HIGH-THROUGHPUT CONTINUOUS CVD REACTOR FOR SILICON DEPOSITION

A. Hurrle, S. Reber and N. Schillinger
Fraunhofer Institute for Solar Energy Systems, Heidenhofstrasse 2, D-79110 Freiburg, Germany
Phone +49-761-45885265, Fax: +49-761-45889250, e-mail: albert.hurrle@ise.fraunhofer.de

J. Haase and J.G. Reichart
centrotherm GmbH + Co, Johannes-Schmidt-Strasse 3, D-89143 Blaubeuren, Germany

ABSTRACT: A prototype of a high-throughput APCVD reactor for silicon deposition has been designed and built where two parallel rows of substrates are continuously fed in and out through gas curtains. Such a reactor can fulfil the hard economic requirements for the production of crystalline silicon thin-film solar cells. Special attention has been directed to a save and reliable operation of the gas curtain system. First deposition experiments on mc-Si substrates revealed epitaxial layers of high crystal quality and homogeneity, deposition rates >3µm/min and a conversion efficiency Si (gas)→Si (solid) up to 30%.

Keywords: CVD Based Deposition, Si-Films, Epitaxy

1 INTRODUCTION

A crucial step of the production process of crystalline silicon thin-film solar cells is the deposition of the silicon layer. As we follow the high temperature approach the most favoured method is the thermal APCVD due to its high deposition rates in the order of several µm/min. It is widely used in research and production of electronic devices and delivers silicon layers of high quality. But up to now no reactor is available which fulfils the hard economic requirements for the production of thin-film solar cells. High throughput and high conversion efficiency of the utilised precursor gases are the predominant requirements in order to reach the cost goals.

Since several years Fraunhofer ISE has developed lab-type CVD-reactors [1, 2]. These experiences led to the innovative concept of a high-throughput reactor where two parallel rows of substrates are continuously fed in and out through gas curtains. Earlier work based on similar principles [3, 4] seem to have not been further continued. The purpose of the work described here was to construct a reactor according to this concept and to prove its usability.

2 APPARATUS

2.1 Principle

In order to achieve a high conversion efficiency Si(gas)→ Si(solid) with only minor parasitic depositions our optically heated lab-type reactors use a tube-in-tube concept. The rectangular substrates form the side walls of the reaction chamber (the inner tube) and constitute the largest part of its inner surface. The chamber is placed within the outer tube, flooded by hydrogen or inert gas. The reactive gases, a mixture of TCS and hydrogen, are fed into the chamber and deposition occurs only onto the inner surfaces.

The same principle is realised in the new apparatus, where the two rows of substrates slide continuously along the chamber, as shown in fig. 1. To prevent or at least reduce the outdiffusion of reactive gases from the chamber into the outer tube, a small overpressure is maintained in the tube and a flow from tube to chamber is established.

The continuous movement of the substrates avoids the detrimental influence of precursor depletion and temperature variations along the chamber and should lead to a homogeneous deposition profile along the movement direction. Due to the fact, that the precursors are allowed to be highly depleted , a further enhancement of the conversion efficiency is expected.

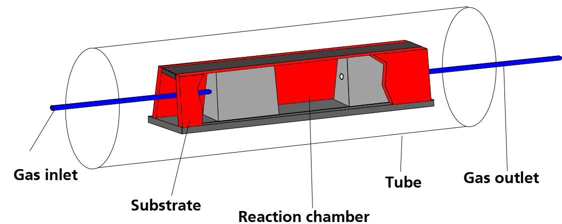

Fig. 1: Principle of continuous CVD

2.2 Gas curtain system

A gas curtain system has been designed which allows to feed the substrates into and out of the reactor in a continuous way without gas exchange between reactor and laboratory. It is based on the behaviour of a gas diffusing against the flow of another gas. Already a small flow in the order of some cm/s reduces the concentration of the diffusing gas after a few centimetres against the flow direction to negligible values. Fig. 2 shows the principle of the gas curtain systems which are installed at both ends of the reactor tube.

