Silane decomposition by injection into molten silicon

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Abstract

The aim of the present study was to test the principal possibility of polycrystalline silicon production for solar applications by silane decomposition in molten silicon. The decomposition was carried out by injection of a gas mixture (20 vol. % silane-80 vol. % hydrogen) into liquid silicon at 1500°C.

Using a water model it was tried to predict physical behaviours for silane injection. An experimental set-up was built and several tests were carried out. It appeared that there are complex technical issues to be solved: thermal insulation of the cooled lance, heat balance, formation of silicon powder, splashing of molten silicon.

Introduction

The cost factor remains a main obstacle for growth of photovoltaic application of silicon. The purity requirement for photovoltaic (PV) silicon is lower than for electronic grade (EG) silicon. However PV silicon is produced mainly as EG silicon using processes such as Siemens, Komatsu or variants of these. Other methods like the reduction of pure silicon compounds (e.g. halides) by pure metals or a metallurgical upgrading route have so far not been able to achieve the PV grade[1] requirements.

The commercial processes for production of electronic grade polysilicon apply thermal decomposition of $SiHCl_3$ (Siemens process) or SiH_4 (Komatsu process and MEMC Silane Fluid Bed process). EG polysilicon is mainly produced by the Siemens process, which is an energy intensive and low efficiency process with corrosive and hazardous by-products.

The driving idea of this work is to inject silane into molten silicon at temperature above its melting point what should ensure almost complete decomposition rate. The gas jet should provide sufficient contact time of the gas with the silicon melt in order to allow decomposition of most of the injected silane. A further challenge was the collection of the produced silicon by the melt avoiding dust formation. The lance should stay cold to avoid a preliminary thermal decomposition of the silane which can lead to plugging of the lance nozzle by the deposited silicon metal.

As a first step a water model simulation was carried out to predict the penetration depth of a silane jet, induced by a top blown lance. The aims of the water model study were:

1) To prove the validation of published mathematical models describing the gas injection
2) To study the effect of the lab scale reactor dimensions on the gas jet penetration depth
3) Prediction of the depth of the silane jet in liquid silicon based on the air-water model data

As a second step several silane injection tests were carried out. Silane was injected by a water cooled top injection lance with a nozzle opening of 0.5 mm in diameter.

Prediction of the silane jet penetration depth

The top-blown gas injection into molten metal was studied on a physical model by Tanaka[2], Rizescu[3], Kumagai[4] and Xu[5]. Tanaka[2] found by dimensional analysis the following relation for the gas jet penetration into the liquid bath:

$$\frac{H_C}{H_O} \cdot \left(\frac{H_O + H_C}{H_O} \right)^2 = \frac{15.2^2}{2\pi} \cdot \frac{\dot{P}}{\rho_L g H_O^3} \tag{1}$$

H_o - height of the nozzle from the liquid surface (m); H_c - depth of the gas penetration into the liquid bath (m); $\dot{P} = m_g v_g$, m_g - gas flow (kg/s), v_g - velocity of gas; ρ_L - density of the liquid (kg/m^3); g - gravity acceleration (9.81 m/s^2)

Rizescu[3] obtained a different dependence, shown in (2), the Froude number Fr describes the relationship of the kinetic energy of the gas jet to the buoyancy of the gas in the liquid[3-5]:

$$\frac{H_C}{d_O} = 2.1 \cdot Fr^{0.4} \quad \text{with} \quad Fr = \frac{\rho_g v_g^2}{\rho_L g d_o} \tag{2}$$

H_c - gas jet penetration depth (m); d_o - nozzle opening (m); ρ_g - gas density (kg/m^3); v_g - gas velocity (m/s); ρ_L - density of the liquid (kg/m^3); g - gravity acceleration (9,81 m/s^2); d_o - nozzle opening (m)

Kumagai and Iguchi[4] proposed with Fr_m as a modified Froude number:

$$\frac{H_C}{d_0} = 4.1 \cdot Fr_m^{1/3} \quad \text{with} \quad Fr_m = \frac{(4/\pi)^2 \rho_g (v_g^{'})^2}{\rho_L g d_o} \tag{3}$$

v'_g - the velocity of the gas jet on the surface, which is lower than the nozzle exit velocity v_g (m/s) as follows:

if $H_o/d_o<1.26$ than $v'_{g}=v_g$
if $1.26<H_o/d_o<17.2$ than $v'_{g}=v_g/(0.00523\cdot(H_o/d_o-1.26)^2+1)$
if $17.2<H_o/d_o$ than $v'_{g}=v_g/(0.167\cdot(H_o/d_o-0.543)$

Finally Xu et al[5] investigated the gas injection into the liquid by a submerged lance. Viscosity and surface tension of liquid had no effect on the penetration depth of the gas jet. Equations 1, 2 and 3 resulted in different penetration depth under the same conditions. For this reason the penetration depth of gas injection was studied in a water-air model. Also the effect of the reactor dimension was studied with various nozzle diameters 0.5, 1.0 and 2.0 mm. As reactors a cylindrical container with 8.0 cm and 17.2 cm diameter and a container with a square base of 48x48 cm were used. The experimental results could not be described by one of the equations mentioned above. The equation of Tanaka und Okane[2] was modified (4) and the coefficients were calculated using the method of the least squares (Figure 1):

$$\frac{H_c}{H_o}\cdot\left(\frac{H_o+H_c}{H_o}\right)^2 = 18.297\cdot\left(\frac{\dot{P}}{\rho_L g H_o^3}\right)^{0.9749} \qquad (4)$$

