

DISCLOSING THE POLYSILICON DEPOSITION PROCESS

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ABSTRACT: The chemical route for producing hyperpure silicon, referred to as polysilicon, is energy intensive. In this work two paths are analysed to reduce energy consumption during polysilicon deposition: reduce power loss and increase polysilicon productivity. The solutions proposed for reducing power loss are: enlarging the reactor capacities and increasing the wall reflectivity. The proposals for increasing the productivity are: working at the optimum deposition conditions, that maximises the polysilicon growth rate, and stopping the process at higher rod diameters. By doing so, the process uses the energy more efficiently.

Keywords: Polysilicon, chemical route, trichlorosilane.

1 INTRODUCTION

The chemical route for the production of polysilicon consists of three steps. The first is the synthesis of a volatile silicon hydride from metallurgical grade silicon (MG-Si). The second is the purification of the synthesised silicon hydride. The third consists in decomposition of the silicon hydride into polysilicon.

The silicon hydride most commonly used in the industry is trichlorosilane (TCS, HSiCl_3). The synthesis of trichlorosilane is carried out in a fluidized bed reactor, where a chloride gas (HCl or SiCl_4) reacts with MG-Si. The products are silicon hydrides ($\text{H}_{x-4}\text{SiCl}_x$, $x=0,\dots,4$) and gases containing the impurities extracted from the MG-Si [1]. In the next step, the chemical compounds resulting from the synthesis are separated by distillation. Trichlorosilane is purified and supplied to the decomposition step, the remaining silicon hydrides are somewhat recycled into the system, and the impurities are removed [2]. The last step consists in reducing trichlorosilane and hydrogen to polysilicon in a chemical vapour deposition (CVD) reactor [3].

Silane is also used in the industry as the precursor gas instead of trichlorosilane. In this case, the silane is produced by several intermediate catalytic rearrangement steps using the synthesised trichlorosilane as the raw material [4]. Then, the silane is purified by distillation and introduced into the CVD reactor, where it is reduced [5].

The research efforts in the chemical route are directed toward the reduction of production cost and the reduction of energy consumption. These three steps (synthesis, distillation and decomposition) are strongly interlinked. Reducing the energy consumption of the overall process requires understanding each step and their interactions. It should be noted that more than 60% of the energy used in producing polysilicon is consumed in the decomposition process [6, 7].

The polysilicon CVD reactor, also called a *Siemens* reactor, consists of a gas-tight chamber where several high-purity silicon slim rods are heated by an electric current flowing through them, and polysilicon is deposited on the seed rods through the thermal decomposition of trichlorosilane in a hy-

drogen environment [8–10].

The polysilicon deposition is a highly energy intensive process, and polysilicon producers and R&D institutions are working on diminishing the energy consumption per kg of polysilicon produced. There are two main paths, as seen in figure 1, to reduce the energy consumed during the decomposition, per kg of polysilicon produced:

- Reducing the power loss, where the radiative power loss is 70% of the total power loss
- Increasing the polysilicon productivity ($\text{kg}\cdot\text{h}^{-1}$): increasing the polysilicon growth rate and increasing the maximum rod diameter before stopping the process

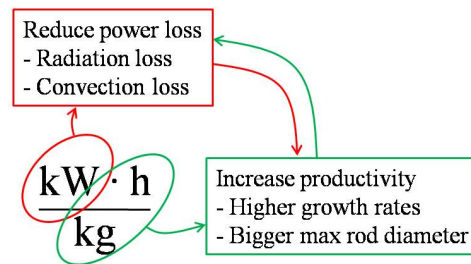


Figure 1: Indications of the basic approaches for reducing the energy consumption of the polysilicon deposition process.

2 REDUCING THE POWER LOSS

The power loss in the CVD reactor has three contributions: the power loss by convection, the power loss by radiation and the power consumed in the chemical decomposition of TCS. The power given to the gases by convection heats them up, and leaves the reactor with the exhaust gases or is exchanged with the reactor cold wall. The power radiated is emitted by the polysilicon rods toward the reactor cold wall. The power consumed in the chemical decomposition of TCS, compared to the other two contributions, can be disregarded.