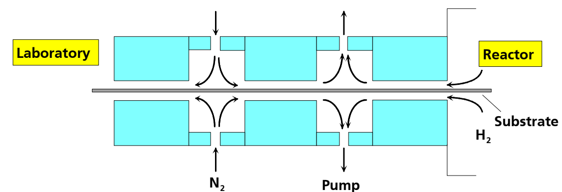

Fig. 2: Principle of the gas curtain system

Each gas curtain system is a unit containing five segments thereof three ones with slits which fit the sample carriers, one showerhead and one pumping chamber. Jetpumps which don't need power supply are used for safety reasons and as their pumping speed can

be easily regulated by the propellant flow. The proper operation is controlled by a H_2-sensor in the outermost (left in fig. 2) and a O_2-sensor in the innermost segment and regulated by adjusting the gas flows in the shower heads and the propellant flows of the jet pumps. An additional jet pump removes the exhaust gases from the reaction chamber.

The gas curtains are only a part of the whole gas flow system which is schematically shown in fig.3 including typical gas flows and pumping speeds. In reality the reaction chamber is inside the tube but for clarity reasons it is drawn outside.

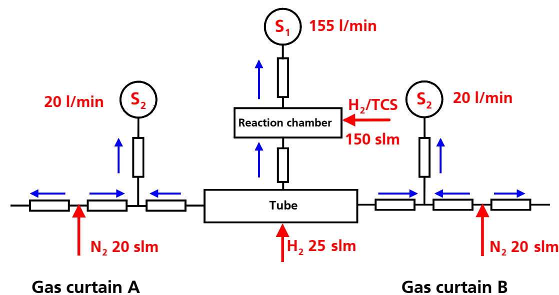

Fig. 3: Gas flow scheme

Slits and pipelines are represented by appropriate conductances and all gas flows and pressures can be calculated on different conditions according to the scheme.

The pressure differences across the slits in the gas curtains are in the order of less than 0.1 Pa at gas flows of some 10 slm whereas the fluctuations of the atmospheric pressure are in the order of 1 Pa. Moreover the laboratory is ventilated and its atmospheric pressure is about 5 Pa lower than outside. Thus the question arises, if the stability of the system is maintained in case of atmospheric pressure drops in this order, e.g. due to opening doors or windows. Fig. 4 shows the dynamic behaviour of two representative gas flows after a sudden atmospheric pressure jump of +5 Pa under flow conditions as in fig. 3.

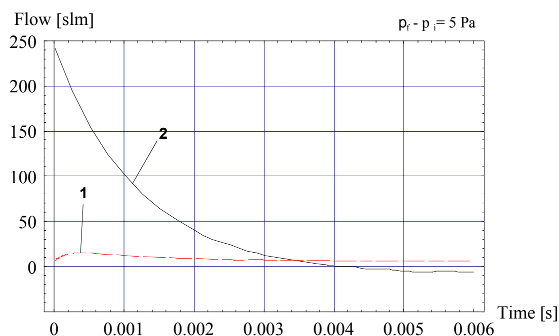

Fig. 4: Gas flows after a atmospheric pressure jump of +5 Pa. (explication in the text)

Graph 1 is the flow from the tube into the reaction chamber. It is only slightly affected by the pressure jump. Graph 2 is the flow in the outermost left slit segment of fig. 3. On equilibrium conditions this flow has a negative value (from right to left as in fig. 3) of about 10 slm. Immediately after the pressure jump there is a very high flow from left to right, but after 4 ms it reverses and approaches rapidly the equilibrium value. The gas volume, transported during this time in the "wrong" direction is about 4.3 standard cm³. This is only 2% of the volume within the slits of a gas curtain segment, i.e. no gas exchange occurs in this time and the stability of the system is maintained. A simple consideration confirms these results: a gas amount of 5 x 0.2 Pa m^3 = 10 standard cm³ is necessary to increase the pressure in the tube of 200 l volume by 5 Pa. This is about twice the calculated amount which flows in each of the two gas curtains from the outside inwards.

2.3 General features

The most important features of the reactor are summarised as follows:

- Open system with gas curtains and two rows of continuously moving substrates
- Total length: 540 cm
- Resistance heating
- Substrate temperature up to 1300 °C
- Reactor tube SiC, 30 cm Ø
- Reaction chamber: graphite, 40 cm long
- Two rows of graphite carriers for the substrates: substrate width 10 or 20 cm, substrate length up to 40 cm; substrates of 10 cm width are placed in two rows one upon the other on each carrier
- In-situ etching of parasitic deposits by HCl
- Gas lines into the reaction chamber for H_2, $SiHCl_3$ and B_2H_6, for H_2 or inert gas into the tube
- Production rate at 5µm/min average deposition rate: 1.4 m²/h for Si layers of 30 µm thickness

In case of emergency (electrical breakdown or exceeded thresholds values of the gas sensors) all dangerous gases are shut off, but the propellant flow for the jetpumps and an inert gas flow into the tube are sustained at predefined values. This is accomplished by bypass lines with normally open valves. Fig. 5 shows a total view of the apparatus.

