FIRST SOLAR CELLS ON SILICON RIBBONS OBTAINED BY FAST CVD FROM SILANE

C. R. Pinto, J. M. Serra, M. C. Brito, J.Silva, J. Maia Alves, A. M. Vallêra
CFMC / Faculdade de Ciências da Universidade de Lisboa
Campo Grande, 1749-016 Lisboa, Portugal

ABSTRACT: : In this paper we report our first results on solar cells made on silicon ribbons obtained by a two-step process: pre-ribbons obtained by CVD followed by zone melting recrystallization (ZMR)
Silicon ribbons were obtained by a fast CVD step using silane. These intrinsic ribbons are self-supported with a porous and microcrystalline structure and therefore must be doped to make them suitable as base material for solar cells. To this purpose the ribbons were recrystallized by ZMR using this step to perform also the boron doping process based on sprayed boric acid method. Solar cells were made using a basic procedure; aluminium back contacts; Ti/Pd/Ag front grid contacts; no anti-reflective coatings, no doping optimization, no passivation nor gettering. I-V measurements of the basic solar cells showed V_{oc}~500 mV and J_{sc} ~ 16-17 mA/cm^2. Minority carrier diffusion length measured from spectral response at long wavelengths gave values of Ln ~ 50-60 μm.
Keywords: Silicon, Ribbon, Solar cell

1 INTRODUCTION

A lot of effort has been put in research to try to reduce the costs of solar cells by short-circuiting the ingot/wafering path, which is the dominant industrial process as of today.

Already in the early days of solar cells it was realised that such a wastefull process could be avoided by ribbon growth techniques. Although easy to enunciate, this problem proved very difficult to solve. This is demonstrated by the fact that even today most of the solar cell industrial production still relies on silicon crystallization in ingot form, followed by wafering. Out of many proposed and researched alternatives, only two processes of sheet growth (the EFG process and String Ribbon) have very recently reached significant industrial production, still accounting for only ~5% of production volume.

Silicon ribbons can be obtained by:

i) Direct growth of self supported silicon ribbon from the melt. That's the case of EFG[1] and String Ribbon[2].

ii) Growth on a substrate, remaining attached to it. We mention here the research done at FhISE[3] and IMEC[4] as examples of silicon growth on a low-cost silicon substrate.

iii) Growth on a substrate, later detached from it. RGS[5] and SSP[6] ribbons are two representative cases of this group.

All these techniques present different problems associated with impurity contamination related to the dies or substrates used. This is true even for processes that use Chemical Vapour Deposition (CVD) of silicon films on large area substrates. Despite numerous attempts, no foreign substrate process has proved outstandingly attractive so far.

Silicon sheet formation from the gas phase needs a substrate. Previous R&D has focused on non-detachable silicon films on cheap substrates (with systematic poor results for material quality and final efficiency) or on detachable films on high quality substrates (with resulting good quality films but high cost). In the SDS approach: (i) we use a bed of silicon dust both as a cheap substrate and as a "sacrificial detachment layer", part of it being incorporated into a (ii) thick film obtained by fast CVD at low temperature and ambient pressure; (iii) the detached, free standing, film is then crystallized by a floating molten zone technique. The process is best suited for silane as feedstock, because of its homogeneous nucleation and high deposition rates at low temperatures and high pressures. Pre-ribbons of high purity are prepared by fast CVD deposition from silane.

This paper describes the experimental details and of the SDS (Silicon Dust Sheet) process. The advantages of the SDS process are: (i) no substrate (therefore no cost and no contamination); (ii) low thermal budget (ambient pressure, low temperature CVD); (iii) high quality, free standing, crystalline silicon sheet (float zone crystallisation, no contact with foreign materials).

2 EXPERIMENTAL PROCEDURE

2.1 SDS process overview

Silicon is deposited by CVD on a layer of silicon powder. The deposited layer is easily separated from the quartz substrate and constitutes a self supported pre-ribbon. By ZMR processing it is converted into a multicrystalline ribbon that can be used as substrate for solar cells.

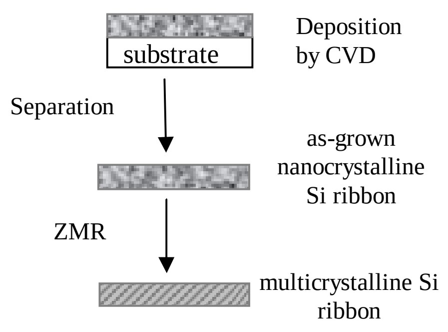

Fig.1- Process sequence of the SDS technique.

