Available online at www.sciencedirect.com
ScienceDirect
Journal of Crystal Growth 299 (2007) 165–170
JOURNAL OF CRYSTAL GROWTH
www.elsevier.com/locate/jcrysgro

Temperature homogeneity of polysilicon rods in a Siemens reactor

G. del Coso*, I. Tobías, C. Cañizo, A. Luque

Instituto de Energía Solar, Universidad Politécnica de Madrid, E.T.S.I. Telecomunicación, Ciudad Universitaria, 28040 Madrid, Spain

Received 7 July 2006; received in revised form 14 November 2006; accepted 5 December 2006
Communicated by J.J. Derby
Available online 22 January 2007

Abstract

Siemens process productivity can be limited by non-homogeneous temperature profile in polysilicon rods. To overcome this limitation high-frequency current sources have been proposed. An analysis is presented which, based on electromagnetic and heat transfer theory, studies temperature and current density profiles within the rods. Two linked differential equations have been numerically solved by use of non-linear methods. The solution of these equations shows that by means of an increase in current frequency, skin effect takes place, heat generation in the inner part of the rod is decreased and therefore temperature homogeneity increases. The effect of the reflectivity of reactor walls is also analysed and reveals that temperature homogeneity can be improved by minimizing radiation losses better than by heating with high-frequency current sources.

PACS: 40/44

Keywords: A1. Heat transfer; A1. Magnetic fields; A2. Siemens process; B2. Semiconducting silicon

0. Introduction

The strong photovoltaic (PV) market growth relies on crystalline silicon, using as raw material highly purified silicon, which is known as polysilicon. Traditionally, polysilicon for the solar industry has been obtained from the microelectronic industry, using off-spec material or the excess of installed capacity of polysilicon producers. But the tremendous growth of the PV industry has produced a quick change of the situation: while in 2000 PV only demanded 10% of the polysilicon, in 2005 PV demand has become comparable to that of the microelectronic industry, in the range of 15.000 t [1], and demand is exceeding production capacity. A scenario of silicon shortage is threatening already the growth of the PV sector, making the need of an independent source of polysilicon a strategic issue for the future of PV. Besides, optimization of the purification process to address solar cell requirements must be pursued in order to reduce the cost of the material as much as possible.

For the moment, the only route in the market to produce polysilicon is based on the synthesis and purification of chlorosilanes (monosilane MS—SiH_4—or trichlorosilane TCS—$SiHCl_3$), and their subsequent reduction in a chemical vapor deposition (CVD) reactor to solid Si. Nowadays, almost 77% of the polysilicon produced worldwide is obtained from TCS in a CVD reactor known as "Siemens reactor" [2].

The Siemens reactor consists of a 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 thermal decomposition of TCS in a hydrogen environment. The experimental conditions that have to be met to achieve a successful growth are somewhat complex. For example, electric current flowing through the rod generates an uneven temperature profile within the rod, mainly due to: (a) the inner part of the carrier rod is thermally insulated by the outer region or "skin", becoming progressively hotter relative to the surrounding outer region; and (b) silicon electric conductivity increases with temperature, then when the centre of the rod becomes hotter conductivity increases in that region, even more current flows there and more heat is

*Corresponding author. Tel.: +34 91 544 10 60; fax: +34 91 544 63 41.
E-mail address: gdelcoso@ies-def.upm.es (G. del Coso).

0022-0248/$ - see front matter
doi:10.1016/j.jcrysgro.2006.12.004

created. Care must be taken, because with such an uneven temperature profile, thermal stresses could break the rod, and temperature on the rod centre must be under melting temperature (1687 K) in order to avoid its breaking-down. These effects limit the maximum rod diameter that can be achieved, and so process productivity.

A way to overcome this limitation has been proposed, based on the use of high-frequency current sources to heat the rods [3]; due to the well-known skin effect in a conductor [4], most of current density migrates to the outer region. In a semiconductor the skin effect does not work exactly as in a conductor, as will be explained later, but qualitatively it can be expected that in a Siemens reactor with rods heated by a high-frequency current source the Si rod will experience two opposed effects: the higher temperature on the centre would cause that more current density flows by the inner region, but on the other hand, the high-frequency current would push current density to the outer region. By improving temperature profile uniformity, the danger of rod collapse by reaching melting temperature is diminished, and maximum rod diameter can be increased and so process productivity.

