On track for Solar Grade Silicon through a Siemens process-type laboratory reactor: operating conditions and energy savings

A. Ramos\textsuperscript{1)}, C. del Cañizo\textsuperscript{1)}, J. Valdehita\textsuperscript{1)}, J.C. Zamorano\textsuperscript{1)}, A. Rodríguez\textsuperscript{2)} and A. Luque\textsuperscript{1)}

\textsuperscript{1)} Instituto de Energía Solar - Universidad Politécnica de Madrid, ETSI Telecomunicación, Avda. Complutense 30, 28040 Madrid, Spain

\textsuperscript{2)} Departamento de Ingeniería Química, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040, Madrid, Spain

Abstract

Polysilicon cost impacts significantly on the photovoltaics (PV) cost and on the energy payback time. Nowadays, the besetting production process is the so called Siemens process, polysilicon deposition by chemical vapor deposition (CVD) from Trichlorosilane. Polysilicon purification level for PV is to a certain extent less demanding that for microelectronics.

At the Instituto de Energía Solar (IES) research on this subject is performed through a Siemens process-type laboratory reactor. Through the laboratory CVD prototype at the IES laboratories, valuable information about the phenomena involved in the polysilicon deposition process and the operating conditions is obtained.

Polysilicon deposition by CVD is a complex process due to the big number of parameters involved. A study on the influence of temperature and inlet gas mixture composition on the polysilicon deposition growth rate, based on experimental experience, is shown.

Moreover, CVD process accounts for the largest contribution to the energy consumption of the polysilicon production. In addition, radiation phenomenon is the major responsible for low energetic efficiency of the whole process. This work presents a model of radiation heat loss, and the theoretical calculations are confirmed experimentally through a prototype reactor at our disposal, yielding a valuable know-how for energy consumption reduction at industrial Siemens reactors.

Introduction

For the first time in 2006, polysilicon for photovoltaics (PV) demand exceeded that for microelectronics \cite{1}. Polysilicon cost impacts significantly on the PV cost and on the energy payback time. In addition, polysilicon purification level for PV is to a certain extent not as critical as for microelectronics (it may be in the ~ 99.99999% purity range rather than in the 99.999999999%).

The lower purity requirements for PV polysilicon, called Solar Grade Silicon, allows process simplifications that lead to cost reductions \cite{2,3}. There exist different routes for
Solar Grade Silicon production. However, the so called chemical route (based on synthesis, distillation and deposition of chlorosilanes) is the besetting one.

At the Instituto de Energía Solar (IES), research on this topic is centered on the chemical route, the so-called Siemens process. In particular, it is focused on the polysilicon deposition step by chemical vapor deposition (CVD) from Trichlorosilane [4]. Note that the CVD step accounts for the largest contribution to the energy consumption of the polysilicon production process. In addition, this feedstock is responsible for a great part of the consumed energy in producing c-Si PV modules, by 28% [5].

Moreover, if analyzing the different contributions to the energy consumption of the CVD process, major losses are due to radiation. Other contributions to the energy consumption are heat loss due to convection, thermal conduction and the consumed heat due to the chemical reactions taking place.

Although there are theoretical models to calculate radiation heat loss in a CVD reactor [6], a deeper knowledge of the heat radiation behavior remains necessary, which is considered a key step in the overall process.

One of these models is presented in this paper, and the theoretical calculations are confirmed experimentally through a prototype reactor at our disposal. Then, this theoretical model is considered valid for radiation heat loss calculations in an industrial Siemens reactor to achieve ultimately, lower energy consumption.

Hereunder, we first report on some of the experiments that have been successfully carried out and the learnings involved. The complexity of the process due to the big number of parameters involved is shown. In particular, the influence of the temperature and the reactive gases concentration on the growth rate and power consumption, are introduced.

After stating our empirical experience of the CVD process, the peculiarities of our system and the complexity of operation, a theoretical model for radiation heat loss calculations is presented for both, an industrial size CVD reactor and our laboratory prototype. Finally, the validation of this theoretical model on the basis of empirical experience is presented and different scenarios, in order to achieve the goal of lower radiation heat losses, are proposed.

