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Comparative study of rapid and classical thermal phosphorus diffusion on polycrystalline silicon thin films

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Abstract

In this paper, the emitter formation on polycrystalline silicon (with grain size of 0.5–10 μm) deposited by chemical vapour deposition (CVD) on foreign substrates (thermal SiO_2 and mullite ceramic) is studied. Phosphorus doping efficiency by $POCl_3$ diffusion, APCVD + drive-in diffusion, and also rapid-thermal diffusion (RTD) from spin-on doping (SOD) sources were compared. For the first time, we report on photovoltaic results obtained on RTD-diffused emitters on pc-Si active layers deposited by rapid-thermal CVD, thus opening the way to an all rapid-thermal process for solar cell fabrication. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Phosphorus diffusion; Polycrystalline silicon

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1. Introduction

In the past 10 years, the junction formation on silicon by rapid-thermal diffusion (RTD) of phosphorus from spin-on doping (SOD) sources has gained increasing interest in the photovoltaic field because of an overall thermal budget reduction. It has been successfully used on single-crystal (sc-Si) [1] and multi-crystalline silicon (mc-Si) with grain sizes ranging from 1 mm to a few centimetres. Here, we demonstrate for the

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first time that RTD can be successfully applied on smaller-grained and rough polycrystalline silicon (pc-Si) with grain-size ranging from 0.5 to 10 μm microns. This grain-size offers significant impact of both the grain boundaries (GBs) and the inner crystal grains on the phosphorus diffusion mechanisms. In particular, the enhanced diffusion at GBs [2,3] will result in a junction that is far from exactly flat and parallel to the surface [4]. In order to get a better insight into the mechanisms and to control the properties of the diffused emitter, not only RTD diffusion is studied but also compared to standard $POCl_3$ diffusion, as well as atmospheric pressure chemical vapour deposition (AP CVD) + drive-in diffusion.

In the first part of this paper, we report on the diffusion results obtained with each process. The influence of the diffusion temperature, time, and especially the source concentration was investigated, and characterised by sheet resistance measurements with the four-point-probe method, secondary ion mass spectrometry (SIMS) and spreading resistance profiling (SRP).

In the second part, the three diffusion processes are compared and the results are summarised. Finally, first solar cells with RTD emitters on pc-Si are compared to classical emitter, on the basis of internal quantum efficiency (IQE) curves as well as photovoltaic parameters deduced from $I(V)$ characteristics under illumination.

The polycrystalline silicon (pc-Si) thin films (5–20 μm thick) used in this study were deposited by lamps-heated CVD reactors at high temperatures (> 1000°C) and high growth rates (1–5 μm/min) on laboratory-made mullite tape-casted ceramic substrates as well as on thermally oxidised Si (thereafter named SiO_2 substrates). Mullite is chosen for its favourable mechanical and optical properties [5], while SiO_2 was used as a reference. The grain sizes ranged from 0.5 to 2 μm, and the doping level was 2×10^{17} boron at/cm^3.

2. Phosphorus diffusion results

2.1. Classical phosphorus diffusion

This diffusion process was performed in a conventional open quartz tube furnace, under nitrogen flux saturated with $POCl_3$, and oxygen. The diffusion time was 15 min. As shown in Fig. 1, the resulting sheet resistance $R_\square$ of the junction on pc-Si is quite lower than on single-crystal silicon (sc-Si, (1 0 0) Cz-Si, 1 Ω cm), thus confirming similar results recently obtained by Van Zutphen et al. [7]. The continuous arrival of phosphorus from the gas phase implies that the formed surface oxide can be seen as an infinite diffusion source.

2.2. Rapid-thermal phosphorus diffusion

The samples were spin-on coated with phosphorus liquid sources P506, P507, and P509 (from Filmtronics, USA). The P-concentrations in these silica-based sources are 3×10^{20}, 5×10^{20} and 2×10^{21} at/cm^3, respectively. The RTD was performed in a cold wall furnace with halogen lamps as heating source, at various temperatures during

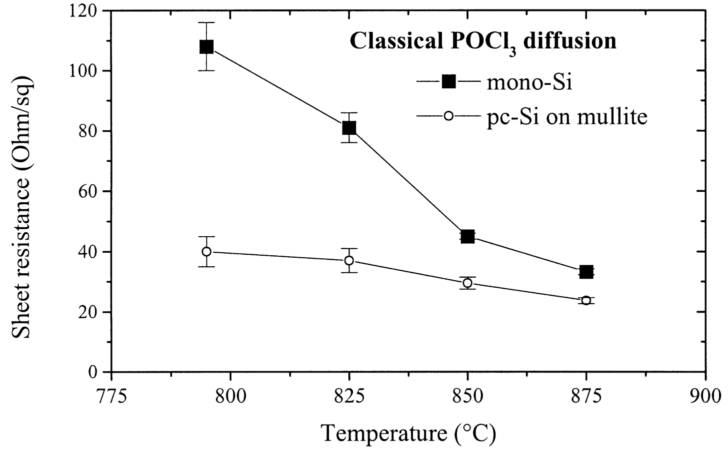

Fig. 1. Sheet resistance vs. diffusion temperature for 15 min $POCl_3$ diffusion (under $O_2 + N_2/POCl_3/O_2$ ambient).