The aim of this paper is to discuss the convenience of using high-frequency current sources in a Siemens reactor, analysing the influence of frequency in temperature and current density profiles of silicon rods and evaluating some other alternatives to minimize break-down risk.

1. Thermal and electrical model for the Siemens reactor

Consider a cylindrical silicon rod, vertically placed, with an arbitrary radius R. A mixture of hydrogen and TCS flows around it from bottom to top, and the whole system is surrounded by a cylindrical reflective wall, with a radius R_{outer}, characterized by its emissivity ξ_0. This is a simplified, symmetric model of a rod inside the deposition reactor, where the mirror simulates radiation coming from other rods or reflected at the wall.

A time-harmonic electrical current passes through the Si rod, and due to the symmetry of the problem, far away enough from the bottom and top edges current density J flows exclusively in the z-direction, and there is not any dependence with θ or z coordinates ($\mathbf{J} = J(r)\cdot\mathbf{u}_z$) [5,6]. Note that in the last formula J is a complex magnitude, the real current density being $J(r,t) = \mathrm{Re}(J(r)\mathrm{e}^{\mathrm{j}\omega t})$, where j stands for $\sqrt{-1}$ and ω is the current angular frequency. The electric field, $\mathbf{E}$, that generates this current density has the same direction as $\mathbf{J}$, according to $\mathbf{J} = \sigma\cdot\mathbf{E}$. Thus $\mathbf{E} = E(r)\cdot\mathbf{u}_z$, E being a complex magnitude as well.

Heat inside the semiconductor is generated by Joule effect, giving a radial-dependent temperature distribution $T(r)$. There is a strong dependence of electric conductivity σ with temperature, so that there is also a radial non-uniform conductivity, which causes a modification of the current density inside the rod. Assuming that at high temperatures the silicon material behaves as intrinsic, carrier densities increase with temperature so that even though electron and hole mobilities decrease, conductivity increases with higher temperatures. An analytical expression for $\sigma(T)$ can be deduced from Refs. [7,8].

Maxwell's equations inside the semiconductor lead to the following Helmholtz equation for the electric field:

$$\nabla^2 E + \kappa^2 E = 0, \tag{1}$$

where $\kappa^2 = \mu\omega^2\varepsilon - \mathrm{j}\omega\mu\sigma(T(r))$, with $\mu = \mu_0$ the magnetic permeability and $\varepsilon = 11.9\cdot\varepsilon_0$ the dielectric permeability. Steady state has been considered and therefore temperature dependence on time has been neglected. It is a good assumption because the temperature evolves much slower than the electric field.

It should be noted that the current density $\mathbf{J} = \sigma\cdot\mathbf{E}$ does not satisfy Eq. (1) due to the temperature dependence—and therefore radial dependence—of σ.

Regarding the heat transfer within the semiconductor, the following equation is fulfilled under steady-state conditions [9]:

$$\nabla(k\nabla T) + q = 0, \tag{2}$$

where k is the thermal conductivity of Si, and q the heat generation per unit of volume, defined as $q(T,r) = |J(r)|^2/\sigma(T)$ [10].

Steady-state condition is considered also in this case; although deposition takes place and changes geometry, conduction sets a temperature profile much faster.

Dependence of k on temperature and its derivative, k', can be obtained by linear interpolation of tabulated data (from 200 to 1681 K) presented in Ref. [11].