2.1 Radiation

The temperature of the rods within the reactor vessel is roughly 1100 °C and the reactor wall is cold, so the hot silicon rods are radiating toward the reactor wall, and losing a big amount of energy [11]. There are some alternatives for diminishing the radiative power loss:

- Increasing the number of rods within the reactor vessel. When increasing the number of rods, part of the radiation from one rod does not leave the reactor, since it can be absorbed by another rod. In this work the term rod will denote the vertical part of the U-rod, the U-shaped combination of rods.
- Introducing a high reflectivity reactor wall. Increasing the reflectivity of the reactor wall by making it of silver or silver-plated steel reduces the amount of radiation energy absorbed by the wall [12]. However, care must be taken to avoid the contamination of the polysilicon produced.

In order to analyse the influence of increasing the number of rods, three state-of-the-art configurations are studied: 36 rods arranged in 3 ring, 48 rods arranged in 3 rings and 60 rods arranged in 4 rings. The power emitted per rod, being the surface temperature 1150 °C, is presented in figure 2.

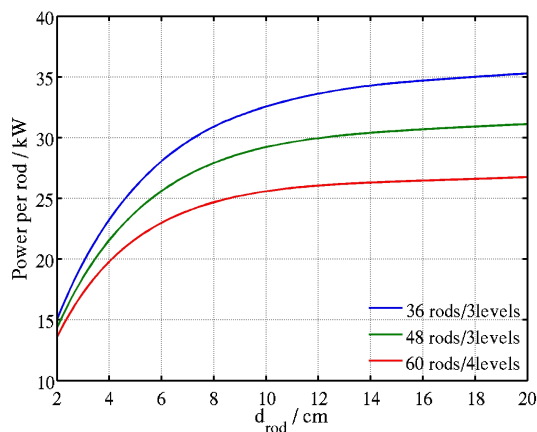


Figure 2: Power emitted per rod and absorbed by the reactor wall for different reactor configurations. U-rod length = 4 m.

The wall emissivity has a strong influence on the radiative power loss. When the emissivity increases, the reflectivity of the wall decreases and the power absorbed increases, as seen in figure 3. It is shown that if the emissivity of the wall reaches $\epsilon = 0.7$ the power is increased around 400 kW, respect to $\epsilon = 0.5$, at the end of the process.

The energy radiated has a noteworthy variation for different values of the wall emissivity, as seen in figure 4, where a growth rate of $7 \mu\text{m}\cdot\text{min}^{-1}$ is considered.

2.2 Convection

The power loss by convection depends on the deposition conditions: the reactor pressure, the rod surface temperature, the gas mixture flow and the gas composition [13].

For a constant pressure, $p=6$ atm, the convection loss throughout the process are depicted in figure 5, for different values of the rod surface temperature. It can be seen that the convection loss is lower than the radiation loss, being the convection loss around 30% of the total power loss.

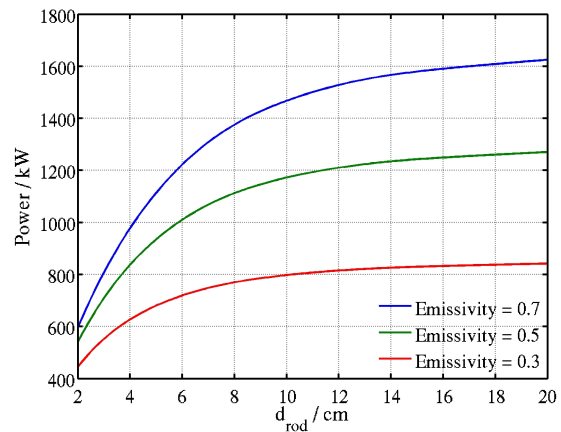


Figure 3: Power radiated by the silicon rods and absorbed by the reactor wall in a 36 rods CVD reactor for different wall emissivities. U-rod length = 4 m.