Fig.5: Total view of the apparatus

The load station is located at the left side where the rear substrate row with mc-Si substrates is visible. The front row is removed in the picture. The unload station is at the right end of the apparatus and not visible in the picture.

Fig. 6 shows more details of the load station. In the foreground right one sees the infeed machine for the substrate carriers, thereof left the first segments of the gas curtain system. One of the both slits for the substrate carriers, inclined by 5° to the plumb line, is visible.

Fig. 6: Load station

3 DEPOSITION EXPERIMENTS

In spite of several technical problems which appeared during the development of the project promising deposition experiments could be performed.

A main and up to now not satisfactorily solved problem was the high oxygen concentration (ca. 100ppm) in the tube, when the tube was flooded by hydrogen. With nitrogen or argon in the tube, the oxygen concentration could be kept below 10 ppm. The reason are small leaks at the interface between flange and adjacent gas curtain element, which are much more efficient in the presence of hydrogen than of nitrogen or argon due to a larger diffusion coefficient.

Another problem were deposits at the nozzle of the exhaust-jetpump when nitrogen was used as propellant (fig.7). A stable operation was not possible on these conditions.

Fig.7: Deposits at jetpump nozzle using nitrogen as propellant

The deposits are soluble in water and consist probably of Ammoniumchloride NH_4Cl. They are strongly reduced with argon as propellant and disappear when the tube is additionally flooded by argon instead of nitrogen.

Most depostion experiments were performed under equal conditions except the gas atmosphere (H_2, N_2 or Ar) in the tube:

- Deposition temperature. 1130 °C (measured in the tube near the reaction chamber
- 50 slm H_2 and 3 slm $SiHCl_3$ fed in the reaction chamber
- Carrier velocity 9 cm/min resulting in a deposition time of 4.5 min
- 10 x 10 cm² mc-Si substrates etched by CP133

Additionally to the gases fed directly into the chamber a small but not controlled amount of gas (ca. 5 slm) flows from the tube into the chamber.

3.1 Depositions with H_2 in the tube

Due to the high oxygen concentration (see above) the deposition experiments under these conditions were not successful. The deposited layers were only partially epitaxial and yellow colored in some areas. Fig. 8 shows as an example a carrier with the 8 substrates after the deposition.

Fig. 8: Partially epitaxial deposition (H_2 in the tube)

3.2 Depositions with N_2 or Ar in the tube

Much better results have been obtained with the tube filled by N_2 or Ar. An operation under these conditions is also preferred due to safety reasons. Visual inspection indicates epitaxially grown layers as it is shown in fig. 9.

Fig 9: Epitaxial deposition (N_2 in the tube)

Fig 10 shows a typical part of a secco-etched cross section of the samples of fig.9, perpendicular to the gas flow and carrier movement direction.

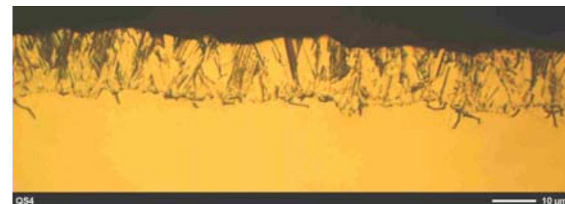

Fig.10: Secco-etched cross section of a deposited layer (N_2 in the tube)

The layer thickness is here about 15 µm, corresponding to a deposition rate of 3.3 µm/min. It decreases slightly from bottom to top, but with the mean layer thickness of 14 µm the conversion efficiency Si(gas)→Si(solid) can be calculated to 30%. This is an

excellent result compared with the value of 34% for chemical eqilibrium, in view of parasitic deposits within the reaction chamber, which reduce the experimental value.

As one can see from fig. 10, the layer, deposited with N_2 in the tube, is rather defective. Layers of much higher quality were obtained with Ar in the tube. Fig. 11 shows an example.

