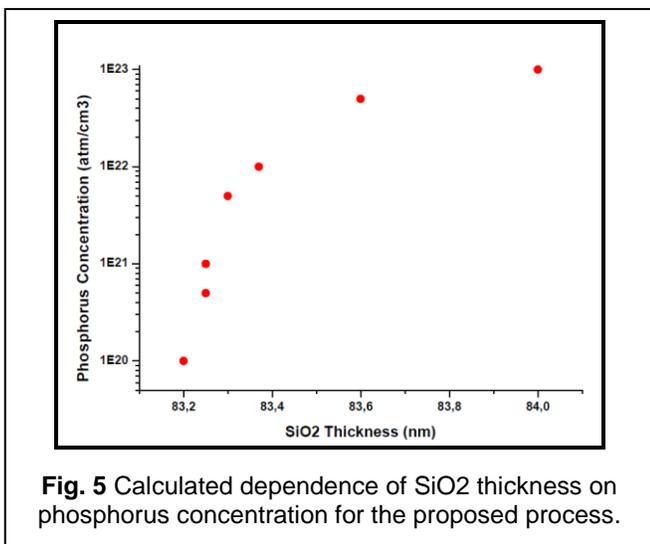

Fig. 5 Calculated dependence of SiO2 thickness on phosphorus concentration for the proposed process.

3.4 Emitter optimization by controlling phosphorus diffusion profile

At this stage of the present study, we propose a thin layer of silicon oxide able to reduce the dead layer zone. In the next part, we demonstrate that we can improve the emitter fulfilment and the solar cell performance by only the manipulation of diffusion profile and without any change in the

manufacturing process. To carry out the analysis of phosphorus profile and his influence on solar cell characteristics, we built a solar cell structure under the Atlas Silvaco® simulator [7] at the same conditions of process described previously in sec.2.1.
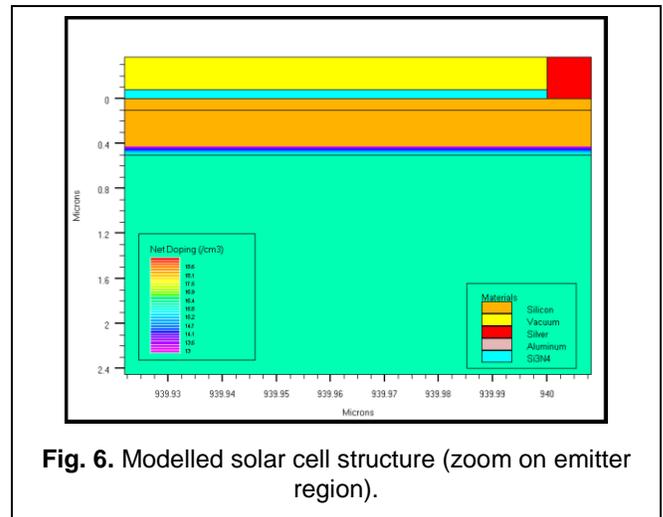

Fig. 6. Modelled solar cell structure (zoom on emitter region).