Taking into account the symmetries in the problem, Eqs. (1) and (2) yield

$$\frac{\partial^2 E}{\partial r^2} + \frac{1}{r}\frac{\partial E}{\partial r} + \kappa^2\cdot E = 0, \tag{3}$$

$$\left(\frac{\mathrm{d}^2 T}{\mathrm{d}r^2} + \frac{1}{r}\frac{\mathrm{d}T}{\mathrm{d}r}\right) + \frac{k'(T)}{k(T)}\left(\frac{\mathrm{d}T}{\mathrm{d}r}\right)^2 + \frac{\sigma(T)|E(r)|^2}{k(T)} = 0 \tag{4}$$

with boundary conditions for Eq. (3):

$$\frac{\partial E}{\partial r} = 0 \quad \text{on } r = 0, \tag{5}$$

$$I_{\text{tot}} + 0\cdot j = \int_\Omega \sigma\cdot E\,\mathrm{d}\Omega \tag{6}$$

and for Eq. (4):

$$\frac{\partial T}{\partial r} = 0 \quad \text{on } r = 0, \tag{7}$$

$$-k\frac{\partial T}{\partial r} = h(T - T_{\mathrm{g}}) + q_{\text{net}} + P_{\text{reaction}} \quad \text{on } r = R, \tag{8}$$

where Ω is rod's circular section, h is the convection coefficient, P_{reaction} means power consumed by the chemical reaction per surface unit and T_{g} is the gas temperature. q_{net} is the net radiant heat transfer from the silicon rod surface to the outer surface and fulfils the following expression [9]:

$$q_{\text{net}} = \xi \frac{\xi_0}{\xi_0 + \xi(1-\xi_0)R/R_{\text{outer}}} \vartheta(T^4 - T_0^4)$$

∂ being Stephan–Boltzmann constant, ξ is silicon emissivity, ξ_0 is wall emissivity and T_0 is outer surface temperature. Assuming that the outer surface is made of opaque material its reflectivity is $1-\xi_0$. Eq. (6) sets that electric current through the rod is I_{tot}, and Eq. (8) sets that the inner heat, transferred to surface by conduction, is dissipated on the surface by convection, radiation and endothermic reaction.

1.1. Convection coefficient estimation

The convection coefficient depends on the gas mixture (species and composition) and the flow regime within the reactor chamber. It is necessary to know if convection is forced or free, because different analogies would be used to estimate convection coefficient [9]. Therefore, to take a decision about that, the characteristic velocities for the forced flow and for the buoyancy have been compared. For the forced flow the characteristic velocity is the volumetric flow divided by cross-sectional area, and the characteristic measure for the velocity driven by buoyancy is defined by $v_{\text{buoyant}} = (g\beta\Delta TL)^{1/2}$ [12], where g is gravitation constant, β is thermal expansivity of the gas, ΔT is the temperature difference between that of the entering gas and that of the surface and L is the length of the rod.

Under reactor conditions presented in Table 1 [13], and assuming a chemical reaction efficiency of 30%, convection can be sorted as free.

The convection coefficient can then be estimated at $T_{\text{m}} = (T_{\text{s}} + T_{\text{g}})/2$ from [9]

$$h = \frac{k}{L}\left[0.825 + 0.387Ra^{1/6}\left[1+\left(\frac{0.492}{Pr}\right)^{9/16}\right]^{-8/27}\right]^2, \tag{9}$$

where Re is the Reynolds Number, Pr the Prandtl Number and Ra the Rayleigh number. The value of h and other parameters related to the fluid dynamics are presented in Table 2.

Some transport properties of the gas mixture, such us viscosity, thermal conductivity, specific heat or density, have been estimated theoretically with methods described in Refs. [12,14,15].

1.2. Power reaction estimation

Even though the Si deposition reaction taking place on the rod surface is assumed to be a two-step reaction [13,16], it can be simplified as follows [17]:

$$SiHCl_3 + H_2 \leftrightarrow Si + 3HCl. \tag{10}$$

Thus, power dissipated on the chemical reaction, per surface unit, is

$$P_{\text{reaction}} = \Delta H_{\text{r}} \rho_{\text{si}} v_{\text{g}}, \tag{11}$$

where ΔH_{r} is reaction enthalpy and v_{g} is silicon growth rate. ΔH_{r} is calculated by means of the equation

$$\Delta H_{\text{r}}(T_{\text{s}}) = \Delta H_{\text{r}}^0 + \int_{T_0}^{T_{\text{s}}} \Delta C_p \mathrm{d}T, \tag{12}$$

where index 0 means standard conditions (0 °C, 1 atm) and Δ is an operator that stands for subtraction of reactants properties, weighted by its stoichiometric coefficients, from product properties, weighted as well. Reaction enthalpy is obtained applying Δ operator to formation enthalpy. Under the conditions presented in Table 1 the values listed in Table 3 are obtained.

