



Effect of POCl_3 bubbler temperature on solar cells emitter characteristics

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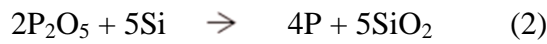
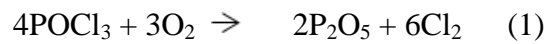
Abstract

The effect of POCl_3 bubbler temperature on silicon n⁺/p solar cells emitter characteristics is investigated in this paper. By increasing the bubbler temperature, calculations and secondary ion mass spectroscopy characterization showed that the amount of phosphorus entering the diffusion tube has significantly increased. On the contrary, emitter sheet resistances remain constant. This was confirmed and explained by emitters depth profiling of the electrically active phosphorus. Besides that, the minority carrier lifetime measured by means of Quasi-Steady-State Photoconductance technique decreased indicating that the excess of phosphorus deposited on emitter surface degrades the emitter electrical performance. The same trend has been observed for the implied open circuit voltage. It decreased from 632 mV at 15 °C to 602 mV at 26 °C. In conclusion, we have shown that the temperature of the POCl_3 bubbler is also an important parameter that controls the emitter properties.

Key words: Silicon, Diffusion, POCl_3 .

1. Introduction

The solar cells emitter formation process using liquid Phosphorus Oxychloride (POCl_3) consists of a deposition step where a dopant layer is formed, followed by a drive-in step during which the bubbled N_2 - POCl_3 gas flow is turned off and the wafers are kept at high temperature in a gas ambient. During deposition step, POCl_3 oxidizes with oxygen to form Phosphorus Pentoxide (P_2O_5) as illustrated in equation 1. This material reacts with the silicon (Si) exposed at the surface of the wafer to form elemental phosphorous (P) and silicon dioxide (SiO_2) (equation 2). At this point the phosphorus diffuses into the silicon at a rate determined by the process temperature and process duration.



In addition, both by-products, SiO_2 and P_2O_5 , form the phosphosilicate glass layer (PSG) which also acts as a dopant source during the drive-in step (equation 3).



In the drive-in step, the phosphorus is driven- in further into the silicon wafer.

Because of the lower solid solubility limit of phosphorus in crystalline Si than in PSG, the phosphorus concentration near the Si surface is over saturated and exceeds the electrically active concentration in equilibrium. This leads to the formation of an excess phosphorus concentration region near the emitter surface. This region, called dead layer, is formed by electrically inactive precipitates [1,2,3] which act as Shockley Reade Hall recombination center for charge carriers [4]. In addition, the charge carriers increase due to a high concentration of the active P causes the Auger recombination increase. Thus, the emitter region contains significant opportunities for charge carriers recombination which limit the solar cells performance. So, a homogeneous emitter designed for performant Si solar cells needs to fulfill specific requirements: (1) a reduced dead layer and (2) a low surface concentration of phosphorus dopant to keep Auger recombination as low as possible.

To meet these requirements, it is necessary to control the amount of phosphorus during the emitter formation and mainly in the deposition step. The P concentration available at this step is determined by the POCl_3 and O_2 reaction (equations 1 and 2) and its process parameters. The parameters that control the deposition step are the process time, oxygen and N_2 - POCl_3 carrier flow rates deposition temperature. They have a decisive influence on the phosphorus

surface concentration. Several studies have been devoted on these parameters [5, 6]. In general, the works on this topic do not mention the temperature of the liquid POCl₃ bubbler. The manufacturer *Air Products and Chemicals, Inc.* [7] recommends to set this temperature at 20 °C. In the present work we will show if the variation of this parameter has or not an impact on n⁺/p silicon solar cells emitter quality and what is its importance among the other diffusion parameters.

2. Background

The POCl₃ is a liquid Phosphorus source used to form n⁺/p or n⁺/n layers in several applications. Figure 1 represents the scheme of the system used to realize these structures where the diffusion process is carried out at reduced pressure.

The dopant amount deposited on silicon wafers depends mainly on the phosphorus entering the quartz tube. This quantity is calculated as follows.

The amount of phosphorus (mp) entering the quartz diffusion tube is expressed as:

$$mp \text{ (gr)} = [M_w(P)/M_w(POCl_3)] \cdot MFR_{POCl_3} \cdot t \quad (4)$$

Where,

M_w(P) is molecular weight of P (31 gr/mole);

M_w (POCl₃) is the molecular weight of POCl₃ (153.33 gr/mole);

MFR_{POCl₃} is the massic flow rate of POCl₃;

t is the diffusion process time (min).