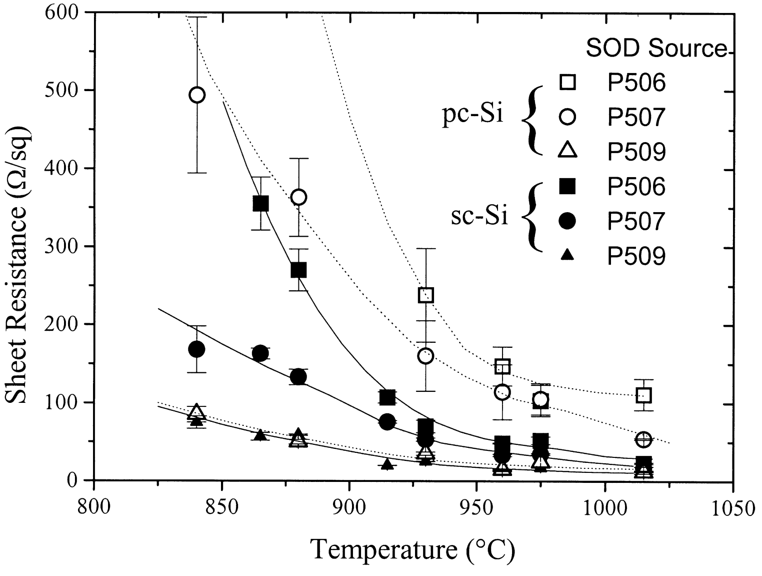

Fig. 2. Effect of temperature and P-concentration of emitters diffused by RTD (30 s under Ar) on sc-Si and pc-Si on mullite. For corresponding P concentration, see text.

30 s. We demonstrate for the first time the possibility to realise an emitter from a SOD source on as-grown pc-Si with grain size and surface roughness of a few microns. In contrast to $POCl_3$ diffusion, the present RTD conditions on pc-Si yield higher sheet resistance values than on sc-Si (Fig. 2). Similar results were obtained in our experiments as a function of time from 15 to 90 s. With the highly P-doped P509 source

Table 1
Sheet resistance values measured on emitters realised by APCVD. A constant sheet resistance was aimed at, while changing two parameters: the temperature and the source concentration

P (w%)	T (°C)	Sheet resistance ($\Omega_\square$)	
		sc-Si	pc-Si
29.4	820	196	114
24	860	85	128
20.5	910	53	118

however, closer values are obtained. In this case, the sheet resistance appears controlled by the surface concentration and the grain boundaries seem to play only a minor role.

2.3. *APCVD + drive-in phosphorus diffusion*

The deposition of the doped oxide by APCVD allows tailoring the P-concentration of the oxide. The diffusion was then performed at various temperatures for 30 min. In the experiments reported in Table 1, a constant sheet resistance on pc-Si was aimed at. As expected, the temperature has to be increased (deeper junction) while the source concentration is decreased (lower surface concentration). However, the differences between sc-Si and pc-Si confirm the above remark that using lightly (heavily) doped source results in higher (lower) sheet resistance on pc-Si. This is also in agreement with previous studies on similarly deposited pc-Si. Starting from a 15 wt % P-rich source, and after diffusion at 1000°C for 2 h, Kamins [3] found sheet resistance values of 18 and 20–37 $\Omega/_\square$ for sc-Si and pc-Si, respectively.

3. Comparative results and discussion

Fig. 3 shows SIMS phosphorus profiles of emitters diffused by the three described processes, at nearly the same temperature (850°C–860°C). First, the RTD applied to sc-Si (case B, 30 s) allows the realisation of similar junctions with reduced thermal budget, when compared to standard $POCl_3$ diffusion (case A, 30 min), thus highlighting the advantage of RTP. It has recently been suggested that this apparently accelerated P-diffusion during RTD can be explained by an out-of-equilibrium injection of phosphorus at the surface from the SOD source under lamp radiation [6]. For the pc-Si cases (C, D, and E), SIMS profiles are characterised by a deep penetration because of fast diffusion along the grain boundaries. Cases C ($POCl_3$, 15 min) and D (RTD, 30 s) reveal clearly that enhanced diffusion during RTD holds true in the polycrystalline material. Though not realised on same starting pc-Si material, an APCVD + drive-in diffused-emitter with 37.6% P-doped source, is also shown in Fig. 3 (case E). In this case, the diffusion queue is also observed and is more