Four different groups of solar cells are investigated. At each time, we change the shape of diffusion profile. The 1st group have an erfc profile, the 2nd a Gaussian profile, the 3rd a double Gaussian profile, and the last one (4th) with our model: erfc profile followed by a Gaussian distribution for a specific phosphorus concentration of 1×10^{22} atm/cm3 and a junction depth of 0.5µm.
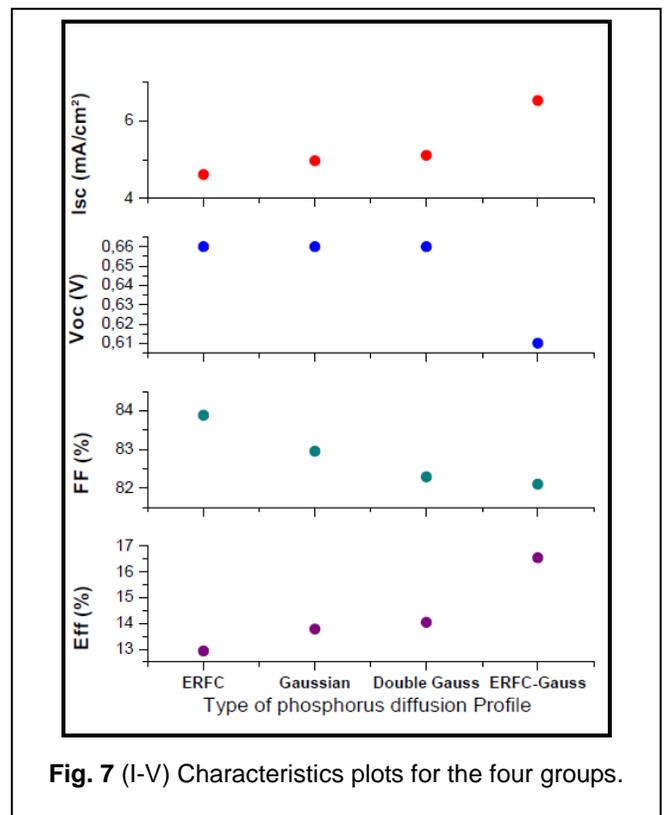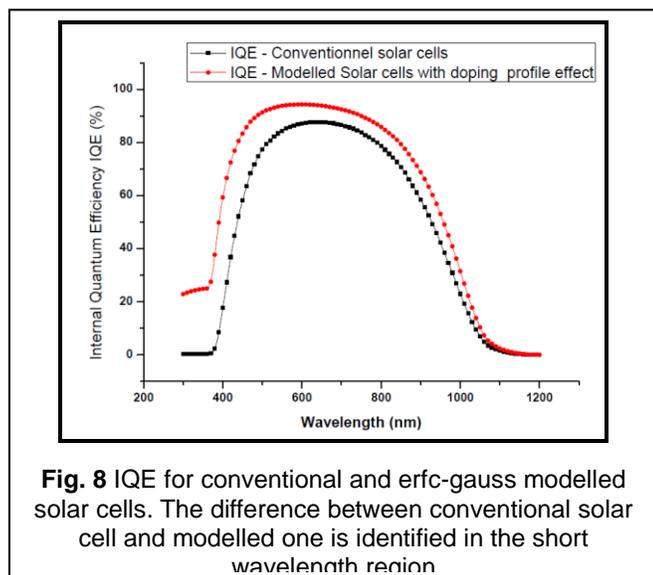

Fig. 7 (I-V) Characteristics plots for the four groups.

The (I-V) characteristics are investigated for each group. Isc: Short Circuit Current, the Voc: Open Circuit Voltage, the FF: Fill factor and the Eff.: Efficiency are plotted for the different groups and showed in Figure 7. We consider the 1st group as a reference solar cell. For the 2nd and 3rd group the I-V characteristics changes moderately. The observation of these parameters for the modelled solar cells leads us to an increase in Isc and cell's efficiency simultaneously for the 4th group. The diminution in Voc and FF for our model can be explained by the remained of some inactive phosphorus atoms and to the non optimized contact formation process not taken in account in our simulation, but the values found for the efficiency imply the key for our study. We are now able to produce doping profiles by this means. Also, implementing an erfc and Gaussian profile is demonstrated to improve the doping profile manipulation without increasing the total process.

3.5 Internal Quantum Efficiency results

Another quantity to characterize the emitter quality of solar cells is the internal quantum efficiency in the short wavelength regime (300-500 nm), since light in this wavelength range is absorbed in the emitter. Solar cells should have a significantly higher IQE in this range. As a consequence, Isc of these cells should be higher. In figure 8, IQEs of solar cells for the 1st and the 4th group were calculated with PC1D [31] in order to support our last results. The IQE of the solar cell subjected to the phosphorus profile manipulation exhibits a clear enhancement in the short wavelength region (350-480 nm) of about 23%. These enhancements are responsible to the elevation of Isc shown in figure 7 and this means that the profile manipulation have an effect on emitter region of solar cell.

Fig. 8 IQE for conventional and erfc-gauss modelled solar cells. The difference between conventional solar cell and modelled one is identified in the short wavelength region.

4   CONCLUSION

An established phosphorus diffusion model was performed to show that practical diffusion times and temperatures can control the junction depth as well as the formed emitter quality. This theoretical study results guide us to achieve the phosphorus diffusion process optimization and correlation between doping profile and solar cells performance. The output data delineate directions for solar cells efficiency improvement through focus on the exact SiO2 barrier layer thickness and phosphors profile management. By the manipulation of the phosphorus emitter profile we demonstrate that we can improve the emitter efficiency and then the solar cells performances by 2.78%. This result was being approval by the IQE calculus with a very noticeable increase for short wavelengths of about 23%.

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