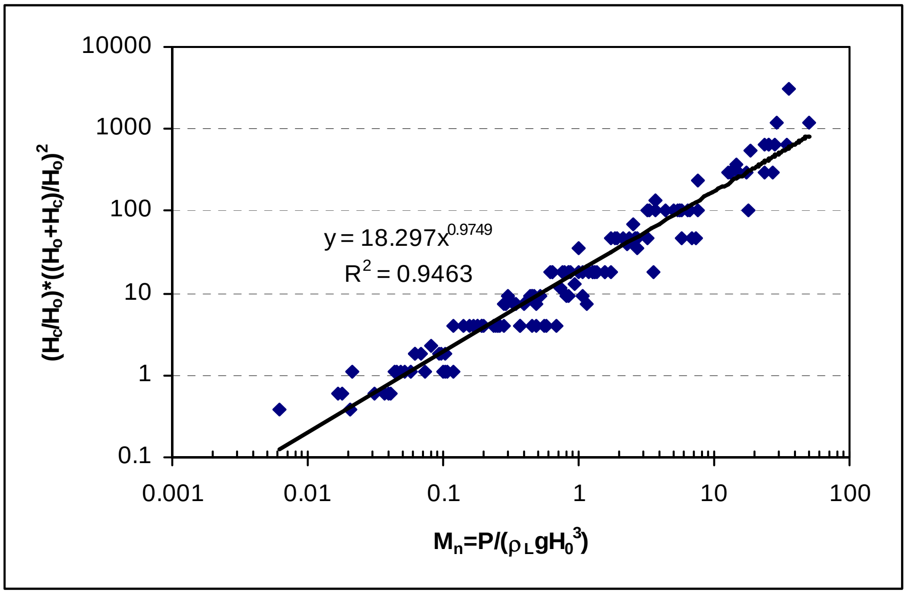

Figure 1: Gas jet penetration depth into liquid (eq. 4)

The container dimension had no significant effect on the penetration depth using a 0.5 mm nozzle (Figure 2, left). With a 1 mm nozzle a lower penetration depth was observed if a container of 8 cm diameter is used (Figure 2, right).

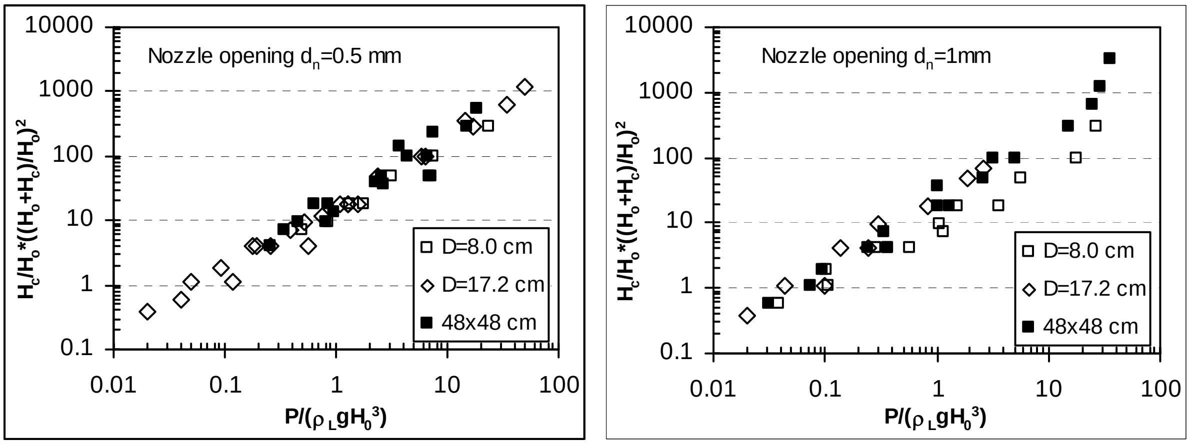

Figure 2: Jet penetration curves for various nozzle opening diameters d and container size diameters D

Based on equation 4, the silane injection depth into the silicon melt was predicted for various nozzle openings. The left graph (Figure 3) shows the predicted values of the 20 vol. % silane-80 vol. % hydrogen jet penetration depth into silicon with the assumption that there is no thermal expansion of the silane-hydrogen mix due to the contact with molten silicon, the right graph takes the heating effects in account. The 3 lines represent nozzle openings of 0.25 mm, 0.5 mm and 1.0 mm. The distance between the nozzle exit and the melt surface was 1.0 cm. The right ends of the lines correspond to a gas pressure of about 500 kPa in the nozzle.

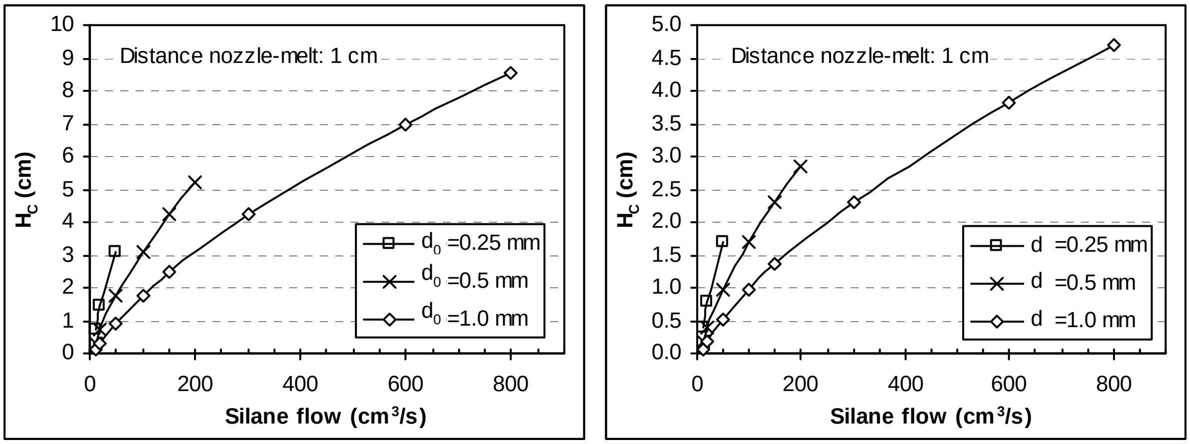

Figure 3: Predicted penetration depth of 20 vol. % silane-80 vol. % hydrogen jet into a silicon melt (left for "cold jet" and right for "hot jet") for three different injector opening diameters d

According to Tanaka[2] $\dot{P}=m_g v_g$ doesn't change with the thermal expansion of silane, consequently the penetration depth doesn't change too. The change of the difference between the gas mixture and silicon densities can be neglected, since the density of the molten silicon (2550 kg/m^3) is very high in comparison to the gas mixture density.

