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On elimination of inactive phosphorus in industrial $POCl_3$ diffused emitters for high efficiency silicon solar cells

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ABSTRACT

It is compelling to eliminate inactive phosphorus in industrial $POCl_3$ diffused emitters for high efficiency silicon solar cells. Several approaches were reported to significantly reduce inactive phosphorus in the literature. However, the underlying physical mechanisms are not fully understood. In this work, we conduct a systematic investigation and fabricate eight emitters involving two $POCl_3$:O_2 ratios at pre-deposition and both inert and oxidising scenarios at drive-in. Characterization techniques such as secondary ion mass spectrometry and X-ray photoelectron spectroscopy are carried out with an emphasis on the phosphosilicate glass. To provide a consistent interpretation of our results and those in the literature, we suggest a probable reaction, “free phosphorus oxidation”, as the dominant mechanism to unveil the role and impact of oxygen during $POCl_3$ diffusion. We further propose that various industrial $POCl_3$ emitters can be fabricated inactive phosphorus free without drive-in or a pre-grown oxide. Among the eight emitters, three emitters are free from inactive phosphorus with a sheet resistance range from 65 to 140 Ω/□, featuring a surface doping from 1×10^{20} to $3 \times 10^{20}\ cm^{-3}$ and a remarkably low emitter saturation current density down to 51 fA/cm^2.

1. Introduction

For *p*-type silicon (Si) substrates, the chosen phosphorus (P) diffusion technology has a big impact on the solar cell performance. Due to the cost effectiveness, $POCl_3$ tube diffusion process is the dominant industrial P diffusion technology to fabricate *n*-type emitters [1]. During the process, both phosphosilicate glass (PSG) deposition and P diffusion are performed inside one quartz tube at elevated temperatures. PSG deposition is accomplished by exposing the Si surface to a gas mixture of $POCl_3$ (carried by nitrogen) and oxygen (O_2) to grow a PSG layer at about 800–900 °C. P diffusion takes place simultaneously with PSG deposition and even afterwards at an elevated temperature. The following three chemical reactions are typically used to describe $POCl_3$ diffusion [2–4]:

$$4POCl_3 + 3O_2 \rightarrow 2P_2O_5 + 6Cl_2 \quad (1)$$

$$Si + O_2 \rightarrow SiO_2 \quad (2)$$

$$2P_2O_5 + 5Si \rightarrow 4P + 5SiO_2 \quad (3)$$

With the presence of SiO_2 and P_2O_5 under an elevated temperature, both materials react and form PSG of different compositions [2,5–7].

$$xSiO_2 + yP_2O_5 \rightarrow x(SiO_2)\cdot y(P_2O_5) \quad (4)$$

As P diffusivity in Si scales up exponentially with temperature [8], a two-step diffusion approach is typically adopted, where PSG deposition is carried out at a rather low temperature (about 800 °C) to minimise P diffusion (‘pre-deposition step’), while subsequently, $POCl_3$ supply is stopped and significant P diffusion takes place at a rather high temperature (‘drive-in step’). In contrast, both PSG deposition and P diffusion occur under the same constant gas flow and medium temperature in a one-step diffusion approach. To give a clear overview of the $POCl_3$ diffusion process, a schematic temperature-time profile as well as gas flow-time profile for both the one- and two-step diffusion are shown in Fig. 1.

Due to the relative simplicity, screen printing technology is the most mature choice of industrial metallization for contacting $POCl_3$ diffused emitters. To ensure a low contact resistance of the screen-printed contact, a high active P concentration at the surface above $3.5 \times 10^{20}\ cm^{-3}$ was a prerequisite for industrial silicon solar cells fabricated in the last few decades [9]. This requirement unfortunately resulted in severe recombination losses in the $POCl_3$ diffused emitters. Firstly, Auger recombination is the dominant loss [10] as it approximately scales with the square of the P concentration [11,12]. Secondly, surface recombination was also found to increase with the surface P

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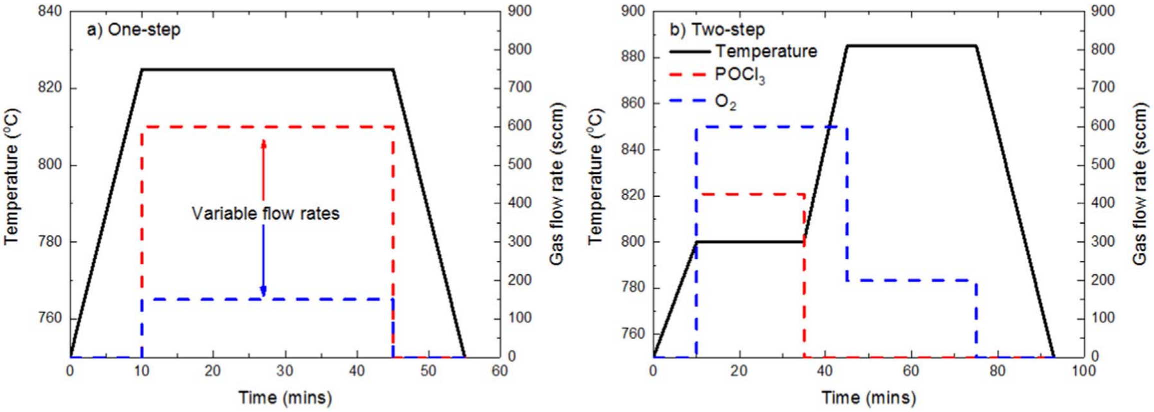