2. Results

Interesting conclusions can be derived by solving the system of linked differential Eqs. (3), (4). They were numerically solved considering non-linear methods. First, both equations were approximated by finite difference, using numerical derivatives that provide a system of non-linear equations. The system was solved, mainly, by

Table 2
Flow calculated values

Mixture gasses flow	$468.47\,\text{l}\,\text{min}^{-1}$
Forced flow velocity	$0.029\,\text{m}\,\text{s}^{-1}$
Buoyancy velocity	$3.813\,\text{m}\,\text{s}^{-1}$
Pr	0.874
Re	297.51
Ra	5.23×10^9
Convection coefficient h	$19.33\,\text{W}\,\text{m}^{-2}\,\text{K}^{-1}$

Table 3
Reaction parameters

ΔH_{r}	$235.41\,\text{kJ}\,\text{mol}^{-1}$
P_{reaction}	$2604.64\,\text{W}\,\text{m}^{-2}$

Table 1
Set of conditions for the Siemens process

Rod surface temp. T_{s}	1423 K	$SiHCl_3$ molar fraction	0.05	Pressure	1 atm
Gas temp. T_{g}	673 K	H_2 molar fraction	0.95	Si growth rate	$8\,\mu\text{m}\,\text{min}^{-1}$
Rod radius	7.5 cm	Reflective wall radius	15 cm	Rod length L	1 m
Wall reflectivity	0.8				

Newton method, although other non-linear methods were used to improve the convergence. Note that while Eq. (3) has complex magnitudes, Eq. (4) is composed of real magnitudes and both are linked by E and T. E appears in Helmholtz Eq. (3), as a complex and in Eq. (4) as a complex modulus. This link forces us to separate the system into two different non-linear subsystems, corresponding to each equation, one that belongs to complex field and other that belongs to real field. By means of an iterative method the linked system can be solved by solving separately each subsystem.

The finite-difference system is made of 500 nodes along the radius, which means 1000 unknowns and 1000 non-linear equations. The calculations in this study are performed on a personal computer Pentium 4 with 4 GB RAM. To solve the system 40% of CPU and 1% of RAM are used during 10 min.

2.1. Temperature profiles as a function of frequency

In Fig. 1 temperature profiles within the silicon rod are presented, showing the dependency on the current frequency, while in Fig. 2 current densities that generate those temperature profiles are shown. Reactor conditions are those shown in Tables 1–3.

At low frequency, more current density tends to flow by the hotter centre than by the surface, but when frequency increases current density is pushed to the outer region of the semiconductor rod due to the skin effect, and, therefore, heat generation on the inner region decreases. Thus temperature profile close to the centre becomes flatter with frequency rising.

It can be seen that, even though at 50 kHz the skin effect begins to be noticed, the temperature profile is still quite uneven. Precise information about the importance of the effect is given in Fig. 3, showing the difference between temperature at the centre and at the surface as a function of frequency.

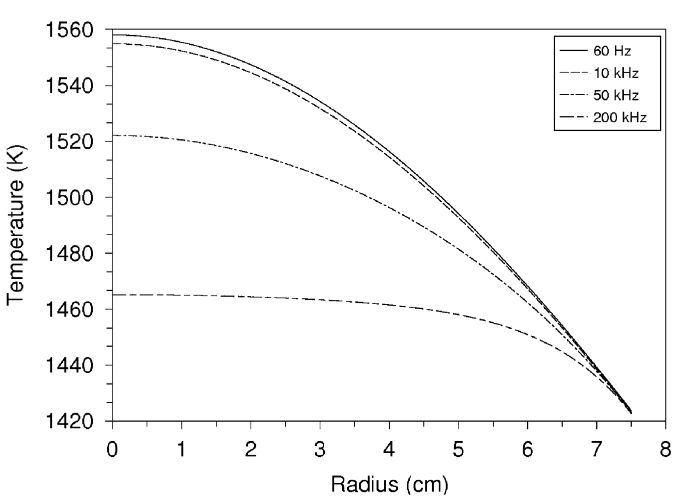

Fig. 1. Temperature profiles within the silicon rod depending on current frequency.