According to Riezscu[3] (eq. 2) and Kumagai[4] (eq. 4) the silane volume rise due to the thermal expansion (1500°C/20°C=1773K/293K=6.05 times) will decrease the penetration depth. Another rise of gas volume is contributed by thermal decomposition of silane. In our case the injected gas contains 20 vol. % silane and 80 vol. % H_2. The thermal decomposition of silane according to the equation $SiH_4=Si+2H_2$ results in additional 20 % increase in volume which results in the total increase in volume of 6.05×1.2=7.26 times. The penetration depth of the gas jet depends on Froude number in exponent 2/5 or 1/3 (eq. 2 and 3). The penetration depth will be $(7.26)^{1/3}\sim 1.9$ or $(7.26)^{0.4}\sim 2.2$ times less (Figure 3, right). The penetration depth is 2 cm for the 0.5 mm nozzle at a silane flow of ~125 cm^3/s=450 l/h from the 1 cm height from the silicon melt surface. In the water model the used air pressure was up to 450-500 kPa. A pressure higher than the Laval pressure can lead to jet perturbations[6].

Based on the calculations it was decided to use a 0.5 mm nozzle which reaches a penetration depth of 2 cm by injecting 20 vol. % silane-80 vol. % hydrogen from 1 cm from the surface at gas mixture flow about 0.2 l/s=720 l/h or 0.05 g/s=180 g/h silicon.

Enthalpy of the silane decomposition

The reaction of the silane decomposition is exothermic if silane is decomposed under the melting point of silicon. The decomposition is endothermic if the decomposition temperature is over the melting point of silicon (Figure 4).

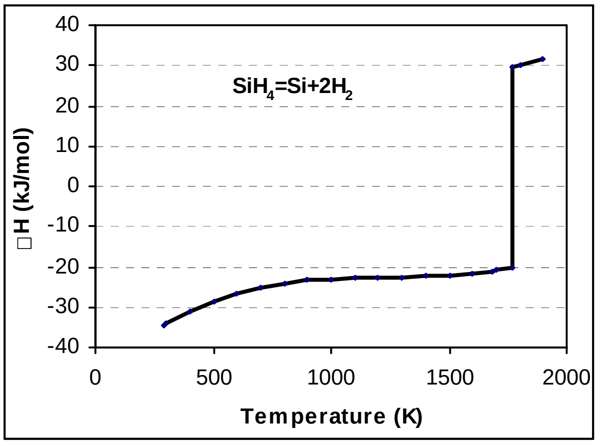

Figure 4: Enthalpy of silane decomposition reaction

For the specified conditions of the laboratory set up it was estimated that the gas mixture flow should be lower than 125 cm^3/s to avoid the solidification of the silicon melt with an assumption that there is no heat exchange between lance and melt.

Test set-up

The experimental set-up scheme is shown on Figure 5. The test set-up is based on a Leybold-Hereaus (now ALD, Hanau) vacuum induction furnace. Vacuum pumps allow to evacuate the furnace chamber down to 10^{-4} bar. Argon was used as a flush gas to displace air from the system. A gas rotameter calibrated for 20% silane and 80% hydrogen was installed in the silane line. Off-gases (hydrogen and silane) were burned continuously by means of a propane burner. The solenoid valves were controlled by the automatic burner control system. In case when of no flame the 3 solenoid valves were closed:

- Silane line
- Off-gase line
- Propane line

Automatic flame-arresting non-return valves blocked automatically the back flow of gas. The temperature of the water cooled lance was controlled by means of a Ni-NiCr-thermocouple installed inside the nozzle close to the nozzle exit and by two in-line-Ni-NiCr-thermocouples controlling the temperature of the cooling water. The cooling water flow is measured by means of an in-line flow meter.

