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**HILTON WAIKOLOA VILLAGE**
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# VOLUME II




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# LOW TEMPERATURE FORMATION OF EMITTER AND BSF BY RAPID THERMAL CO-DIFFUSION OF P, Al or B

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## ABSTRACT

Rapid thermal processing (RTP) is now emerging as a promising simplified process for manufacturing of terrestrial solar cells in a continuous way. In earlier works, we have shown that RTP can advantageously replace classical furnace for performing emitter, BSF and surface passivation in addition to an efficient gettering of metallic impurities during these steps.

In this work, we present results about co-diffusion of two dopant elements in a single rapid thermal cycle at low temperature in order to form emitter and BSF simultaneously. We have, in particular, found that the diffusion kinetics of dopant elements are enhanced during rapid thermal co-diffusion of P, Al or B and lead to the optimal dopant activity and profile for high efficiency silicon solar cells at low temperature. Additionally, the gettering effect induced by the co-diffusion of P and Al is more efficient than can be achieved by a single diffusion of these two elements. Finally, test solar cells were performed on these structures and gave, for a low processing temperature (800°C/60 s), an efficiency of 11 % on polished FZ mono-crystalline substrates without antireflecting coating.

## INTRODUCTION

Rapid thermal processing (RTP) based on incoherent sources of light is seen for more than ten years as a very promising candidate to replace conventional furnace annealing. These optical heating techniques have many advantages as being rapid, dry and clean. The energy is directly transfered to the sample without significant heating of the reactor. Moreover, it has been shown that all the kinetics of diffusion, gettering, oxidation and annealing are enhanced as compared to classical thermal processing [1, 2].

RTP also offers many other technical advantages over classical thermal steps since in such closed reactor the lamps (used as heating source) are turned on only during the short duration of the thermal cycle. The major benefit of this kind of process is a reduction in the thermal budget and potentially of the pay-back time. On the other hand, due its safety in handling, the spin-on coating from liquid source can easily be associated to RTP for the preparation of low-cost silicon solar cells in a continuous way.

In previous works, we have shown that the use of RTP for specific thermal steps in the solar cell manufacturing may lead to relatively high efficiency. As a first example, rapid thermal annealing in oxygen atmosphere has been performed on structures with a conventional diffused emitter and Al evaporation on the back. Using this procedure, a 16.6 % efficiency [3] has been obtained on single silicon substrates. On the other hand, rapid thermal co-diffusion into Polix material of phosphorus and boron from doped oxide layers followed by a conventional thermal oxidation leads to the formation of solar cells with a 15.1 % efficiency [4]. In a near future, we expect that all the thermal steps including surface passivation, AR coating and contact sintering can be performed by RTP with a minimum number of cycles. This will contribute to simplify the production lines of large scale manufacturing processes.

In this work, we will show that rapid thermal co-diffusion of P, Al or B is very efficient to perform emitter and BSF for silicon solar cells at a lower temperature compared to those used during a single diffusion. The explanation of this phenomena is probably due to the mutual influence of one doping element on the another though injection of point defects during their co-diffusion in silicon. This enhancement of the diffusion kinetics leads to lower sheet resistance of the diffused layer and deeper profiles of the dopant elements.

## EXPERIMENTAL PROCEDURE

1 Ωcm p-type float-zone (FZ) single silicon wafers and Polix multicrystalline material from Photowatt have been processed. Two different dopant sources have been used : phosphorus doped glass films deposited by the spin-on technique from liquid solution or AP-CVD oxides in order to form the emitter and Al evaporation or boron doped AP-CVD oxides for the formation of the BSF.

The RTP unit used here was model FAV4 of Jipelec (Grenoble, France), which is characterized by "cold walls" (< 250°C for a wafer processed at 1100°C) and programmable temperatures, ramps and steps. The temperature was measured by an infrared pyrometer. The characteristic features of the temperature profile are a heating rate of 250°Cs$^{-1}$, then a plateau at a temperature T with time duration $\Delta t$ (from 5 to 120 s), followed by a rapid cool-down with a rate typically around 80°Cs$^{-1}$, which will inherently include a "quenching step". The total time taken to reach room temperature was less than 1 min. The RTP cycles were generally done under a pure argon flow and the plateau temperatures ranged between 800 and 1100°C.