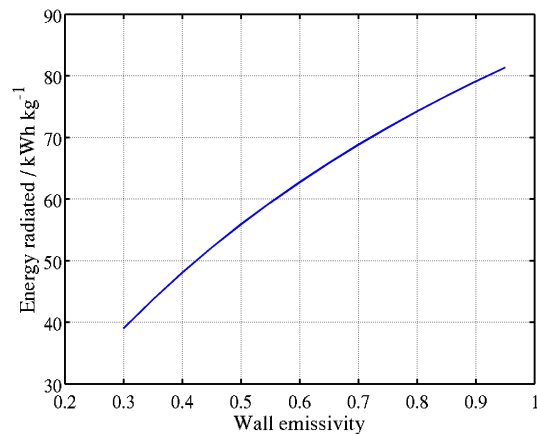


Figure 4: Energy radiated per kilogram of polysilicon produced in a 36 rods CVD reactor for different values of the wall emissivity. The average polysilicon growth rate is $7 \mu\text{m}\cdot\text{min}^{-1}$. U-rod length = 4 m.

The polysilicon productivity and the power loss by convection are interlinked, since both depends on the deposition conditions, and they cannot be increased and reduced at the same time. For instance, the gas flow rate can be raised to increase the productivity, but that would also increase the convection loss.

3 INCREASING THE POLYSILICON PRODUCTIVITY

To increase the productivity it is necessary to understand the effect of the process variables on the deposition process, and to find the best conditions to increase polysilicon growth rate and decrease energy consumption. Not only the deposition conditions but also the maximum rod diameter before stopping the process increases the polysilicon productivity, since the rod's surface area where the deposition takes place increases tremendously at the end of the process.

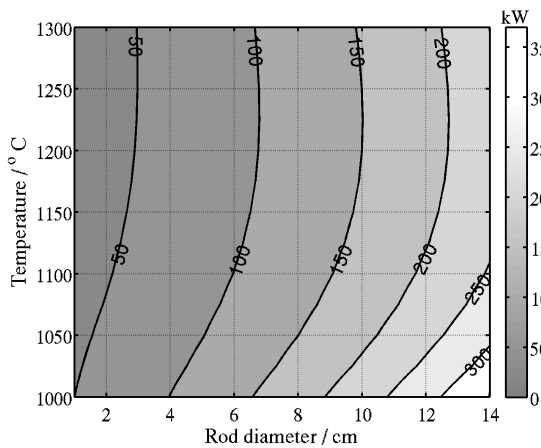


Figure 5: Power loss by convection, expressed in kW, dependence on the rod surface temperature and the rod diameter. U-rod length = 4 m.

3.1 Influence of the deposition conditions

It is important to analyse the optimum inlet gas composition, reactor pressure and rod temperature for growing polysilicon, since a bad choice of them can produce a very slow polysilicon growth rate, and therefore a very high energy consumption.

The inlet gas compositions where the maximum growth rates are reached, for different surface temperatures and pressures, are presented in figure 6. It is shown that the optimum hydrogen molar fraction decreases when increasing the pressure and the rod surface temperature.

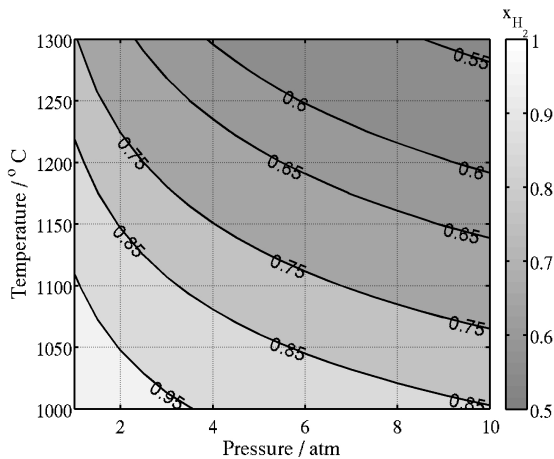


Figure 6: Inlet gas compositions, expressed as the hydrogen molar fraction, that achieve the maximum growth rate for different rod surface temperatures and reactor pressures. Re = 2300, U-rod length = 4 m, rod radius = 1 cm.