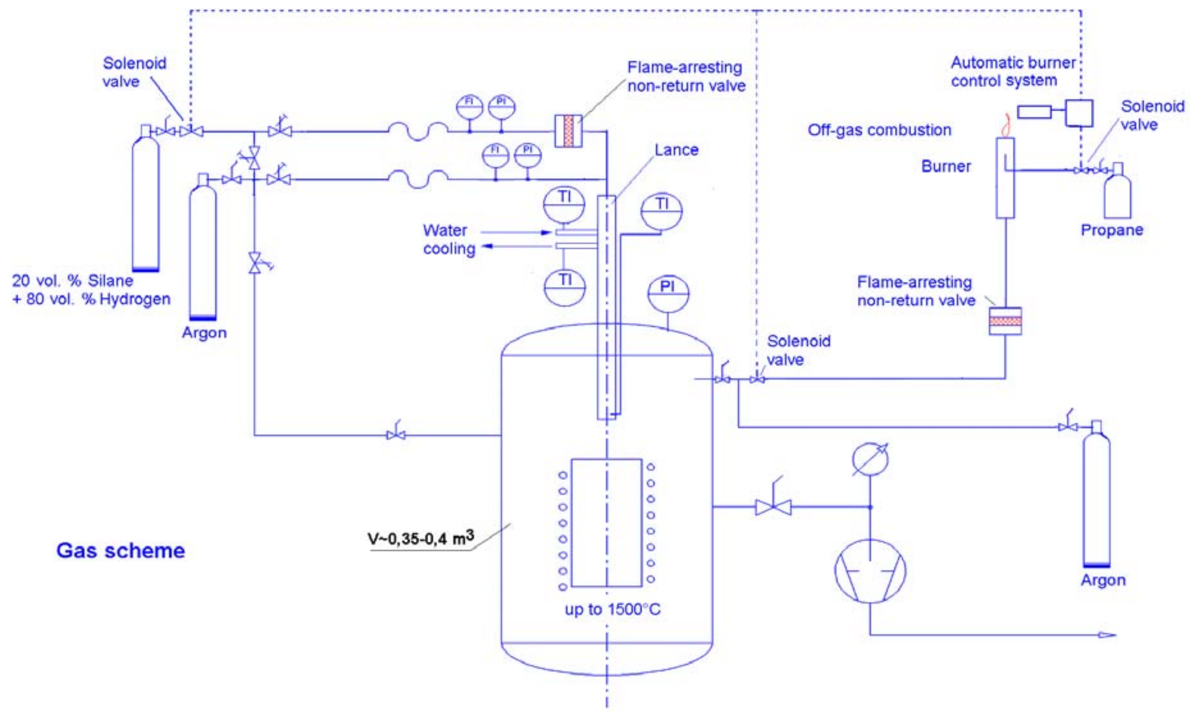

Figure 5: Experimental set-up for silane decomposition in a liquid silicon melt

The water cooled lance was an in-house development and made from coaxial copper tubes (Figure 6). The outer diameter was 25 mm. A rubber ring sealing between the lance and furnace mantle allowed moving the lance up and down without gas leakage.

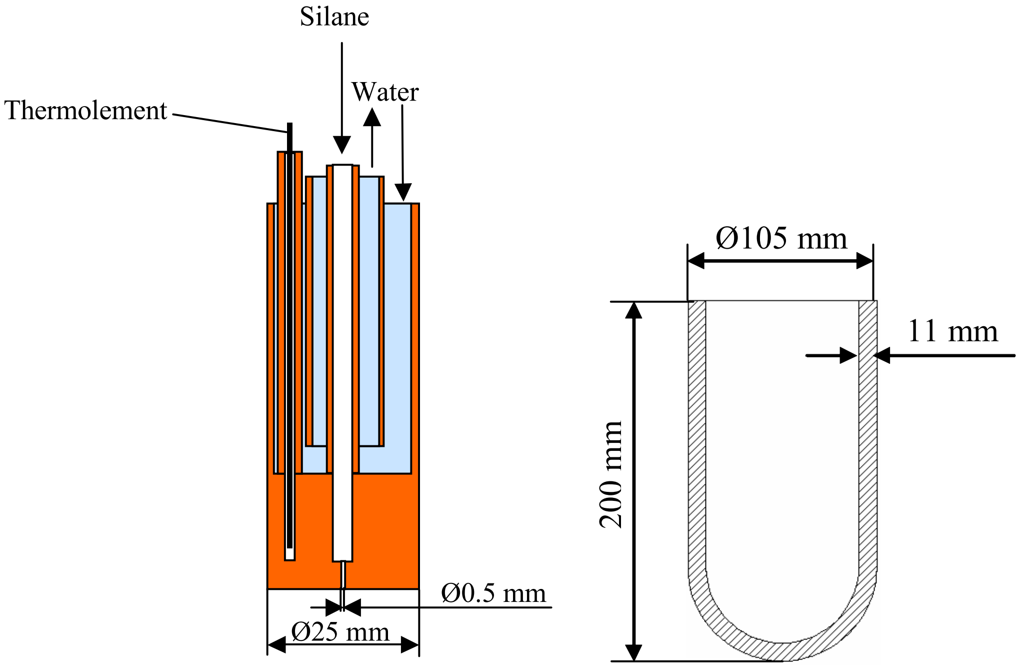

Figure 6: Water cooled lance nozzle (left) and quartz crucible used to melt (right)

At 1500°C the main part of heat transfer takes place by heat radiation. 4 layers of 0.13 mm graphite foil protected the lance from the foreside. The heat insulation of the lance sides consisted of an 6 mm graphite felt. A quartz tube protected the heat isolation of the lance from the molten silicon. The outer diameter of the quartz tube was 43 mm and the inside diameter was 37.5 mm.

The furnace inductor could be tilted to pour the molten silicon into a fire clay mould inside of the furnace chamber (Figure 7). Since a Pt-PtRh-thermocouple installed in the graphite susceptor didn’t work properly at high temperatures due to interaction between platinum and carbon, it was replaced by a W-WRe-thermocouple and mounted in a protective tube between crucible and graphite susceptor. 1000 g of high grade polycrystalline silicone were melted in each test.