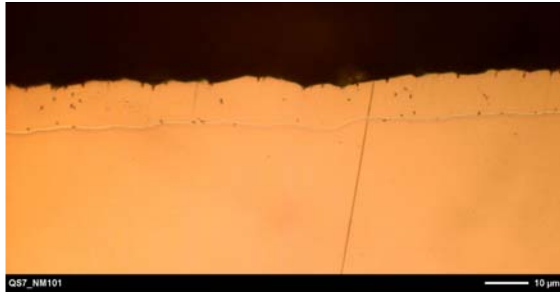

Fig.11: Secco-etched cross section of a deposited layer (Ar in the tube)

Compared to Fig.10 the number of defects is drastically reduced. The layer thickness is about 35% lower than in Fig. 10. The reason is not clear, but it may be caused by a lower substrate temperature than indicated.

The whole cross section extended over the the total height of a lower and upper substrate at the same horizontal position and the layer thickness was measured in this range. Fig. 12 shows the result.

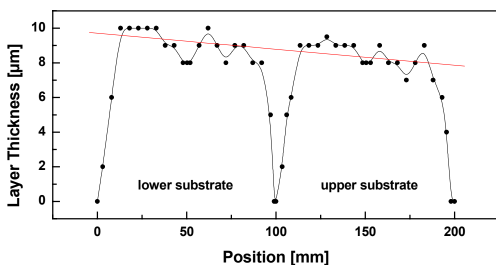

Fig.12: Deposition profile perpendicular to gas flow direction (Ar in the tube)

Apart from the sharp drops at the ends of both substrates due to the mounting, the layer thickness decreases only slightly from bottom to top. This may arise from the asymmetry of the reaction chamber due to the inclined substrate holders.

The deposition profiles of the 16 substrates in two opposite carriers along the gas flow and carrier movement direction has been obtained by weighing the substrates before and after the deposition (fig.13). The slight decrease of the deposition rate during the process (the left samples in the figure were the last ones to be coated) may be due to a slight decrease of the substrate temperature of about 10°C.

In order to get more insight into the processes within the reaction chamber, a stationary deposition without substrate movement was performed. In contrast to the profiles of fig. 12 the amount of deposited silicon varies strongly along the reaction chamber as well as, more surprisingly, from bottom to top substrates. At the end of the reaction chamber much more silicon is deposited on the lower substrates than on the upper ones. This is apparently compensated in case of moving substrates by the higher deposition on the upper substrates at the beginning. The large improvement of the deposition profiles by moving the substrates is clearly demonstrated.

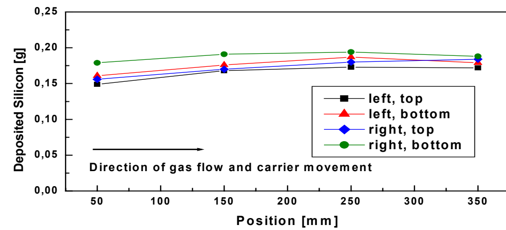

Fig. 13: Deposition profile in gas flow direction with moving substrates (Ar in the tube)

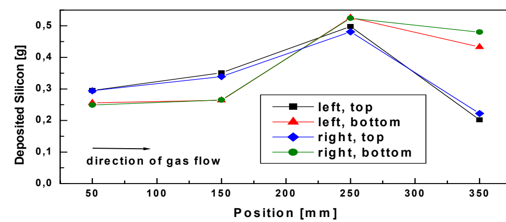

Fig. 14: Deposition profile in gas flow direction with stationary substrates (N_2 in the tube)

4 CONCLUSIONS

A continuously running APCVD reactor with a reliable gas curtain system was built and proved. In spite of the restricted number of experiments made up to now, epitaxial layers of high crystal quality and good homogeneity over the whole substrate area could be deposited at high conversion efficiency. Further work is necessary to prove the long-term behaviour, to optimise the process with respect to substrate temperature and gas composition and to deposit boron-doped layers for solar cells.

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REFERENCES

[1] F.R. Faller and A. Hurrle, IEEE Trans. Electron Devices, Vol. 46, No. 10 (1999) p. 2048

[2] S. Reber, C. Haase, N. Schillinger, S. Bau and A. Hurrle, Proc. 3rd World Conference on Photovoltaic Energy Consevation, Osaka May 2003, p. 1368

[3] R.N. Anderson, United States Patent No. 4,048,955 Sep. 20, 1977

[4] K.R. Sarma and M.J. Rice, J. Cryst. Growth **56** (1982) p. 313