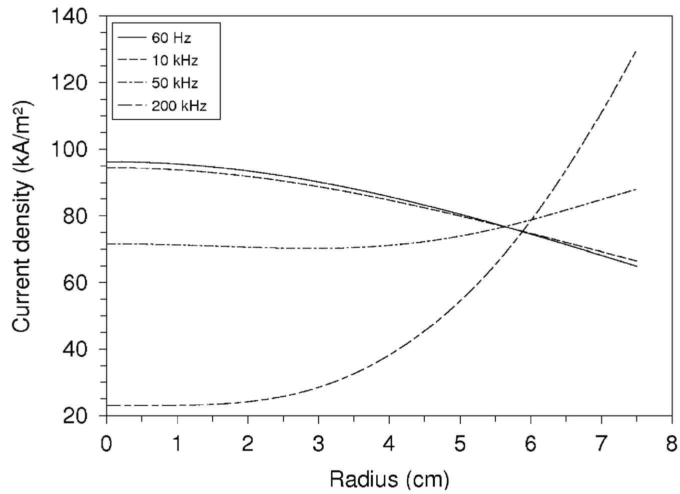

Fig. 2. Current density profiles within silicon rod depending on current frequency. Current density profiles generate temperature profiles presented in Fig. 1.

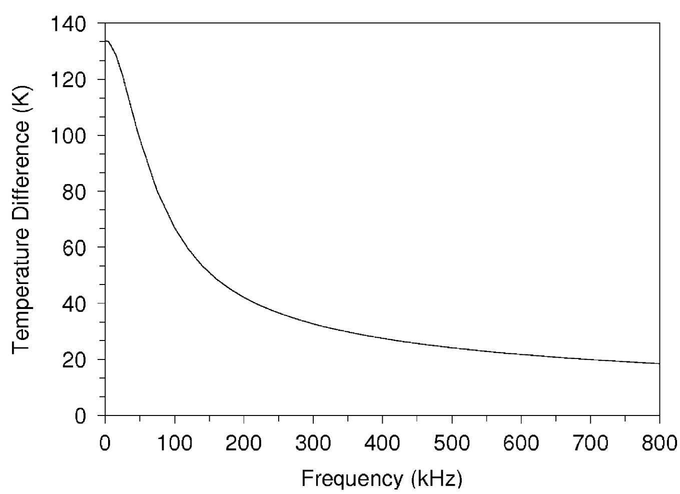

Fig. 3. Temperature difference between rod centre and surface as a function of frequency.

It can be appreciated that the first part of the curve (0–200 kHz) decreases sharply with frequency, and at 200 kHz the temperature difference has already been reduced 70%. For higher frequencies the slope is quite smaller, there is not a noteworthy improvement in temperature flatness by going beyond 200 kHz.

High-frequency current sources not only generate more even temperature profiles, they also require less electric current to set the optimal temperature on the surface rod. Considering that surface temperature is constant, when frequency increases a flatter temperature profile is obtained, with lower temperatures along the rod, and so lower conductivity. Thus, lower current is required to generate the power needed to set the surface temperature. This is confirmed by Fig. 4, in which RMS current needed to obtain a surface temperature of 1423 K is presented.