The maximum growth rate for different surface temperatures and pressures is presented in figure 7. It is seen that the rod surface temperature and the pressure within the reactor vessel have a strong impact on the growth rate. A good combination of both increases the growth rate sixfold. When the rod surface temperature is raised, the kinetic of the silicon deposition is faster because the reactor constants have an exponential dependence on this parameter [14]. When the pres-

sure in the reactor vessel is raised, the growth rate increases because the concentration of reactant species (hydrogen and trichlorosilane) is greater.

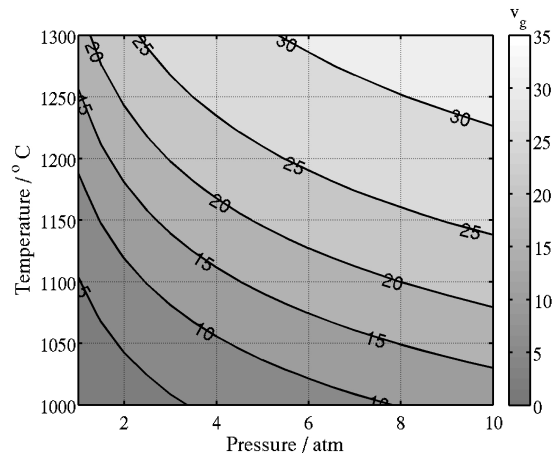


Figure 7: Maximum growth rate, expressed in $\mu\text{m}\cdot\text{min}^{-1}$, dependence on the reactor pressure and rod surface temperature. Re = 2300, U-rod length = 4 m, rod radius = 1 cm.

3.2 Increasing the maximum rod diameter

The deposition process uses energy more efficiently when the rod diameter is high. This has two causes: first, part of the radiation is blocked when the diameter is high; and second, the net deposition surface increases tremendously. When the rod diameter is above 10 cm, the power loss rises slowly, as seen in figure 3, while the mass production rate increases notably, yielding low energy consumption per kg of silicon produced. Figure 8 presents the variation of the energy consumption with maximum rod diameter, considering a 36 rod CVD reactor and an average polysilicon growth rate of $7 \mu\text{m}\cdot\text{min}^{-1}$.

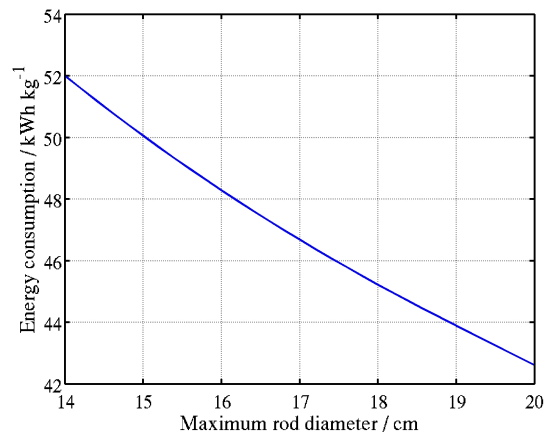


Figure 8: Energy consumption throughout the deposition process for different maximum rod diameters, from 14 to 20cm. A 36 rod CVD reactor is considered, and the average polysilicon growth rate is $7 \mu\text{m}\cdot\text{min}^{-1}$.

The limitation for increasing the maximum rod diameter is found in the risk of melting the rod core. The limiting temperature that the rod surface can reach before melting the rod core

is studied in detail in reference [15]. It is concluded that this limiting temperature is always above the optimum deposition temperature, presented in the next section, considering rod diameters from 1 to 20cm. Thus, melting the rod core does not therefore introduce a limitation for stopping the process before a rod diameter of 20cm is reached. Nevertheless, it must be said that even though the rod core does not melt, the corners of the U-rod may do it.

4 DISCUSSION

The energy radiated by the rods is reduced by 20% when comparing the 60 rod CVD reactor to the 36 rod CVD reactor and it is reduced by 10% when comparing the 48 rod reactor to the 36 rod CVD reactor. If the wall emissivity is improved, by selecting better materials or by surface treatment, the energy radiated is reduced by 30%.