Experience with a laboratory scale reactor: complexity of the polysilicon deposition process

For proper research on Solar Grade Silicon through the Siemens process, it is necessary to know the optimal deposition conditions -fluid dynamics theory-, the thermal radiation effect of hot silicon rods -radiation heat transfer theory- and the electromagnetic theory, as an electric heating of the rod occurs. Research on chemical vapor deposition conditions for solar grade silicon production is performed through a laboratory CVD prototype.

All working conditions of the industrial Siemens process, except the pressure inside the reactor chamber, can be reproduced with our laboratory CVD prototype. Polysilicon deposition processes are developed for safety at a pressure of 800 mbar, instead of the typical industrial pressure of 6 bar. The relation between the main parameters involved in the process and the pressure inside the reactor chamber can be theoretically stated [7]. Therefore, valuable information about the phenomena involved in the deposition process and the operation conditions can be obtained with the laboratory prototype.

First, a high purity silicon rod is introduced inside the reactor. This rod is about 56 cm long, with a diameter around 0.7 cm. The rod is heated up above 1000°C thanks to
the electric current passing through it - joule effect heating. Once the desired conditions of temperature are reached in the reactor chamber, the reactive gases needed for the vapor phase reaction to occur are introduced. These mentioned gases are Hydrogen (H₂) and Trichlorosilane (SiHCl₃, TCS) and due to the CVD process, high purity silicon (polysilicon) is grown on the surface of the rod. Then, the rod diameter increases with time. Note that all the parameters of the polysilicon deposition process, except the pressure inside the reactor chamber, are time dependent along a deposition process.

The polysilicon deposition experiments conducted in this laboratory prototype reactor can be developed at deposition surface temperatures up to 1250°C. The reactive gases concentration at the entrance of the reactor chamber can also be varied.

Several experiments for a constant TCS:H₂ mass ratio and different deposition surface temperatures have been successfully carried out. Furthermore, experiments for different reactive gases concentrations for the same and constant deposition surface temperature had been conducted in the prototype reactor.

**Deposition surface temperature influence on the growth rate**

All experiments performed with the aim of studying the influence of the temperature on the growth rate, have been conducted considering a constant molar fraction and gas flow. The percentage of TCS of the gas mixture is 2% and H₂ is the 98% left. This corresponds to a TCS:H₂ mass ratio of 1.33:1.

Hereunder, the experimental results obtained from three polysilicon deposition processes developed in our laboratory prototype at temperatures of 1000, 1100 and 1150°C are presented in Table 1.

**Table 1**: Polysilicon growth rate at different deposition process temperatures.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>T[°C]</th>
<th>Time[min]</th>
<th>Si deposited[gr]</th>
<th>Growth rate[µm/min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1000</td>
<td>385</td>
<td>23.55</td>
<td>2.08</td>
</tr>
<tr>
<td>B</td>
<td>1100</td>
<td>430</td>
<td>50.46</td>
<td>3.38</td>
</tr>
<tr>
<td>C</td>
<td>1150</td>
<td>540</td>
<td>74.24</td>
<td>3.90</td>
</tr>
</tbody>
</table>

* Reactor chamber pressure: 800 mbar

The maximum growth rate measured is 3.9 µm/min at 1150°C. In Figure 1 the plot represents the growth rate depending on the rod surface temperature. It can be seen that a 62.5% growth rate increment is obtained from 1000 to 1100°C, meanwhile only an improvement of 15.4 % was obtained from 1100 to 1150°C.
Figure 1: Growth rate dependence on the rod surface temperature for polysilicon CVD processes conducted in the laboratory prototype reactor.

The strong dependence with the temperature of the polysilicon growth rate is evidenced. The growth rate decreases when the deposition surface is at 900-1000°C, low temperature regime, while it increases above 1100°C, in the high temperature regime. In Figure 2, a polysilicon seed rod before a deposition process and the rod after the experiment A are shown.