There are other factors that can modify the temperature profile dependence on frequency; in particular, analysis of

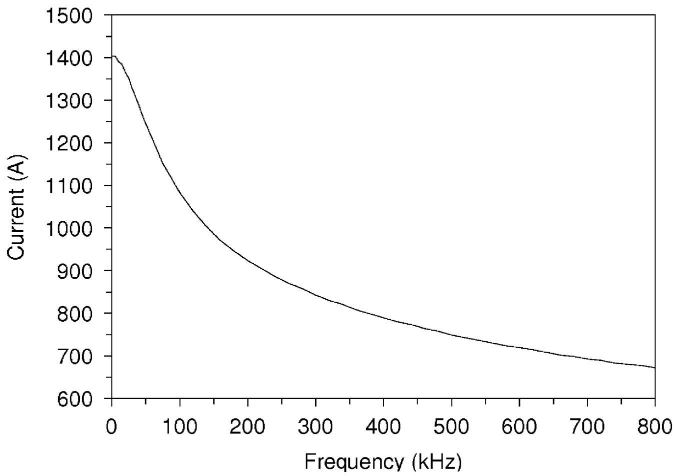

Fig. 4. RMS current needed to set surface temperature at 1423 K.

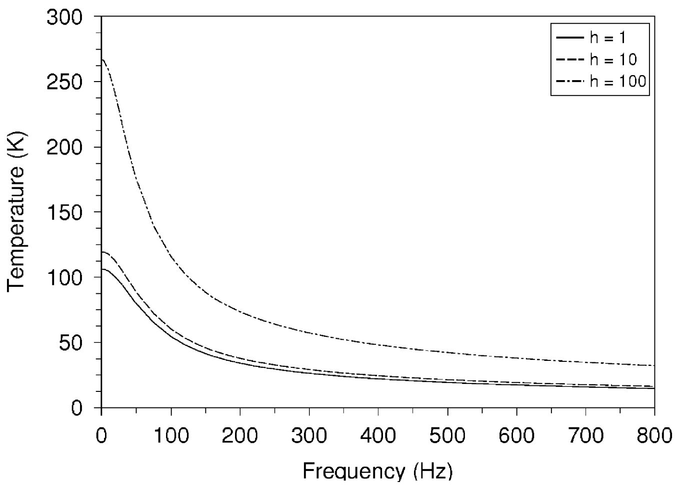

Fig. 5. Dependence on frequency of temperature difference between the centre and the surface of the rod. Three different convection coefficient values are considered, $h = 1$, 10, 100 W m^{-2} K^{-1}. Surface temperature is 1423 K.

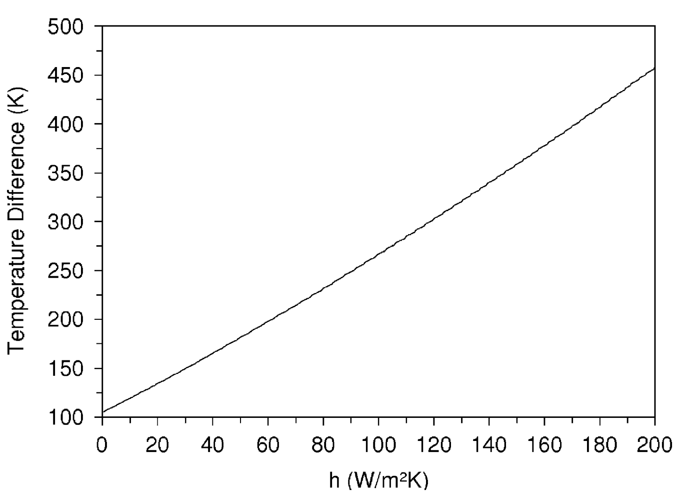

Fig. 6. Dependence on convection coefficient of temperature difference between the centre and the surface of the rod. A 60 Hz current has been considered, surface temperature: 1423 K.

the influence of convection and of wall reflectivity is presented in the next sections.

2.2. The role of heat convection

The role of heat convection on temperature profile is presented in this section, where the convection coefficient h is modified keeping other parameters constant with the values set in Tables 1–3. Fig. 5 shows how temperature dependence on frequency changes as h increases, making the temperature profile more uneven. The reason is that a higher h value cools better the silicon rod, and surface temperature decreases relative to that of the centre region.

For a particular electric current frequency, a linear dependence of temperature difference on convection coefficient is observed, as can be seen in Fig. 6 for the case of 60 Hz.