The optimum deposition conditions are those that reduce the energy consumption per kg of polysilicon produced [15]. When increasing the pressure in the reactor vessel, the growth rate increases and the energy consumption decreases. An optimum pressure can be found at 6 atm, since increasing the pressure above this value does not produce a noteworthy variation in the energy consumption. Regarding the rod surface temperature, an optimum deposition temperature is found between 1100-1200 °C, depending on the rod diameter, that minimises the energy consumption. When the temperature is above this range, the radiation loss increases dramatically while the growth rate increases more slowly, leading to higher energy consumption. When the temperature is below this range, the radiation loss decreases but, in this case, it is the growth rate which decreases dramatically, leading again to higher energy consumption.

The energy consumption is reduced by 22% as a consequence of stopping the process at 20cm instead of 14cm.

5 CONCLUSIONS

The reduction of energy consumption during the polysilicon deposition requires: to reduce the power loss and to increase the polysilicon productivity.

The power loss by radiation can be reduced by enlarging the reactor capacities. By doing so, producing polysilicon in a 60 rod CVD reactor would save 11 kWh·kg⁻¹ compared to producing in a 36 rod CVD reactor. It can also be reduced if the reflectivity of the wall is improved, by selecting better materials or by surface treatment. In this case, the energy saving could be around 17 kWh·kg⁻¹.

The optimum deposition conditions have been presented, identifying the best conditions for increasing polysilicon productivity and decreasing energy consumption. The deposition temperature should be in the range of 1100-1200 °C, the greater the diameter the lower the temperature. The pressure within the reactor vessel should be around 6 atm.

Increasing the maximum rod diameter before stopping the process also increases productivity and reduces energy consumption. The estimated energy saving when increasing this diameter from the established value in the industry, 14cm, to 20cm is 13 kWh·kg⁻¹.

6 ACKNOWLEDGMENT

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REFERENCES

- [1] L. P. Méndez, Síntesis de clorosilanos para la industria fotovoltaica, Ph.D. thesis, Universidad Complutense de Madrid - Facultad de ciencias químicas (2009).
- [2] L. Rogers, Handbook of semiconductor silicon technology, Noyes Publications, 1990, Ch. Polysilicon preparation, pp. 33–94.
- [3] E. Bugl, R. Griesshammer, H. Lorenz, H. Hamster, F. Köppl, Method for the deposition of pure semiconductor material, Patent US4311545 (1982).
- [4] L. Hunt, Handbook of semiconductor silicon technology, Noyes Publications, 1990, Ch. Silicon precursors: their manufacture and properties, pp. 1–32.
- [5] K. Hashimoto, K. Miura, T. Masuda, M. Toma, H. Sawai, M. Kawase, Journal of the Electrochemical Society 137 (1990) 1000–1007.
- [6] A. Mozer, P. Fath, in: 3rd Solar Silicon Conference, 2006.
- [7] J. O. Odden, G. Halvorsen, H. Rong, R. Glockner, in: Silicon for the chemical and solar industry IX, 2008, pp. 75–89.
- [8] H. Schweickert, K. Reuschel, H. Gutsche, Production of high-purity semiconductor materials for electrical purposes, Patent US3011877 (1957).
- [9] H. Gutsche, Method for producing highest-purity silicon for electric semiconductor devices, Patent US3042494 (1962).
- [10] K. Reuschel, A. Kersting, Method for producing hyper-pure silicon, Patent US3057690 (1962).
- [11] G. del Coso, C. del Cañizo, A. Luque, Radiative energy loss in a polysilicon CVD reactor, Solar Energy Materials and Solar Cells, submitted (2010).
- [12] F. Köppl, H. Hamster, R. Griesshammer, H. Lorenz, Process for the deposition of pure semiconductor material, Patent US4179530 (1979).
- [13] G. del Coso, C. del Cañizo, A. Luque, Journal of the Electrochemical Society 155 (2008) D485–D491.
- [14] H. Habuka, T. Nagoya, M. Mayusumi, M. Katayama, M. Shimada, K. Okuyama, Journal of Crystal Growth 169 (1996) 61–72.
- [15] G. del Coso, Chemical decomposition of silanes for the production of solar grade silicon, Ph.D. thesis, Universidad Politécnica de Madrid - ETSIT (2010).