![Figure 2: Polysilicon seed rod before (bottom) and after (top) a CVD process, experiment A.](image)

**Reactive gases concentration influence on the growth rate**

To explore the influence of the reactive gases concentration on the growth rate, different experiments have been carried out at a constant deposition surface temperature of 1100°C. Volume concentrations of TCS of 2, 3 and 4% (TCS:H₂ mass ratio of 1.33:1, 2:1 and 3:1 respectively) were considered for each one of a total of three deposition experiments. The chamber pressure and the inlet gas flow are kept constant for all these experiments.
Polysilicon growth rates obtained are 3.38, 4.05 and 5.98 µm/min for TCS volume concentrations of 2, 3 and 4%, respectively. The strong dependence on the TCS concentration of the growth rate is put forward. Then, for the TCS concentrations range studied, the higher TCS:H₂ mass ratio, the faster the growth rate.

Discussion

It is experimentally tested that the polysilicon growth rate has a strong dependence with the temperature and reactive gases concentration, in particular TCS. For both parameters, the higher the surface temperature and the TCS concentration, the greater growth rate. These results are in agreement with that predicted by theory and simulations, in both trend and magnitude [8,9].

On the one hand, when the rate at which polysilicon deposition occurs is slower than the rate at which unreacted TCS arrives, it is said that the process is surface-reaction-limited. In this case the growth rate is primarily dependent on temperature and reactant concentration.

On the other hand, when the deposition rate becomes faster than the rate at which unreactive TCS arrives at the surface, then the process is said to be mass-transport-limited. Now the growth rate depends primarily on reactant concentration, reactor geometry and gas flow [10,11].

For the experiments A, B and C, we can assert that the process is surface-reaction-limited as the growth rate increases if the temperature does. For these three experiments, a similar gas flow can be assumed. In addition for each experiment, the same TCS:H₂ mass ratio, rod surface temperature and reactor geometry are considered.

Energy savings

A polysilicon deposition process in a CVD reactor comprises three main steps: heating, polysilicon deposition and cooling down. First, silicon seed rods are heated until the deposition process temperature, then the reactive gases begin to go inside the reactor chamber and the polysilicon deposition starts. When the silicon rods reach their maximum diameter, reactive gases go no longer inside the reactor chamber and the cooling down step starts.

In order to reduce the energy consumption of the whole process, the greater energy savings would be achieved diminishing the power requirements of the most energetic steps. Comparing the energy requirements of the heating step and the deposition process, the last one is responsible of the main part. From the experiments developed in our laboratory reactor, we obtain that for 9 hours deposition process at 1150°C, the energy consumption of the rod heating is 3.2% and the deposition process is responsible of the 96.8% left of the total energy consumed. The longer the deposition process, the larger the second percentage (compared to the first one). This can be scaled-up to an industrial Siemens process, with a typical batch time of 80-100 hours.

Energy losses during the deposition step are due to radiation and convection heat loss and chemical reaction heat consumption. For industrial scale Siemens reactors, radiation heat loss can assume between 65-75% of the total power if all the energy radiated by the rods towards the reactor wall is wasted. The heat consumption due to the chemical reaction is typically neglected; it corresponds to less than the 1.5% of the total power required. Convection losses decrease with the increase of the pressure and they sum up to 23.5-33.5% of the total amount of heat losses. Note that at the IES labs, the working pressure of our CVD prototype is 6-7 times lower than that at the industry.
This lower pressure in the prototype reactor causes the convection heat loss to assume a greater percentage of total energy losses.

From the above it is clear why efforts are put into reducing radiation losses for energy saving of the deposition process.

**Theoretical model for radiation heat loss calculations**

During a CVD polysilicon deposition process, in the deposition step, the power consumption is the amount needed to keep the silicon rods surface at the desired temperature, typically around 1150°C. Power supplied instantly must compensate for radiation and convection heat loss and the heat consumed by the chemical deposition reaction. The polysilicon growth rate is very slow; it is about microns per minute, so heat transfer during the deposition step is considered as a steady state process. Radiation heat loss assumes the great part of all power required instantaneously.