2.2 Pre-ribbon formation

A specially designed furnace is used to grow the silicon pre-ribbons. This furnace has a top window through which radiation from halogen lamps is used to heat a layer of silicon powder placed on top of a quartz plate sample holder. The heated silicon powder gives rise to the silane decomposition and act as seed for ribbon growth. We use conditions that are normally avoided in CVD processes: powder formation, and fast, low quality growth. With this approach we are decoupling the CVD step from the crystallization step.

The pre-ribbons are structurally unsuitable for solar cells despite their microcrystalline structure, because of it's high porosity. Several pre-ribbons were prepared, with average sheet densities between 42 and 84 mg/cm^2, corresponding to solid silicon thicknesses between 180 and 360µm, with varying degrees of porosity and homogeneity.

2.2 ZMR

ZMR is performed using an in-house developed furnace. It has two elliptical mirrors that concentrate the radiation of two 1000W halogen lamps [7]. In a typical run, the sample is moved downwards with a 3mm/min velocity and the atmosphere inside the furnace is renewed with a 1 l/min argon flux.

2.3 Ribbon doping

The pre-ribbons obtained in the CVD step are intrinsic and to be used for solar cells they need to be doped.

The doping process is based on the spraying of a solution of boric acid with a concentration of 0,76g/l. Further details are found at [8].

The incorporation of the boron into the samples is achieved during ZMR, according to the equation

$$2B_2O_3(g) + 3Si(s) \rightarrow 3SiO_2(s) + 4B(s)$$

With this technique we successfully combined doping and recrystallization in one step.

3 RESULTS

3.1 CVD deposition

CVD deposition occurs on the layer of silicon powder that is placed on top of a quartz plate inside the CVD reactor. (REC?)

Table 1. Powder details

Density (g/cm3)	Thickness (mm)	Area (cm2)
0,23-0.29	0,5	12

A flux of diluted silane (10% in H2) enters the reactor and decomposes upon reaching the powder layer. Gas convection, gas diffusion and decomposition in the powder bed and its temperature distribution are very important parameters to control pre-ribbon shape and uniformity which are key points to allow successful processing in the second step. The typical conditions for CVD are indicated in Table 2.

Table 2. CVD parameters

Temp.(C)	Flux (l/min)	Dep. Rate(µm/min)
750-800	0.4	6-8

Acording to our measurements, during this process the conversion of silane into silicon is aproximately 60-75%.

We observed that by playing with the gas path inside the furnace and the lamp power we could obtain pre-ribbons with 3 different cross sections: plane-convex, plane-concave or plane-plane.

The porous nature of the pre-ribbon is clearly shown in the top picture of fig.2.

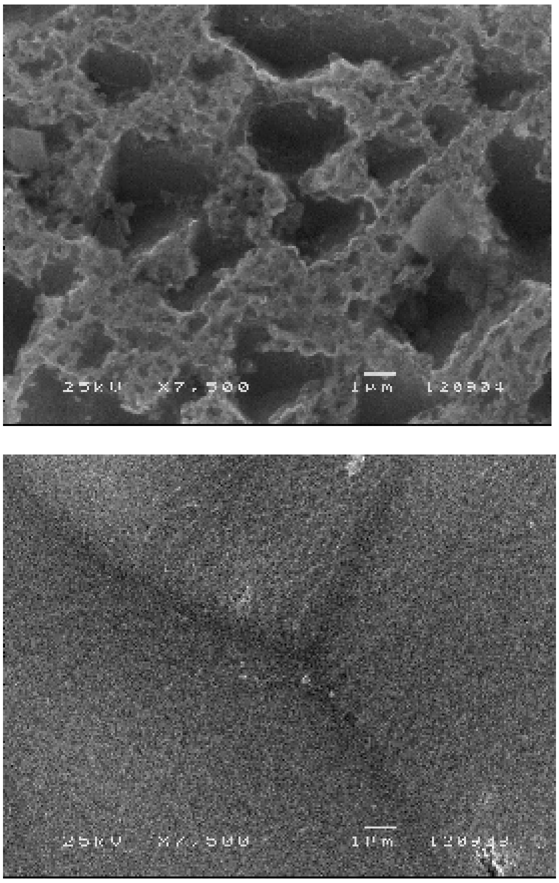

Fig.2 – SEM pictures showing the structure of the ribbon before and after ZMR. Top photograph: as grown CVD pre-ribbon; Bottom photograph: after ZMR.

3.2 ZMR processing

ZMR proved to be more difficult than expected due to the characteristics of the pre-ribbons, that may vary widely according to deposition conditions. As we mentioned, the temperature on the powder layer can give rise to different behaviour of the gas deposition leading to different cross section shapes. plane-plane Plane-convex shape leads to ZMR disruption at the edges of the ribbon; plane-concave shape to holes in the middle. The third shape, plane-plane, is the one that allows successful ZMR provided the pre-ribbon has the right porosity.