Fig. 1. Illustration of a $POCl_3$ time-temperature/gas flow rate profile for emitter formation in both the one-step (a) and two-step (b) diffusion.

concentration [13–16]. Thirdly, such a high P concentration requires diffusing more P atoms into silicon, typically beyond the P solid solubility limit [17]. As a result, a "dead layer" is produced where many P atoms are electrically inactive [18–20]. These inactive dopants present in the form of interstitials, clusters [21,22] and SiP precipitates [5,23–25] and behave as Shockley-Read-Hall (SRH) [26,27] recombination centres [28].

Fortunately this requirement was relaxed lately as the screen printing technology advances. It was reported that a reasonable low contact resistance of about 5 mΩ cm^2 was achieved on a 120 Ω/□ phosphorus emitter with a surface concentration of 1.7×10^{20} cm^{-3} [29]. As a result, the intrinsic Auger recombination was no longer the dominant loss while the SRH recombination due to these inactive P atoms was identified as the major limitation of the industrial $POCl_3$ emitter performance [20,30]. It is compelling to reduce/eliminate inactive P for high efficiency silicon solar cells. Substantial efforts were dedicated to fine tune $POCl_3$ diffusion parameters in the past few decades and may be classified into three approaches: (a) pre-oxidation where an oxide layer is grown prior to $POCl_3$ diffusion [31,32]; (b) lowering the $POCl_3$:O_2 ratio [5,18,32–35]; and (c) post-oxidation where drive-in is performed under an oxidising ambient [36–42].

In the pre-oxidation and post-oxidation approaches, an oxide layer is grown on the Si surface due to Reaction (2). In lowering the $POCl_3$:O_2 ratio, an oxide layer was also identified between the PSG and Si at pre-deposition [33], which holds Reactions (2) and (3) responsible. It appears that all these approaches make use of oxide for inactive P reduction. Since oxide was found to retard the diffusion of certain impurities such as P long ago [6,43], it may be rational to interpret the underlying mechanism as the diffusion barrier theory [35]. While this theory may explain some experimental results straightforwardly, we find that it is also inconsistent with some recent in-depth studies, where a thinner oxide was actually found to be associated with a lower $POCl_3$:O_2 ratio [33,34]. It is contradictory for the diffusion barrier theory to attribute the less severe inactive P to the thinner oxide.

It is crucial to comprehend the right physical mechanisms behind these approaches in order to design various inactive-P-free industrial emitters for high efficiency silicon solar cells. In this study, we carry out a systematic in-depth study with eight process splits, including two $POCl_3$:O_2 ratios, three different temperatures and both inert and oxidising scenarios at drive-in. To unveil the underlying mechanisms, several characterization techniques are applied to all emitters including the electrochemical capacitance-voltage (ECV) technique and the secondary ion mass spectrometry (SIMS). Two emitters are further analysed with the X-ray photoelectron spectroscopy (XPS) technique with a special attention to the elemental distribution in PSG.

2. Experimental

2.1. Sample preparation

The samples used in this work were polished 4″ round float-zone (FZ) grown *p*-type silicon wafers with a nominal bulk resistivity of 2.4 Ω cm and a thickness of 260 µm. After the RCA1 (NH_4OH:H_2O_2:H_2O = 1:1:5) and RCA2 (HCl:H_2O_2:H_2O = 1:1:5) cleaning procedure followed by a final HF dip (2.5% v/v), the wafers were loaded into a quartz tube diffusion furnace (TS8603, Tempress) at 750 °C to start the $POCl_3$ diffusion process. Eight diffusion splits were performed to prepare emitters in either one-step or two-step manner, as listed in Table 1. The temperature ramp rate was set to 10 °C/min for all the heating and cooling steps. After removing the PSG in 2% diluted HF, the samples had a symmetrical n^+pn^+ structure and were symmetrically coated by 100 nm silicon nitride (SiN_x) film with a refractive index of 2.05 using plasma-enhanced chemical vapour deposition (PECVD, MAiA XS, Meyer Burger) for lifetime measurement.

2.2. Characterization

Sheet resistance ρ_{sh} values were measured at 25 points equally spaced over the wafer by a four-point-probe scanner (SheRRescan, Mechatronics). An ECV analyser (CVP21, WEP) was used to measure the electrically active P doping profiles of the centre point of each wafer, calibrated by the ρ_{sh} data near the test location. Time-of-flight

Table 1
Process conditions for eight distinct emitters. The gas flow unit is standard cubic centimetres per minute (sccm).

Steps	Emitters Process parameters	A One-step	B	C	D Two-step	E	F	G	H
PSG deposition	Temperature (°C)	825			795				
	Duration (min)	65	35	65	25 min				
	$POCl_3$:O_2 ratio (sccm:sccm)	600:150		450:600	600:150	450:600			
Ramp-up	O_2 flow rate (sccm)	NA			0	0	450	600	600
Drive-in	Temperature (°C)				885				
	Duration (min)				30				
	O_2 flow rate (sccm)				0	0	0	0	160