The rate of outgoing radiant heat per unit area from a surface, named radiosity, is the sum of the directly emitted heat flux and the incoming radiant heat flux proportionally to the surface reflectivity (Figure 3).

![Diagram of the outgoing radiant heat per unit area from the surface (radiosity).](image)

**Figure 3:** Diagram of the outgoing radiant heat per unit area from the surface (radiosity).

The directly emitted energy flux per unit area \(E\) is dependent on the surface emissivity \(\varepsilon\), the surface temperature \(T\), and the Boltzmann constant \(\sigma\). Then, radiosity \(J\), depends on the same parameters, and furthermore, on the surface reflectivity \(\rho\), and the incoming radiant heat flux per unit area \(G\), (Eqs. 1 and 2). The directly emitted energy flux, the radiosity (sum of the directly emitted and the reflected radiant flux) and the incoming radiant heat flux per unit area are expressed in watts per square meter, W/m².

\[
E = \varepsilon \cdot \sigma \cdot T \quad (1)
\]

\[
J = E + \rho \cdot G \quad (2)
\]

The surface reflectivity is defined as: \(\rho = 1 - \varepsilon\), then, the incoming radiant heat flux per unit area can be expressed as shown in Eq. 3.
\[ G = \frac{1}{1 - \varepsilon} (J - E) \]  

(3)

The net heat flux exchanged \((Q)\) in watts, \(W\), by any surface \(S_i\), is obtained from the difference between the radiosity and the incoming radiant heat flux. The net heat flux exchanged corresponds to the radiation heat losses (Eq. 4).

\[ Q_i = S_i \cdot (J_i - G_i) \]  

(4)

For an industrial size reactor, the net heat flux calculations are not straightforward. The geometrical disposition of the seed rods in the reactor chamber must be considered; for the sum of the radiosity of each surface these need to be weighted by the configuration factors (to consider the heat flux going from one surface to another).

The configuration factor \((F_{i,j})\) is defined as the fraction of energy leaving a certain surface \(i\) that arrives at the surface \(j\). For example, to calculate the incoming radiant heat flux from one rod \(j\) to another rod \(i\) (Eq. 5), the radiosity of the surface \(j\) is weighted by the fraction of energy leaving the surface \(j\) that reaches the surface \(i\) \((F_{j,i})\).

\[ G_j = F_{j,i} \cdot J_i \]  

(5)

The calculation of the configuration factor is done using a geometric method called \textit{Hottel's crossed-string method}\cite{12}. Then, the net radiation heat flux exchanged for a certain surface \(i\) can be expressed as it is shown in Eq. 6. Where \(n\) is the total number of surfaces. Note that for a Siemens reactor, the reactor wall input must be considered.

\[ Q_j = S_j \cdot (J_j - G_j) = S_j \cdot J_j - \sum_{j+1}^n S_j \cdot F_{j,i} \cdot J_i \]  

(6)

Then, for a Siemens reactor of \(n-1\) rods, an \(n\)-equations system (Eq. 7) needs to be solved. Eq. 7 is obtained combining Eqs. 4 and 6. Radiosities of each surface \((J_i)\) are the unknowns of the system. The temperature of the rod surfaces and the reactor wall is known, as well as the corresponding surface emissivities.

\[ A_i \cdot \frac{1}{1 - \varepsilon_i} J_i = \sum_{j=1}^n S_j \cdot F_{i,j} \cdot J_j = A_i \cdot \frac{E_i}{1 - \varepsilon_i} \sigma \cdot T_{i}^4 \]  

\(i = 1, \ldots, n\)  

(7)

Once \(J_i\) is obtained for the \(n\) surfaces, the incoming radiant heat flux per unit area \((G_i)\) is also known (Eq. 3). Thereby, the net radiation heat exchanged by each surface \((Q_i)\) is obtained substituting \(J_i\) and \(G_i\) in Eq. 4.

Detailed application of this model and numerical results for the radiation heat losses calculations for three state-of-the-art industrial size reactor configurations can be found in \cite{6}.

7
Model validation: implementation for a laboratory scale reactor

The final objective is to propose a validation of the theoretical model presented for radiation heat loss calculations on the basis of experimental experience through a laboratory scale reactor.