Convection coefficient cannot help to increase silicon growth, because even for very small h values temperature difference is still high (and therefore an uneven temperature profile is obtained). The reason is that radiation is the main cooling phenomenon. But, on the other hand, if h grows the effect can be very harmful, increasing the temperature difference and thus minimizing maximum silicon rod diameter.

2.3. Influence of wall reflectivity

Inside the reactor the rod is illuminated by neighbouring rods and by the reflecting walls. This is an important effect as shown in the following graphs.

Dependence on frequency of rod temperature difference between the centre and the surface has been calculated for different wall reflectivity values. Results are shown in Fig. 7. Those values are selected according to heat radiation loss, if maximum loss corresponds to $\xi_0 = 1$, the following values correspond, respectively, to 75%,

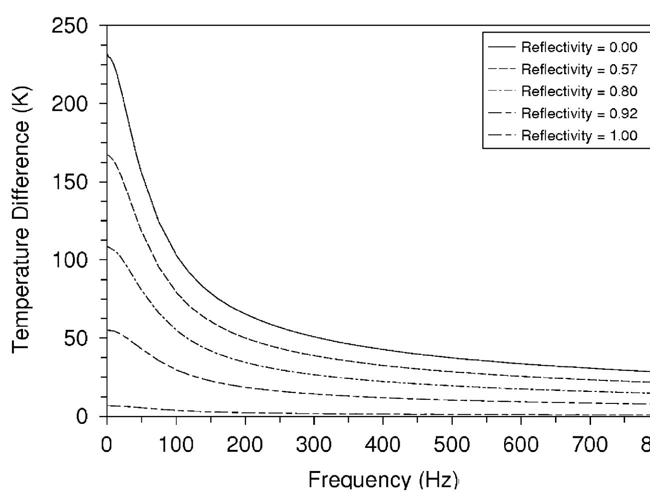

Fig. 7. Dependence on frequency of temperature difference between the centre and the surface of the rod. Five different wall reflection values are considered, surface temperature: 1423 K.

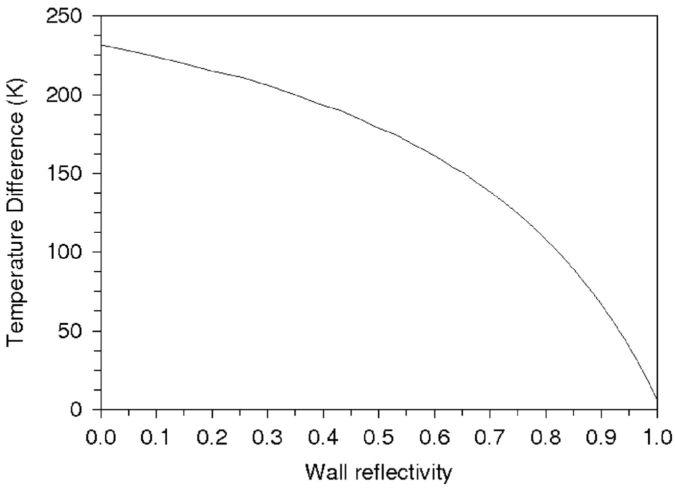

Fig. 8. Dependence on wall reflectivity of temperature difference between the centre and the surface of the rod. A 60 Hz current has been considered, surface temperature: 1423 K.

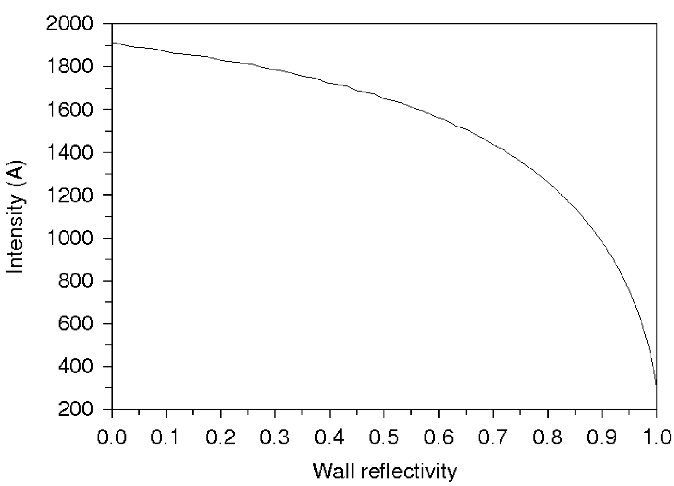

Fig. 9. RMS current needed to set surface temperature at 1423 K. A 60 Hz current has been considered.