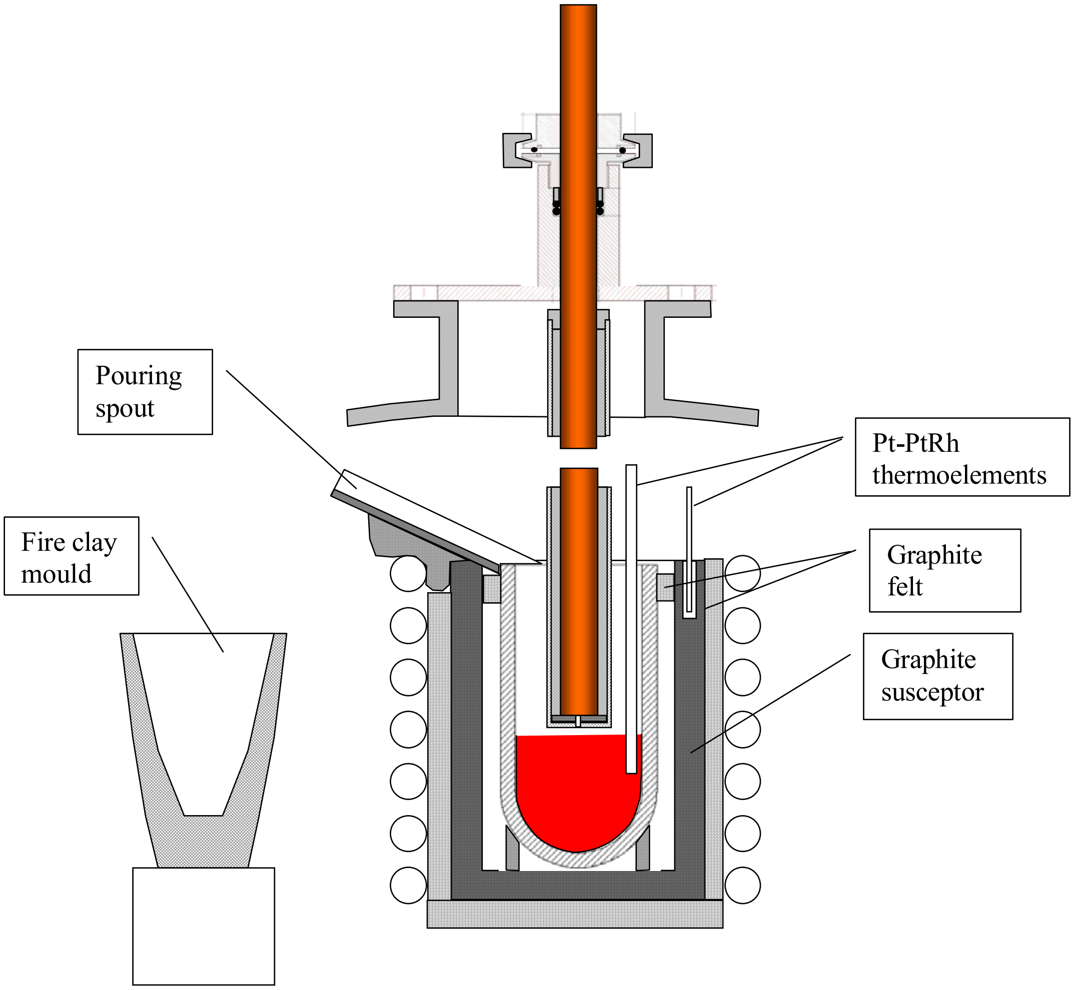

Figure 7: Start up experimental set-up, part of the furnace chamber with non submerged lance, crucible, inductor and mould (set up for test 1)

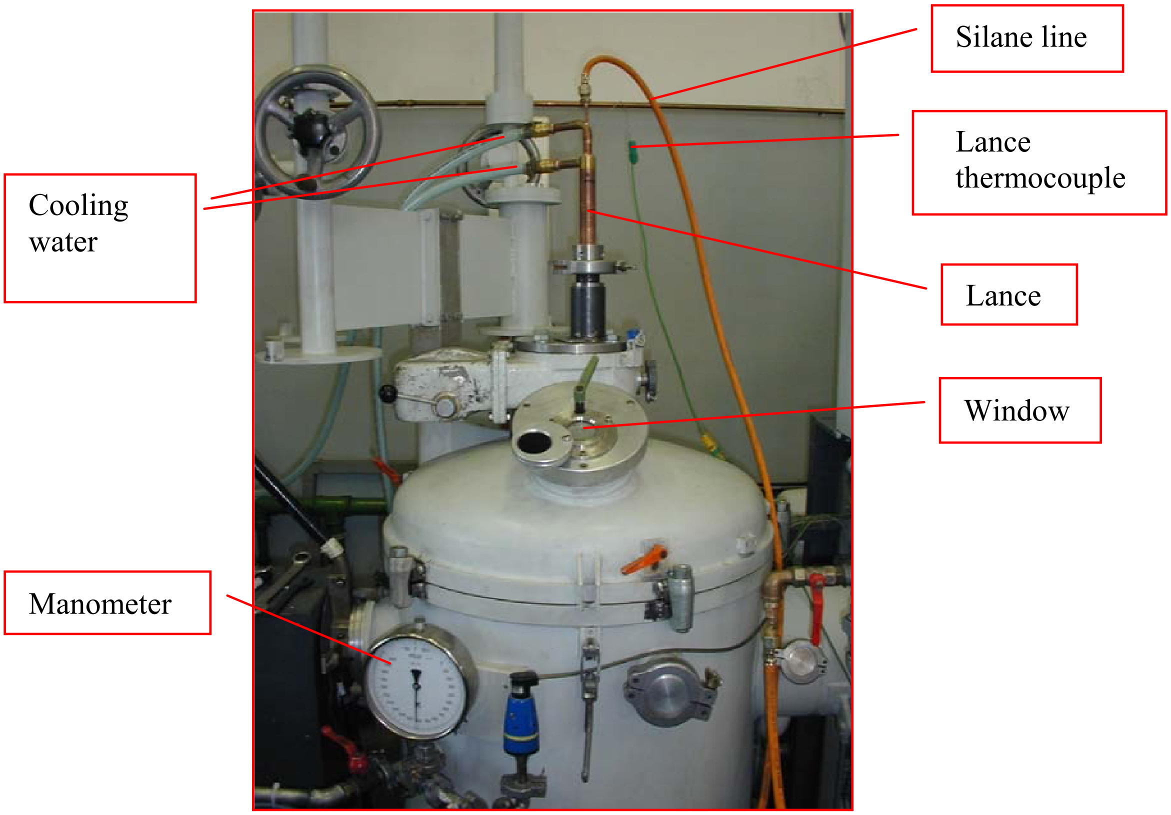

Figure 8: Experimental set up, overview picture

Results

In the first test the furnace chamber was evacuated by the vacuum pump and filled with argon until atmospheric pressure was reached. The injection of the gas mixture (20 vol. % SiH_4 and 80 vol. % H_2) from the non-submerged nozzle (Figure 7) resulted in a strong formation of a yellow-brown powder which covered the inside surface of the furnace chamber. This caused plugging of the fire arrester valve of the off-gas line. To prevent plugging of the fire arrester valve the subsequent test were carried out starting under vacuum and ending when the pressure inside the furnace chamber reached atmospheric pressure. After every test the gases were displaced by argon and burnt using the propane burner (Figure 5).