## JUNCTION FORMATION AT A LOWER TEMPERATURE

Shallow junctions can be formed in silicon by diffusion using RTP in a few tens of seconds compared to the classical furnace diffusions for relatively longer time. There are different propositions to explain the acceleration of diffusion kinetics of metallic elements. Two of them are : (i) the effect of temperature gradients [5] and (ii) the effect of light especially the near UV [6]. According to the first proposition, too large temperature gradients imply the generation of constraints in the material and that these constraints are accompanied by the injection of large concentration of point defects (vacancies, auto-interstitials). The dopants and the



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metallic elements diffuse by the intermediary of these defects, resulting in an accelerated diffusion of the elements. According to the second proposition, the energetic light (from UV to visible) of the lamps (whose filaments are at much higher temperatures than the substrate, unlike the case in classical furnaces) can cause certain chemical processes (i.e. bond braking) having higher activation energies allowing the creation of point defects and facilitating pairing just as the creation of electron-hole pairs which influence the state of charge of chemical species and accelerate their diffusion.

### Mutual enhancement of the dopant diffusion kinetics in a co-diffusion processing step

In Fig.1 we report Secondary Ion Mass Spectroscopy (SIMS) profiles of phosphorus diffused or co-diffused with aluminium for different time-temperature cycles in a rapid thermal furnace. They show an enhancement of the phosphorus diffusion in the case of RTP co-diffusion of P and Al. This result can be probably explained by a mutual influence of Al on P (P on Al) through the injection of point defects during their diffusion in silicon. We have probably the same phenomena as the "pull" [7] effect in microelectronics in which the diffusion kinetics of one dopant is accelerated by the other. This enhancement is also present in the case of a co-diffusion of boron and phosphorus, as shown on Fig. 2. The same phenomena can also be observed when the co-diffusion of the P and B are performed from AP-CVD silicate sources.

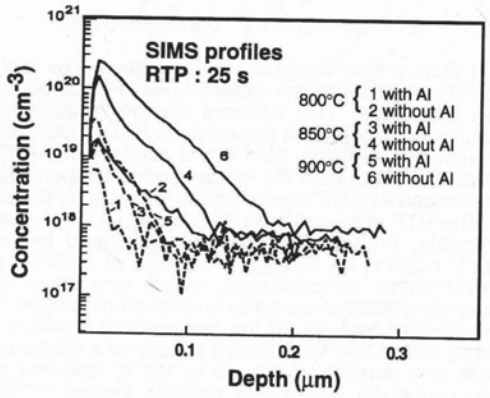



Fig. 1. Phosphorus diffusion enhancement during co-diffusion with Al.

### Dopant activity enhancement due to co-diffusion

Figure 3 shows the evolution of the sheet resistance ($R_\square$)values of phosphorus diffused or co-diffused samples with aluminium on the back for various time-temperature cycles in the lamp furnace.

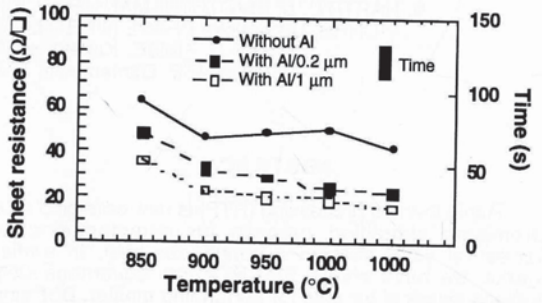



Fig. 3. Evolution of the sheet resistance of phosphorus doped layers after a single diffusion and after co-diffusion of P and Al for two different thicknesses.

We can observe a systematic decrease of the $R_\square$ with increasing diffusion temperatures. The values after co-diffusion were systematically lower than those achieved by single diffusion. This is probably due to a higher phosphorus activity and, as reported before, to a deeper profile of phosphorus after co-diffusion.

To summarize this section, we can point out that co-diffusion processing by RTP can offer the possibility to lower the temperature of the thermal cycle if it is necessary (as we will show it in the case of the use of a multicrystalline substrate) or at the same time to avoid too shallow junctions by keeping the temperature at a higher level. Although shallow junctions with high surface dopant concentrations can be a good way for homogeneous emitter of laboratory solar cells as the metallization procedure can be adapted, too shallow junctions can result more generally in shunting and fill factor losses in an industrial processing using screen printed contacts.

## EFFECTS ON THE BULK

A major obstacle for the use of RTP in photovoltaics is the generation of electrically active defects which degrade the minority carrier lifetime in silicon so that processing conditions which induce a gettering are of atmost importance in order to counterpart this negative effect.