50%, 25% and 0% of this maximum loss. The analysis is completed by a particularization for a 60 Hz current source, presented in Fig. 8.

It can be realized that wall reflectivity has a strong influence on temperature profile, being a parameter that can help to minimize temperature gradients within the rod. If wall reflectivity is increased, heat radiated by the rod is sent back and therefore cooling is reduced. As long as cooling becomes lower, surface temperature will tend to be closer to that of the centre.

A smoother temperature profile requires less RMS current, as can be seen in Fig. 9, and, in this case, also less electric power to set deposition temperature on the surface. When radiation losses decrease, the power needed to heat the rod is lower. It does not happen when high-frequency current sources are used, even though less RMS current is required when frequency is increased, the power needed remains constant.

3. Conclusions

Different alternatives have been analysed in order to improve Siemens process. High-frequency current sources produce the so-called skin effect, making temperature profile within the rod smoother. This is quite important in order to avoid the thermal stresses breaking slim rods and therefore more silicon can be deposited before stopping the process. Wall reflection can help to reduce thermal stresses. By increasing wall reflection, effective radiation is decreased in the rod and an even temperature profile is obtained. Gas flow inside the reactor vessel is another important factor to take into account, because a high convection coefficient can be harmful for silicon growth, limiting maximum rod diameter.

In order to increase silicon growth per silicon rod, high-frequency current sources and sufficiently reflective walls are improvements that can be implemented. Thermal stresses would decrease and maximum diameter would increase. But although high-frequency current source generates higher temperature homogeneity in the rod, that could be achieved better by minimization of radiation losses.

References

[1] M. Rogol, Silicon and the solar sector, in: The Third Solar Silicon Conference, Munich, 2006.
[2] B. Ceccaroli, in: A. Luque, S. Hegedus (Eds.), Handbook of Photovoltaic Science and Engineering, Wiley, New Jersey, 2003, p. 156.
[3] Chemical vapor deposition system for polycrystalline silicon rod production, US Patent 2003/0127045, 2003.
[4] L. Knockaert, IEEE/ACES International Conference on Wireless Communications and Applied Computational Electromagnetics, 2005, pp. 309–312.
[5] M.J. Tsuk, J.A. Kong, IEEE Trans. Microwave Theory Tech. 39 (8) (1991) 1338.
[6] L. Knockaert, Microwave Opt. Technol. Lett. 43 (1) (2005) 1.
[7] S. Grove, Physics and Technology of Semiconductor Devices, Wiley, New York, 1967.
[8] D.M. Caughey, R.E. Thomas, Proc. IEEE 55 (1967) 2192.
[9] A.J. Chapman, Heat Transfer, fourth ed., Macmillan, New York, 1984.
[10] V.T. Morgan, N.G. Barton, J. Phys. D: 19 (1986) 975.
[11] R. Hull (Ed.), Properties of Crystalline Silicon, IEE, London, 1999.
[12] D.E. Rosner, Transport Processes in Chemically Reacting Flow Systems, Dover, New York, 1986.
[13] S. Bau, High-temperature CVD silicon films for crystalline silicon thin-film solar cells, Ph.D. Thesis, Fraunhofer Institut für Solare Energiesysteme, 2003.
[14] R.B. Bird, W.E. Steward, E.N. Lightfoot, Transport Phenomena, second ed., Wiley, New York, 2002.
[15] P.D. Neufeld, A.R. Janzen, R.A. Aziz, J. Chem. Phys. 57 (1972) 1100.
[16] H. Habuka, et al., J. Crystal Growth 169 (1996) 61.
[17] A. Luque, H. Rodríguez, I. Tobías, J. Alonso, J. Crystal Growth 283 (2005) 198.