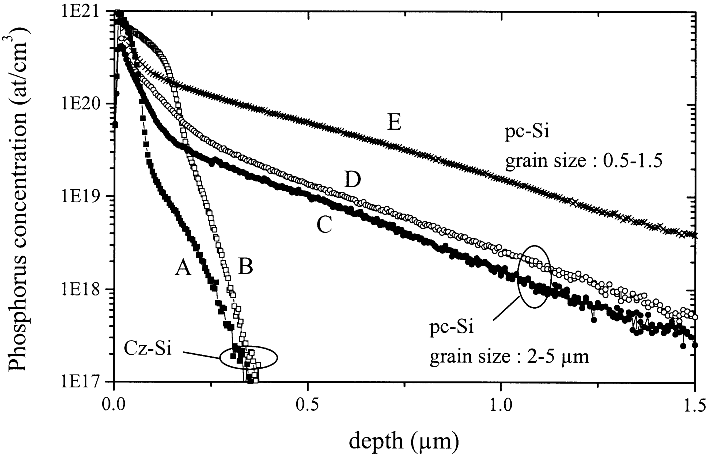

Fig. 3. SIMS profiles of Phosphorus-diffused emitters in pc-Si and sc-Si with various processes: (A, C) $POCl_3$ diffusion at 850°C for 15 min; (B, D) RTD diffusion (P509 source) 850°C, 60 s; (E) AP-CVD + drive-in 860°C, 30 min.

pronounced because of a smaller grain size and higher thermal budget (time and temperature). Spreading resistance profiling on this sample gave a junction depth of 1.3 μm, compared to nearly 2 μm needed for the P profile to reach down the B doping level of $5\times10^{17}\,cm^{-3}$. In a general manner, the junction depth that can be deduced from the phosphorus SIMS profile is higher than that obtained from SRP measurement. The latter is attributed to the planar junction in the grains, whereas the SIMS concentrations below this depth are mean values between P-rich GB's and Si grains. This corresponds to a type B diffusion mechanism in the Harrison's classification [2]. The junction is not flat (type A) but has a three-dimensional shape (type B), as directly evidenced in Ref. [4]. The observed differences in sheet resistance between sc-Si and pc-Si depending on source concentration can be explained on the basis of phosphorus concentration/ de-activation in the defects and grain boundaries of pc-Si. Phosphorus diffusion from a lightly doped source can result in higher sheet resistances on pc-Si because of trapping of dopant atoms at defects and GB's. The enhanced diffusion at grain boundaries can also accelerate the source depletion. Furthermore, the mobility in polycrystalline Si is lower than in sc-Si because of carrier trapping at grain boundaries. On the other hand, an infinite phosphorus source (e.g. $POCl_3$ diffusion) allows a massive diffusion to occur in the GB's and from the GB's to the grains, with no source depletion. In this case, even if trapping of dopants can occur, the total amount of diffused phosphorus is sufficient to provide active dopants that contribute to lower the sheet resistance.

Finally, Fig. 4 shows IQE curves of 1 cm^2 photovoltaic devices realised with 2 different emitters. The pc-Si active layers were deposited in two successive and identical runs on thermal SiO_2 in the RT-CVD reactor (T = 1100°C, 6 min deposition time). Compared to the standard APCVD + drive-in emitter (here 71 $\Omega/_\square$), the result obtained from the RTD emitter appears quite promising. Further improvements can

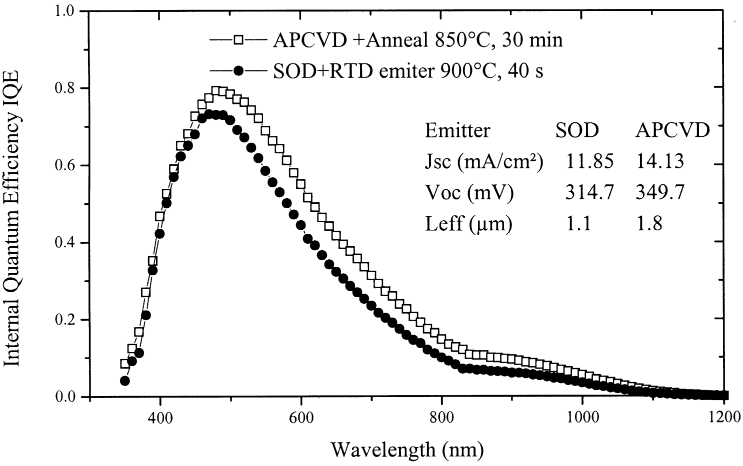

Fig. 4. IQE curves of pc-Si Solar cells on thermal SiO_2.

be expected by using a lower-doped SOD source (following recent results on sc-Si [8]), but while keeping a sheet resistance low enough.

4. Conclusion

Three different phosphorus diffusion processes were studied for emitter formation on small-grained (0.5–2 μm grain size) polycrystalline silicon on foreign substrates (mullite, thermal SiO_2). The common feature is that enhanced diffusion along GB's cannot be avoided, even for very short diffusion time (< 60 s). The sheet resistance differences between pc-Si and sc-Si are reduced with increased temperature. This difference is positive for the lightly concentrated P-sources, and negative for heavily doped diffusion source. For the first time, rapid-thermal diffusion (RTD) was successfully used on such pc-Si layers to realise photovoltaic devices with characteristics comparable to standard phosphorus diffusion methods. In combination with the rapid-thermal CVD technique to grow the active layer on substrate, this opens a new way for a completely rapid-thermal solar cell fabrication.

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