For the laboratory scale reactor, the above equations have an easier application. We can consider one or more rods and different dispositions in order to prove that the radiation heat loss predicted by the theoretical model is in agreement with the empirical results obtained.

Three different scenarios are presented in Figure 4. In the scenario 1 it is considered one single rod placed in the center of the IES prototype CVD reactor. The scenarios 2 and 3 consider two and four rods placed inside the reactor chamber as it is shown in Figure 4.

Now, the theoretical model for the radiation heat loss calculations is applied for the different proposed scenarios. The three of all can be reproduced in our prototype CVD reactor. Note that for the further model validation, all the numerical results showed below correspond to the particular CVD prototype geometry.

Then, for the calculations hereunder presented, the emissivity of the silicon rods is assumed to be 0.7 and that of the reactor wall, made of stainless steel, 0.5. The inner diameter of the reactor wall is 15.5 cm and the initial rod diameter is 0.7 cm. Reactor wall temperature is kept constant at 80°C and the rods surface temperature is 1150°C. In addition, the rod radius growth along a polysilicon deposition process is taken into account.

For the scenarios 1, 2 and 3, a 2, 3 and 5-equations system need to be solved, respectively. For all the three cases the system of equations can be expressed as Eq. 8.

\[
\begin{bmatrix}
A \\
J
\end{bmatrix}
= 
\begin{bmatrix}
B
\end{bmatrix}
\]

(8)

Eqs. 9, 10 and 11 describe the elements of the matrices in Eq. 8.

\[
A(i, j) = -S_{ij}F_{ij}, \quad i \neq j, \quad i, j = 1, \ldots, n
\]

(9)

\[
S_{ij} = \frac{2\pi R_i R_j}{\pi (R_i + R_j)^2}
\]

(10)

\[
F_{ij} = \frac{\frac{R_i}{R_i + R_j}}{\frac{R_i}{R_i + R_j} + \frac{R_j}{R_i + R_j}}
\]

(11)
\[ A(i,j) = S_j \left( \frac{1}{1 - \varepsilon_j} - F_{i,j} \right) \quad i = 1, \ldots, n \]  
\[ B(i) = S_i \frac{\varepsilon_i}{1 - \varepsilon_i} \sigma T_i^4 \quad i = 1, \ldots, n \]

**Scenario 1**

In this case, one single rod is placed in the center of the prototype reactor chamber. Then, all heat radiated from the rod arrives at the reactor wall, the main part is absorbed by the wall and a little part is reflected back. There is also a small amount of direct emitted radiation flux from the wall inside the reactor chamber, but notice that this small amount, plus the reflected part from the incoming flux, is not only reaching the rod surface, but also the reactor inner wall.

Geometrical factors for this scenario are calculated for a rod diameter from 0.7 to 3.0 cm. According to Eq. 8, the 2-equations system is raised and the radiosities for the silicon rod and the reactor wall are obtained. Then the net radiation heat exchanged of the rod is calculated (Eq. 4). In Figure 5 numerical results are presented.

In Figure 5, it can be observed how the radiosity of the rod (due to its emissivity and higher temperature) is much higher than the radiosity of the wall. As the silicon rod gets thicker the radiosities raise, as the power loss through radiation does. However, the radiated power loss per unit area decreases as the rod diameter increases. This can be explained because the greater the rod diameter, the larger the incoming flux from the wall reaching its surface.

**Figure 5:** Radiated power loss [W/m²] (dashed line), total radiated power loss [W] (solid line), rod radiosity [W/m²] (crosses) and wall radiosity [W/m²] (bullets). Scenario 1.
Scenario 2
In this scenario, two rods are placed in the middle of the prototype reactor chamber. All heat radiated from each rod arrives at the reactor wall and also reaches the other rod.
Again, geometrical factors for this scenario are calculated, and according to Eq. 8, the 3-equations system is solved. There is a 4 cm separation between the two rods. The same tendencies as in Figure 5 would be shown if the radiosities, the radiated power loss per unit area and the total radiated power are plotted.