MFR_{POCl₃} is given by the following relation:

$$MFR_{POCl_3} \text{ (gr/min)} = [P_{vap}/P_{bu} - P_{vap}] \cdot [FR \cdot M_w(POCl_3)/22414] \quad (5)$$

Where,

P_{vap} is the vapor pressure of POCl₃ at bubbler temperature (Torr);

P_{bu}, is the pressure in the bubbler (atmospheric pressure in Torr);

FR is the N₂ carrier flow rate (sccm);

22414 cc/mole is the molar volume at Normal Condition of Temperature and Pressure.

The simplified form of equation (4) is:

$$mp (gr) = 0,0013.FR.t.[Pvap/Pbu-Pvap] \quad (6)$$

3. Experimental

Four-inch CZ p-type <100> monocrystalline silicon wafers were used. The bulk resistivity and thickness are 1 Ω .cm and 320 μ m, respectively. After NaOH etching and Radio Corporation of America (RCA) cleaning, the wafers were processed in batch-type POCl₃ diffusion closed tube furnace (figure 1). The emitter sheet resistance was measured using a Four-Point probe. The total and active phosphorus profiles were performed by Secondary Ion Mass Spectroscopy (SIMS) and Electrochemical Capacitance-Voltage profiler (ECV), respectively. The effective carrier lifetime was measured by mean of Quasi Steady State Photo-Conductance decay (Sinton WCT 120-QSSPC) on wafers passivated on both sides with iodine ethanol. The surface light reflectance was carried out using a Varian Cary 500 UV–VIS–NIR spectrophotometer operating at 632.8 nm.

Each set of experiment consists of five silicon wafers loaded on quartz boat. Three test-wafers were used for characterization and two dummy wafers were placed at both ends of the batch to ensure uniform distribution of the gases flow. As illustrated in figure 1, the diffusion furnace is a closed tube where the process is carried out at a reduced pressure of 300 mbar. The POCl₃ bubbler is equipped with a temperature control system which provides an accurate (± 0.2 °C) and stable temperature.

4. Results and discussion

4.1. Effect of bubbler temperature on phosphorus amount entering the tube furnace

In this section, the experiments were performed using the following parameters:

- Bubbler temperatures: 10 °C; 15 °C and 25 °C;
- Deposition time: 20 min;
- N₂-POCl₃ bubbling flow rate: 500 standard cubic centimeters (sccm);
- Diffusion process temperature: 870 °C.

Using equation (6), the amount of phosphorus entering the diffusion furnace we calculated for the three temperatures. This amount increases with bubbler temperature as shown in figure 2 and we can notice that the mass of phosphorus has more than doubled; it increases from 0.30

grams to 0.67 grams. This is a direct result of the POCl_3 vapor pressure increase with temperature. Indeed, as the vapor pressure is a relative measure of the tendency to evaporate, the amount of POCl_3 that escapes from its liquid phase increases exponentially with temperature [8].

As shown in figure 3, SIMS depth profiling of PSG-etched emitters confirmed these results. The surface concentration of the total phosphorus deposited onto silicon substrate during diffusion process increases from $2.20 \cdot 10^{20}$ atoms/cm⁻³ to $5.50 \cdot 10^{20}$ atoms/cm⁻³ with increased temperatures.

4.2. Effect of bubbler temperature on emitter characteristics

In the following study the temperature and deposition time were kept constant at 835 °C and 15 minutes, respectively. The N_2 - POCl_3 flow rate was fixed at 500 sccm and the bubbler temperature was varied as follows: 15 °C, 22 °C and 26 °C.

4.2.1. Variation of emitter sheet resistance

Figure 4 represents the average emitters sheet resistance performed at three bubbler temperatures and no significant change can be noticed. This is explained by the same surface concentration of electrically active phosphorus, as illustrated in figure 5. These ECV measurements revealed that the three PSG-etched emitters have an identical phosphorus profiles.

4.2.2. Variation of the effective carrier lifetime

Table 1 shows clearly the decline of the effective carrier lifetime (τ_{eff}) with bubbler temperature increase. The accumulation of electrically inactive phosphorus at the emitter surface is responsible of this degradation. As found in part 1, the amount of phosphorus deposited onto emitter surface increases proportionally to temperature leading to a proportional increase of electrically inactive phosphorus in the highly recombinant dead layer.

As the solar cells open-circuit voltage (V_{oc}) is known to be the measure of the amount of recombination in the emitter, we have also assessed the effect of temperature by implied- V_{oc} deduced from the QSSPC measurement. As shown in table 1, the decrease of implied- V_{oc} with temperature increase means that the recombination of the minority carrier is increased.