In test 2 (Figure 9) was tried to reduce the formation of silicon powder by submerging the lance into the silicon melt. Before submerging the lance into the molten silicon the argon line was opened, which prevented the plugging of the water cooled lance nozzle by solidified silicon. After lance contact with the molten silicon, the silane line was opened and the argon flow was closed. The moment when the lance gets contact to the melt could be clearly noticed by vibration of the lance. Also a vibration of the measuring cone of the silane rotameter could be observed.

At a gas flow of 6 l/min formation of smoke (obviously silicon dust) was observed. The gas flow was gradually reduced to 3 l/min until the smoke disappeared. After 35 min the silane injection was interrupted, because smoke appeared at the outside of the quartz tube.

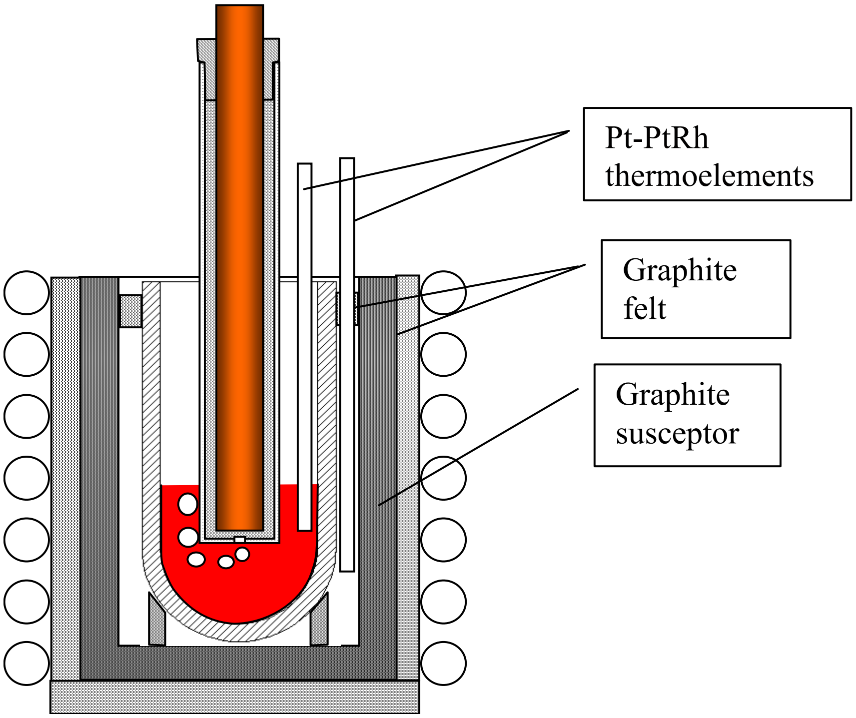

Figure 9: Modified experimental set-up crucible with submerged lance, inductor (set up for test 2)

The inside of the furnace chamber was covered by yellow-brown dust. Submerging the lance caused a freezing of the silicon melt and subsequently plugging of the nozzle (Figure 10). This forced the gas flow to pass through the graphite insulation converting the graphite into SiC (Figure 11).

Figure 10: Test 2. Yellow dust inside on surfaces of the crucible and the lance

There were only a few silicon droplets found on the crucible wall, which indicates that the lance was plugged by frozen silicon shortly after beginning of the silane injection.

Figure 11: Graphite felt and foil insulation converted to SiC due to plugging of the immersed silane-lance by solidified silicon metal

In the test 3 only the internal water cooled copper lance was lifted upwards out of the melt creating a space inside the quartz tube to reduce heat losses from the melt (see figure 11). Silane (20 vol. % SiH_4 and 80 vol. % H_2) was injected onto the silicon melt through the 4 mm nozzle at the bottom end of the quartz tube. The distance/space of the nozzle opening to the end of the quartz tube was approximately 250 mm. The silane flow was adjusted to approx. 1 l/min, where smoke generation was hardly visible. After 160 min of injection again a strong smoke formation appeared on the side of the quartz tube due to a crack. The silane line was closed and the test was stopped.

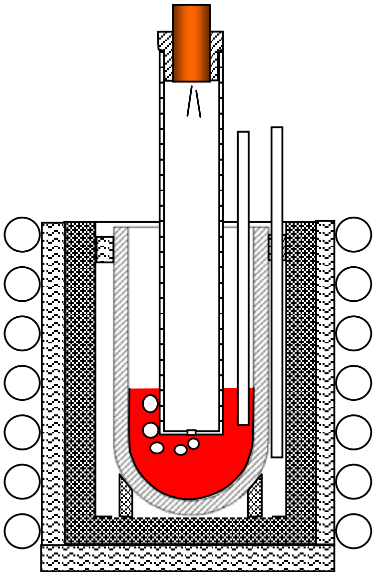

Figure 12: Modified experimental set-up crucible with submerged ceramic tube, 250 mm lifted injector nozzle and inductor (set up for test 3)

Molten silicon splashes built a deposit on the cold zone of the crucible (Figure 13).