Scenario 3
Now, two pairs of rods are placed in the middle of the prototype reactor chamber (Figure 4). Each rod is placed at the corner of a 4 cm side square. As was the case in scenario 2, again all heat radiated from each rod arrives at the reactor wall and also reaches the other rods.
Now a 5-equations system is solved. Again, the same tendencies as in Figure 5, but steeper, would be shown if the radiosities, the radiated power loss per unit area and the total radiated power are plotted.

Comparison of the different scenarios
The average values, from 0.7 to 3 cm rod diameter, of the radiated power loss per unit area and the corresponding savings related to the scenario 1 are collected in Table 2. It is shown that the heat radiation savings per unit area of the scenarios 2 and 3, related to the scenario 1 are similar, 11.2 and 13.9%, respectively.
Therefore, depending on the rods number and disposal inside the reactor chamber, power loss through radiation changes. As radiation loss savings for the cases 2 and 3 are quite close, the scenario 3 is modified to scenario 3bis, in which each rod is placed at the corner of a 3.2 cm side square. For the scenario 3bis the radiation savings increase as the rods are placed closer one to another. The power loss through radiation is now 17.1% lower related to the scenario 1 (Table 2).

Table 2: Radiated power loss per unit area for the three scenarios and heat radiation savings per unit area for all cases, related to the scenario 1.

<table>
<thead>
<tr>
<th>Scenario</th>
<th>Number of rods</th>
<th>Radiated power loss $[\text{W/m}^2]$</th>
<th>Savings [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>$1.50 \times 10^5$</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>2</td>
<td>$1.33 \times 10^5$</td>
<td>11.2</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>$1.29 \times 10^5$</td>
<td>13.9</td>
</tr>
<tr>
<td>3bis</td>
<td>4</td>
<td>$1.24 \times 10^5$</td>
<td>17.1</td>
</tr>
</tbody>
</table>

In Figure 6, the radiated power loss per unit area, in watts per square meter, for all the four scenarios is represented.
Figure 6: Radiated power loss [W/m²] for the four scenarios. Scenario 1 (solid line), scenario 2 (dashed line), scenario 3 (dotted line) and scenario 3bis (bullets).

Regarding to our final aim of validating the theoretical model, scenarios 1, 2 and 3bis are selected (differences in between these three scenarios in terms of radiation heat loss are at least of the 6.7%).

The scenario 1 has already been reproduced in our CVD prototype reactor. The amount of radiated heat loss empirically obtained is very close to the theoretical values showed above (differences under 8%). Next step in progress is to reproduce in the prototype reactor the scenarios 2 and 3bis to validate the theoretical model.

Conclusions
First, the complexity of operation of a CVD prototype reactor is stated and the strong dependence with the temperature and the TCS concentration of the polysilicon growth rate is evidenced, both on the basis of empirical experience. For the range of temperatures and TCS concentrations studied, polysilicon deposition rate increases as one of the parameters does while the other is maintained constant. These results are in agreement with that predicted by simulations and theory.

Furthermore, the polysilicon deposition by CVD accounts for the largest contribution to the energy consumption of the polysilicon production process. In addition, major heat losses along a polysilicon deposition process are due to radiation. Theoretical models to calculate radiation heat loss in a CVD reactor exist. A theoretical model validation for radiation heat loss in an industrial Siemens reactor through a CVD prototype reactor is presented. Three different scenarios are proposed for such validation. The case for one single rod placed in the center of the reactor chamber has already been reproduced in our prototype. The empirical results obtained and the
theoretical values fit together quite well. Next step in progress will be reproducing the two scenarios left, to finally validate the theoretical model for radiation heat loss.

Acknowledgements

Mayte Sanchez and Ana Peral are acknowledged for helpful discussions.

References

2. S. Singer, Photovoltaics: Getting cheaper, Eco Queen of Green, 2007
6. G. del Coso, C. del Cañizo and A. Luque, How to diminish the radiation loss in a Siemens-type reactor, Silicon for the Chemical and Solar Industry X, 2010