We observed that by using CVD growth conditions that give porosities below ~50% allows reproducible ZMR crystallization with low failure rate.

The recrystallized ribbons are 300 µm thick, with a crystalline structure consisting of grains which are a few centimetres long and a few millimetres wide, p-doped, with resistivities around 2.5Ω.cm.

3.3 Solar cell characterization

Since the goal of these preliminary solar cells is to evaluate the suitability of these ribbons for photovoltaic application, cells were just formed to allow some electrical characterization: spectral response and I-V measurements.

The junction was formed by phosphorous diffusion from a solid source. After mesa etching, aluminium back contacts and a grid of Ti/Pd/Ag front contacts were deposited by evaporation, followed by contact annealing. No anti-reflective coatings, no doping optimization, no passivation nor gettering procedures were attempt.

I-V measurements showed V_{oc}~500 mV and J_{sc} ~ 16-17 mA/cm^2 as can be seen on fig.3.

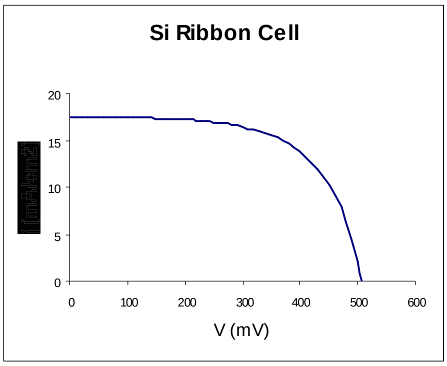

Fig. 3- I-V curve of our best test cell.

Spectral response measurements were done on several cells to evaluate material quality. A typical response in these cells is shown in fig. 4.

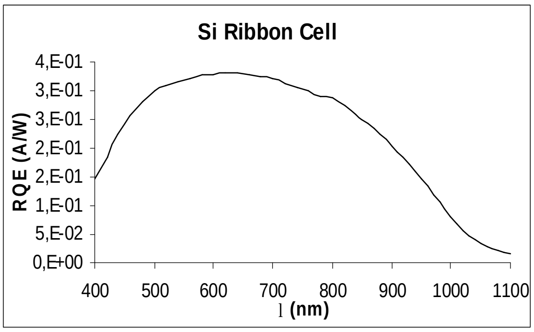

Fig.4- Spectral response of one of these test cells.

Minority carrier diffusion length measured from spectral response at long wavelengths gave values of Ln ~ 50-60 µm.

Minority carrier diffusion length values are lower than the ones obtained in the control samples (multicrystalline cast silicon) which underwent the same ZMR and doping process. We believe that the lower diffusion length values in SDS ribbons can be explained by impurities present in the pre-ribbon powder, given the fact that processing was identical in both cases. That is a subject we are addressing now.

4 CONCLUSIONS

The SDS (Silicon Dust Sheet) method for the formation of silicon ribbons based on CVD from silane was described. The advantages of the SDS process are: (i) no substrate (therefore no cost and no contamination); (ii) low thermal budget (ambient pressure, low temperature CVD); (iii) high quality, free standing, crystalline silicon sheet (float zone crystallisation, no contact with foreign materials).

First test solar cells shown here demonstrate the feasibility of the whole process we have been working on: formation of a pre-ribbon by CVD to a final solar cell.

5 ACKNOWLEDGEMENTS

This work has been partially supported by the following FCT grants:

SFRH/BD/12763/2003 and SFRH/BPD/20660/2004

6 REFERENCES

[1] F.Wald, in “Crystals: Growth, properties and applications” 5 149 (1981)

[2] T.Ciszek, in “Silicon Processing for Photovoltaics I”, 131, Ed. North- Holland (1987)

[3] W.Zimmermann, K.Schmidt, F.Haas and A.Eyer, Proceedings of the 2th world PVSEC,1998

[4] H. Dekkers, S. De Wolf, G. Agostinelli, F. Duerinckx and G. Beaucarne, Solar Energy Materials and Solar Cells. Vol. 90: (18-19) 3244-3250; 2006

[5] W. Koch et al., Proc. 2nd World PVSEC, 1998, p1254

[6] A.Eyer, N.Schillinger, A.Rauber, Proc. 9th EC Photovoltaic Solar Energy Conf., Freiburg, RFA, 1989

[7] C.R Pinto, J.M.Serra, M.C.Brito, R. Gamboa, J. Maia Alves, A.M. Vallêra, Proc.21st European Photovoltaic Solar Energy Conference and Exhibition, Dresden, 2006, p1099.

[8] J. A. Silva, I. Costa, M. C. Brito, J. Maia Alves, J. M. Serra and A. M. Vallêra, Proc. 21st European Photovoltaic Solar Energy Conference and Exhibition, Dresden, 2006, p1064.