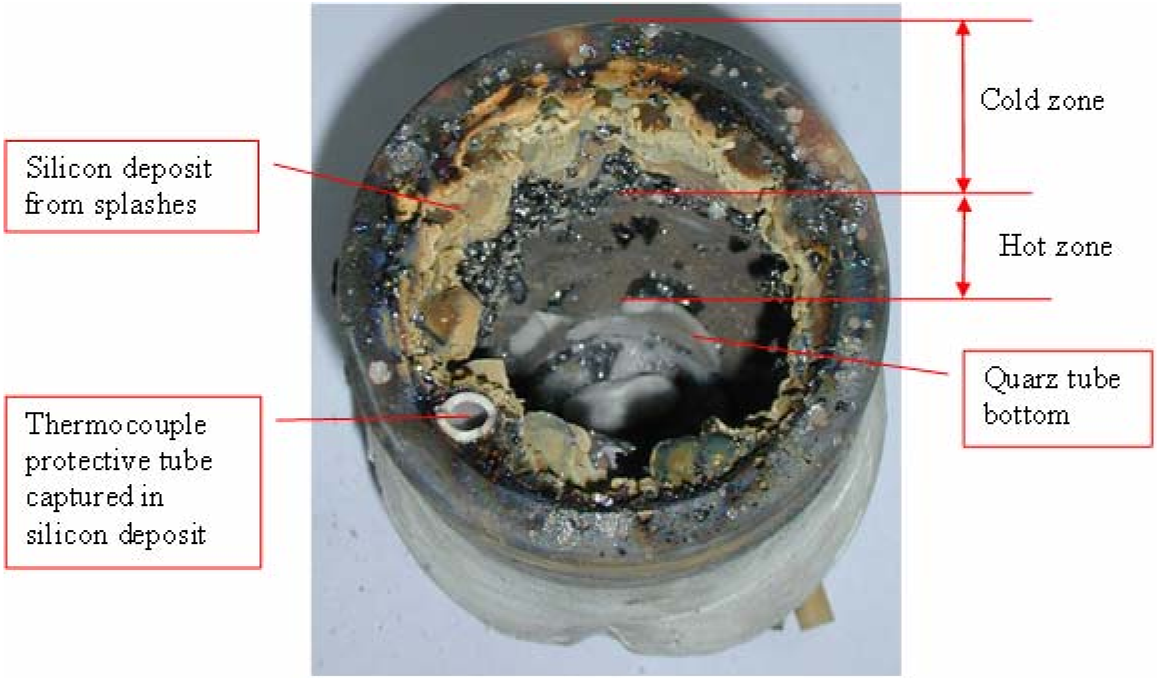

Figure 13: Frozen slicon splashes at the cold area inside the crucible (Test 3)

The outer surface of the quartz tube was covered with a thick layer of yellow-brown dust and silicon splashes (Figure 14). The tube diameter at the bottom end of the tube was expanded by approx. 8 mm. We suppose that the gas pressure inside of the tube caused the cracking of the tube walls. Inside of the quartz tube 4 zones were distinguished:

1. Loose powder deposit zone. The nozzle surface was covered with 3-4 mm thick powder layer.
2. Sintering zone. The dust was sintered forming a dark dense shell.
3. Melting zone. Liquid silicone was deposited inside of the quartz tube showing signs of wax-like flow.
4. Clear zone. Here the temperature was high enough to allow the silicon to flow downward.

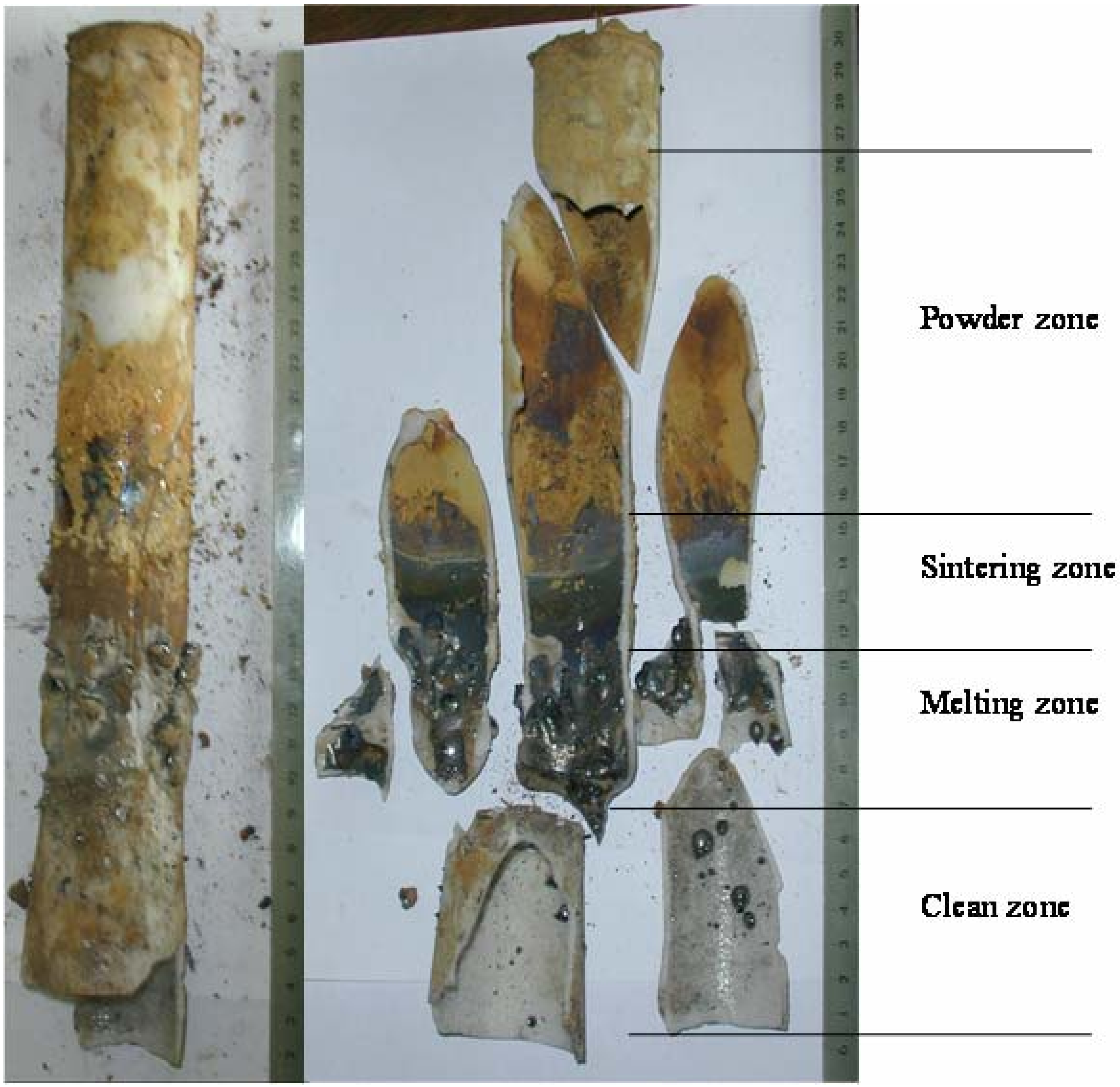

Figure 14: Quartz tube after test 3 (thick layer of yellow-brown dust outside the tube and silicon splashes inside, clean zone proves the principle as produced silicon could flow downwards to the bulk melt)

During this test 25 g of silane–hydrogen mixture (20 vol. % SiH_4 and 80 vol. % H_2) were decomposed, which corresponded to 70 l of the gas mixture. The gas consumption was ~0.44 l/min at normal conditions. The space in the quartz tube was about 290 cm^3. At assumed temperature 1000°C in the quartz tube the gas flow expands to 1.9 l/min. That results in residence time about 7 seconds. The estimated gas velocity was 3 cm/s. Such conditions would provide a complete decomposition of silane[7].