In summary, lowering the bubbler temperature improves the electrical emitter quality. This is consistent with the recommendation mentioned in [7]. Indeed, the dopant product manufacturer recommends to set the bubbler temperature at least 5 °C lower than the air

temperature around the tubing that connects the bubbler to the diffusion furnace to prevent the condensation of the N₂-flushed POCl₃. We note that during the diffusion process, the temperature in the furnace gas cabinet was around 23 °C.

4.2.3. Variation of surface reflectance

The grey color of the as-diffused wafers indicates that the PSG thickness is very thin. Figure 7 shows the light spectral reflectance for silicon substrate wafer and as-diffusion PSG-coated wafers at the three bubbler temperatures. In 400 nm-800 nm wavelength range, the reflectance of as-diffusion wafers covered with PSG is lower than that of silicon substrate. This reflectance reduction is due to the PSG optical properties and particularly its refractive index. As reported in [9], the refractive index of PSG depends on its phosphorus concentration and may be as low as 1.74. This enables this layer to act as a good and low cost antireflective coating [10]. Figure 7 also shows that the variation of the bubbler temperature has no significant effect on the reflectance indicating that the three PSG layers have similar thicknesses.

Conclusions

In this study a liquid POCl₃ was used as a source of phosphorus in n⁺/p silicon based emitter formation. The influence of temperature of this source on emitter characteristics was investigated. We found that the amount of phosphorus entering the tube furnace as flushed-POCl₃ form increases with temperature. Despite of phosphorus amount increase, analyses of emitter formed at three bubbler temperatures revealed that the sheet resistances were similar. On the contrary, the effective carrier lifetime decreased with temperature increase due to inactive phosphorus increase on emitter surface. Furthermore, the PSG layers act as an antireflection coating and its thicknesses are not affected by the bubbler temperature variation. So, the POCl₃ bubbler temperature has a strong effect on the transported amount of POCl₃ to the diffusion tube and consequently on emitter characteristics. This parameter is as critical as the other diffusion parameters.

Acknowledgment

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Table caption

Table 1: Effective carrier lifetime at Δn of $1 \times 10^{15} \text{ cm}^{-3}$ and implied- V_{oc} for three bubbler temperatures.

Table 1

Bubbler temperature ($^{\circ}\text{C}$)	τ_{eff} (μs)	Implied- V_{oc} (mV)
15	58	632
22	47	624
26	38	602

Figures captions

Figure 1: Closed tube phosphorus diffusion system diagram.

Figure 2: Amount of phosphorus entering the diffusion tube as a function of bubbler temperature.

Figure 3: Total phosphorus SIMS depth profiles as a function of bubbler temperature.

Figure 4: Variation of emitter sheet resistance with bubbler temperature.

Figure 5: Phosphorus ECV profiles for three bubbler temperatures.

Figure 6: Spectral surface reflectance of silicon substrate and wafers with PSG formed at three bubbler temperatures.