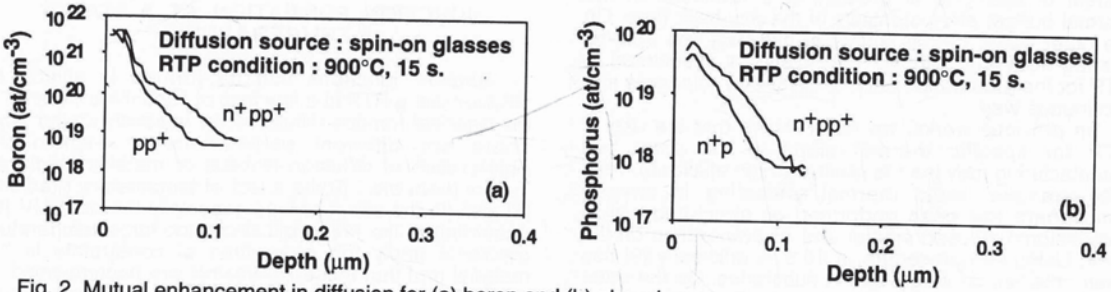



Fig. 2. Mutual enhancement in diffusion for (a) boron and (b) phosphorus.



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### Diffusion length enhancement due to P/Al co-diffusion

Figure 4 shows the evolution of the minority carrier diffusion length ($L_D$) values in P and P/Al co-diffused samples at different temperatures during 25 s. One can see the beneficial effects of the co-diffusion in the improvement of the diffusion length in the material. It results in part from the gettering of metallic impurities during the RTP co-diffusion and secondly by a reflector effect due to the presence of the rear BSF performed by Al alloying.

The evolution of the $L_D$ values for a multicrystalline substrate as Polix is similar, with also an important improvement of the $L_D$ values starting at the lowest temperature range with a maximum at 850°C. However, for higher annealing temperatures, we observe a gradual degradation of the $L_D$ values which could be due to the activation of metallic impurities present in the starting material as we will discuss later on.

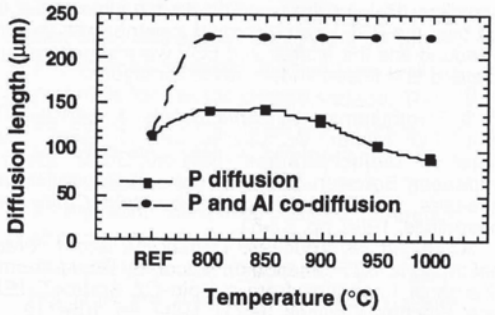



Fig. 4 : Surface PhotoVoltage (SPV) measurements of $L_D$ on monocrystalline silicon after an RTP co-diffusion of P and Al at different temperatures showing the spectacular improvement of $L_D$ up to the sample thickness.

### Necessity of a subsequent classical anneal in the case of a P/B co-diffusion

In Fig. 5, one can note a large degradation in $L_D$ (from an initial value of > 200 µm down to 45 µm) at very high RTP temperature.

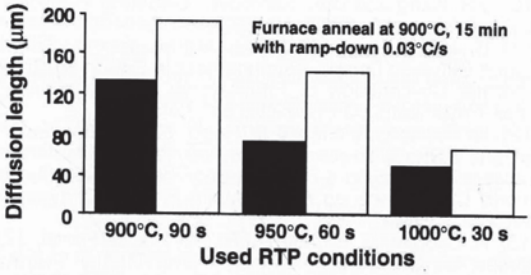



Fig. 5 : SPV measured diffusion length on Polix material after an RTP treatment (in black) and following a subsequent furnace anneal (in white).

This could be due to the reactivation of metallic impurities present into the Polix material, and also due to the activation of grain boundaries after this thermal treatment [8]. At higher temperatures, supersaturated interstitital (metallic) impurity concentration also would be high [9]. The diffusion of dopants such as P and B is accompanied by the dissolution of metallic precipitates, which, once in solution, remain frozen in active sites after the rapid cooling. The partial restoration of $L_D$ observed after the subsequent furnace anneal with slow ramp-down notably in the RTP temperature range 900-950°C (Fig. 5) is mainly due to the precipitation of most of the metallic impurities and defects in electrically inactive form during the slow cooling process (0.03°C/s).

The first conclusion emerging from these measurements is the necessity to keep the processing temperature as low as possible in order to avoid a second thermal treatment in a classical furnace.

The second interesting result to point out is the difference between the two kinds of co-diffusion processes (P-Al, P-B), not in terms of mutual enhancement of the diffusion kinetics, but in terms of effects on the bulk diffusion length, especially in the case of a multicrystalline substrate in which the gettering is more in competition with the activation of residual metallic impurities.