The thermal balance was a main issue in all tests. In test 4 the quartz crucible was surrounded with a 0.5 mm thick SiN coated graphite foil and with a 8 mm cover consisting of 2 layers of graphite felt. This was done in order to avoid freezing silicon splashes. To reduce the heat transfer from the melt to the lance the nozzle of the lance was made from copper in form of a pin. The 0.2 mm pin nozzle was screwed with a 4M thread and soldered with Pb-Sn for better heat transfer. The gap between the nozzle and quartz tube was closed with quartz powder using soluble glass as binder. (Figure 15).

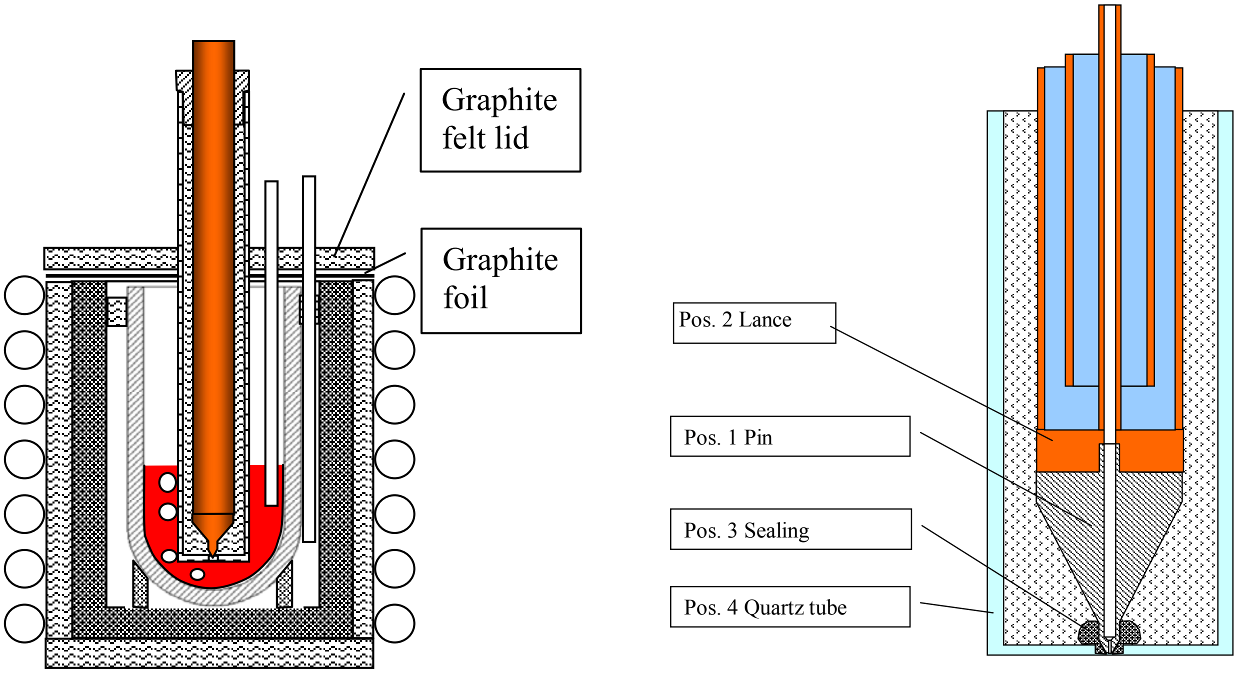

Figure 15: Modified experimental set-up, quartz crucible surrounded with a SiN coated graphite foil and covered with 2 layers of graphite felt, pin shaped injector nozzle and inductor (set up for test 4)

The crucible, quartz tube and thermocouple protective tubes were coated with SiN to reduce the reaction between quartz and graphite at test temperatures, avoiding the formation of volatile silicon oxide. The silane flow decreased continuously and after 6 min the nozzle was plugged and the test had to be stopped. All graphite surfaces were covered with silicon carbide, which wasn't detected in the earlier tests. The reason was the formation of a volatile silicon sub-oxide due to the decreasing heat losses by covering the crucible. After this result it was decided hold the program despite the fact that test 3 proved the principle.

Summary and Conclusions

The principal possibility of polycrystalline silicon production for solar applications by silane decomposition in molten silicon was tested. The decomposition was carried out by injection of a gas mixture (20 vol. % silane - 80 vol. % hydrogen) into molten silicon at 1500°C using a vacuum induction furnace.

Silane jet penetration into silane melt was preliminary predicted in a water model. The theoretical penetration depth of the gas jet was about 2 cm at test conditions (0.5 mm nozzle, 1 cm distance from the melt surface).

The experimental set-up was designed, built and four injector modifications were carried out. The injection of gas mixture over the melt always resulted also in an unwanted silicon powder formation. The project has shown that there are still many complex technical issues to be solved: thermal insulation of the cooled lance, splashing of molten silicon. Another issue is the heat transfer to the melt. The silane decomposition at temperatures above the melting point of silicon is an endothermic process, which is a principal difference to standard decomposition techniques at temperatures below the melting point where the process is exothermic. Nevertheless the test results offer the chance that the presented process idea has a potential to be transferred to practice.

Acknowledgments

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