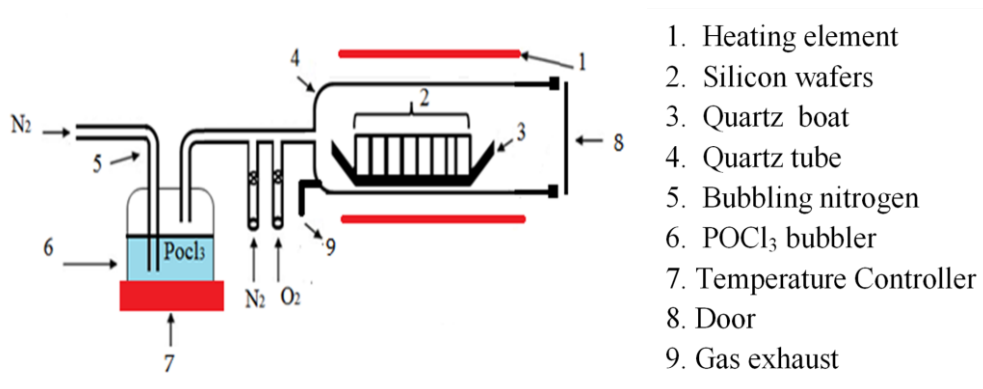


Figure 1

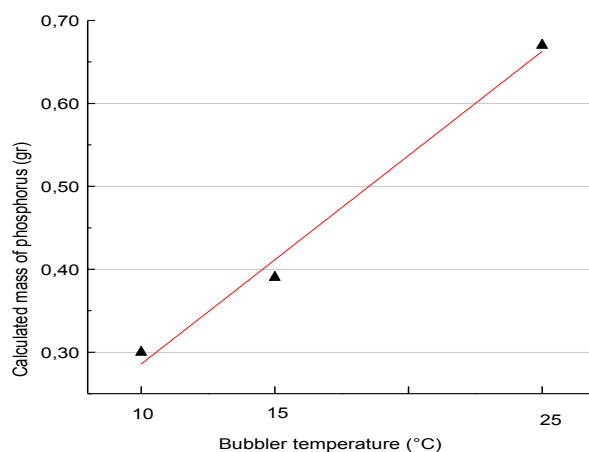


Figure 2

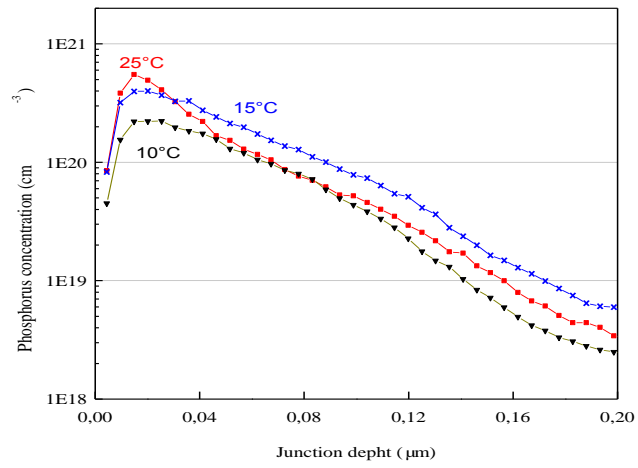


Figure 3

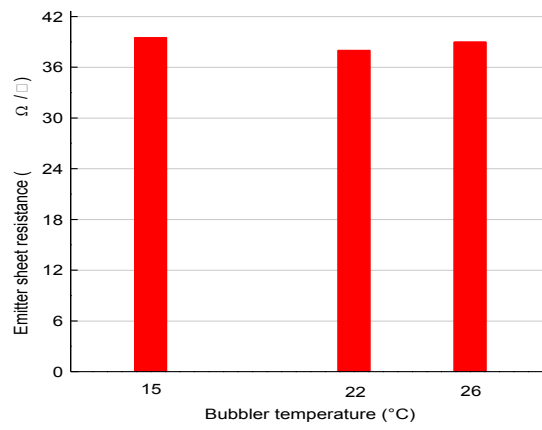


Figure 4

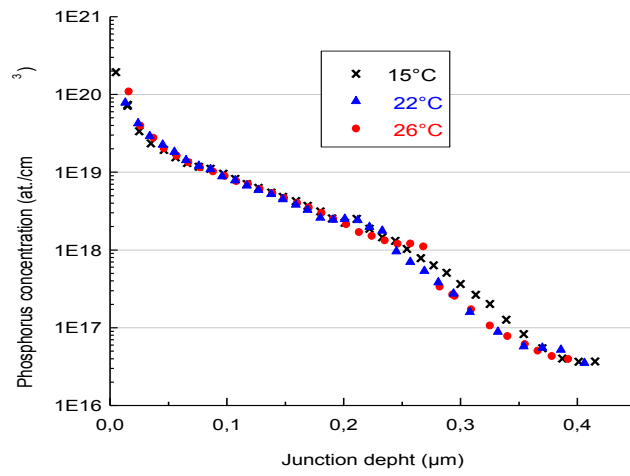


Figure 5

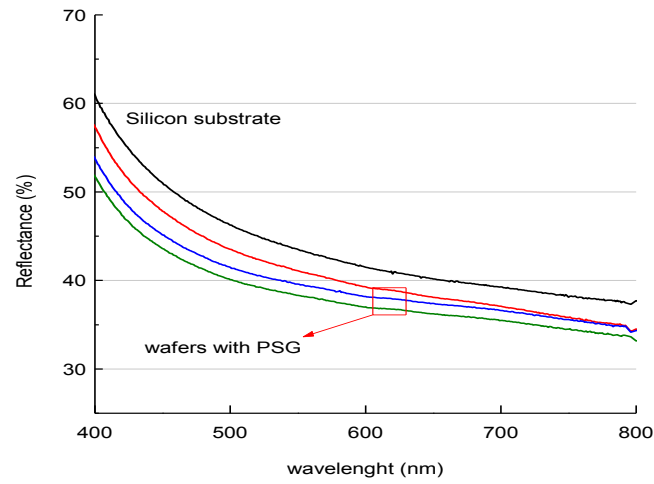


Figure 6

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