It is well known that boron is less efficient that phosphorus in terms of gettering [10] and has not the additional reflector effect of Al [11]. Moreover, as we have, in the case of Al, on the backside an Al-Si eutectic which is molten during the RTP process, the diffusion of silicon self-interstitial ($Si_I$) coming from the front surface will be enhanced in order to fill up the lack of $Si_I$ on the backside induced by the formation of the Al-Si eutectic. This excess of interstitial can simultaneously enhance the P diffusion and transform by the kick-out mechanism the substitutional metal into an interstitial one so that the gettering effect overcomes easier the activation procedure.

## SOLAR CELL TESTING

Our preliminary solar cell evaluation concerns only FZ monocrystalline substrates and in a first run we have only compared structures having roughly the same emitter profile after the RTP cycle.

| RTP cycle | Structure | $V_{OC}$ (mV) | $I_{SC}$ (mA/cm$^2$) | FF (%) | η (%) |
|---|---|---|---|---|---|
| 800°C/60 s | $n^+pp^+$ | 605 | 23.38 | 78 | 11 |
| 950°C/60 s | $n^+p$ | 578 | 22.43 | 77 | 10 |

Table I : Performance of 4 cm$^2$ polished FZ silicon solar cells without antireflecting coating fabricated by RTP co-diffusion of P and Al or by simple P diffusion.

In Table I, we have reported photovoltaic parameter values obtained on polished FZ monocrystalline substrates by rapid thermal P diffusion or P and Al co-diffusion. We can notice that the performance of the co-diffused cells at low temperatures are higher than those achieved after a high processing temperature or after a single diffusion process. The highest efficiency value is 11 % without AR coating for a cell P and Al co-diffused at 800°C/60 s.

This preliminary result is encouraging and an invitation to continue in this way of reduction of the processing temperature, especially for multicrystalline substrates which are more sensitive to the activation of residual impurities during the quenching step induced by the RTP cycle.

On the other hand, if the cell manufacturing procedure at the present time includes a subsequent



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classical oxidation step in the same temperature range that was used for the restoration of $L_D$ in the previous sub-section, we can use higher RTP temperatures for the Polix material as well as P/B doping sources as it is illustrated on Table II.

Moreover, if Al is used as BSF, the classical oxidation step can be replaced by a rapid thermal oxidation which can be performed during the drive-in of the Al as illustrated on Table II for a FZ monocrystalline sample with a classical P diffused emitter.

Anyway, if up to now not all steps are optimized, these conversion efficiencies of RTP cells are very promising and represent the highest values for mono- and multicrystalline cells of this category. Moreover, the future integration of other RTP steps as the surface passivation, which can be combined with the dopant diffusion in a single thermal cycle [12] and of the contact sintering [13] will contribute to reduce the number of manufacturing steps. This simplification of the cell processing together with a reduction of the duration and temperature of the thermal cycles will make this technology more cost-effective.

In summary, these results contribute to the emerging of RTP as an attractive alternative to the classical thermal processes for silicon solar cell manufacturing.

| RTP cycle | Substrate | Structure $n^+pp^+$ | Passivation $SiO_2$ | $V_{OC}$ (mV) | $I_{SC}$ (mA/cm$^2$) | FF (%) | $\eta$ (%) | Ref. |
|---|---|---|---|---|---|---|---|---|
| 1000°C/20 s | mono | P/Al | RTO | 616 | 34.1 | 79 | 16.6 | [3] |
| 950°C/45 s | multi | P/B | CTO | 591 | 32.6 | 78.6 | 15.1 | [4] |

Table II : Best performance of 4 cm$^2$ mono (FZ) and multicrystalline (Polix) silicon solar cells having at least two classical thermal steps replaced by a single RTP cycle. For the first one, the BSF was performed together with the front oxide by introducing oxygen in the RTP furnace (RTO) and for the second one the emitter and BSF were simultaneously diffused from AP-CVD deposited layers. Both cells have been AR coated and tested under AM1.5 conditions.

## CONCLUSION

This study of RTP silicon solar cells on the way of the replacement of all classical thermal steps by a minimum of short duration cycles in a lamp furnace has up to now demonstrated that the emitter and BSF can be performed simultaneously on mono as well as on multicrystalline substrates. Moreover, a significant enhancement of the diffusion kinetics is observed during the co-diffusion of the two dopants which allow us to reduce the processing temperature. For multicrystalline substrates, which are more sensitive to the activation of residual impurities or defects, it is up to now preferable to use Al on the back-side instead B due to its greater gettering efficiency. The future integration of other RTP steps as the surface passivation and contact sintering, which simplify the cell processing and lower the time and power consumption will bring this technology close to its industriability.

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