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Production of polysilicon from silane pyrolysis in a fluidized bed

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Thesis for the degree of Doctor Philosophiae

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Simplicity is the ultimate sophistication
Leonardo da Vinci

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Abstract

The photovoltaic industry has experienced a tremendous growth over the last years. The backbone of the technology has so far been elemental silicon. Silicon is the second most abundant element on the earth, but in order to be utilized for solar panels, it needs to be purified. This purification process is very energy intensive. Behind a finished solar module, up to 30% of the energy goes into purification depending on route, Cucchiella and D´Adamo (2012).

Reducing the energy payback time of solar panels is important, and focus on silicon production is crucial, since this is one of the most energy intensive parts. The production of polysilicon involves production of metallurgical silicon from quartz and further processing into polysilicon. The most common route for the latter step is the Siemens process. In this process, chlorosilane is produced from chlorination of the metallurgical silicon. Subsequently, trichlorosilane is reduced in a decomposition process after some additional refining. The decomposition reactor itself is where the energy consumption becomes large.

The silicon containing reactant starts to decompose at a temperature of typically 350 - 480 °C depending on the process. However, in order to assure correct deposition, the deposition itself has to happen at temperatures as high as 1100°C for trichlorosilane, and about 650°C for monosilane. The layout of the Siemens process is simple. Electrical heating elements of silicon are distributed within a cooled dome. The heating elements are kept at typically 1100°C, while all other surfaces are kept at about 250°C. The process takes days and even weeks, depending on the process optimization, and the heat loss is therefore substantial.

There is one other technology producing polysilicon to the market today, and this is the fluidized bed reactor. In a Fluidized Bed Reactor (FBR), the reactor vessel is filled with silicon particles. A gas is injected at the bottom of the reactor to fluidize the particles. Fluidizing the particles means the drag force on the individual particles is on the same scale as the weight of the particle. In this state, the bed of particles behaves like a liquid, and the flow of gas keeps the bed in continuous motion. The particles are heated to a temperature above the decomposition temperature and the reactant gas is inserted to the bed. Upon decomposition, the silicon deposit on the particles thus making them grow. After some dwell time, the particles have grown to a size suitable for extraction. The finished beads are then extracted, and new small seed particles are inserted to or produced within the bed.

What complicates the picture is the decomposition of the reactant and how this influences growth. Challenges associated with FBR production of polysilicon involves dust (fines) production, unwanted depositions on surfaces other than the beads as well as inadequate quality due to porosity, amorphous inclusions and impurities.

During the PhD project a state of the art fluidized bed has been designed, built and operated. This thesis discloses the design chosen as well as the background for the choices made. Further, the results of the experimental investigations are presented. The project has successfully achieved production of polysilicon. The results demonstrate two different types of silicon growth and how to control the process.

The ability to alternate the nature of the produced material by process parameters has been demonstrated. High-density deposition and low fines production has been demonstrated. Low

density and high fines production modes is also demonstrated and parameters leading to this mode is identified.

Two different sources of fines formation are demonstrated. The first is nucleation and growth in gas phase. The other mechanism is the release of inadequately bound structures from the surface of the silicon beads post deposition.

An ability to scavenge fines through optimization of process parameters is demonstrated. The process was first optimized for large dust production. The beads were then harvested and investigated before being reintroduced to the bed. The process was then optimized for dense depositions leading to a scavenging of the earlier deposited fines. The nature of the finished structures formed by this type of process is also presented in the thesis.

The results of this work have been presented in four published journal papers and four conference proceedings. The design of the reactor is patent pending and the patent application is appended to this thesis.

Further, a set of experiments was performed in a separate hot wall reactor also referred to as a free space reactor. It is known from the literature that silane based fluidized bed material may be associated with a characteristic periodic porous pattern. Through the presented free space experiments, the ability to grow a similar pattern in steady state has been demonstrated, thus indicating that the phenomenon is not directly linked to the fluid mechanics of a fluidized bed.

Acknowledgements

Many people have been of great help, inspiration and support during this project. First and foremost, I owe a great debt of gratitude to my supervisor, Dr. Arve Holt at Ife for offering me the opportunity to study for a PhD degree, and for the continued support and guidance through the many different chapters of this journey.

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Further, I would like to thank all the staff at Ife that has contributed to the progress and results of this project. The devoted Ife team has provided help with solving all types of small and large challenges, and continued to astonish by competence width and depth. I would especially like to thank Hallgeir Klette for all help with getting the experimental rig operational and for continued focus on safety, keeping us all out of harms way.

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I would like to thank my parents Anne Grethe and Josef, for a lifetime of love and support. My thanks also go to my sisters Kristin and Trine along with their husbands for their enduring support. Each and everyone have been most inspirational and helped me celebrate every small step of the way, making the journey seem shorter.

A special thanks goes to my father for inspiring my decision of initiating this task, and to my loving and understanding wife Rakel Elisabeth for giving me room to see it through.

Kjeller   Werner O. Filtvedt
13th February 2013

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Symbol list

Latin symbols:

Symbol	Description	Unit
A	Cross section	$[m^2]$
u	Atomic Mass Unit	$[1.66 \times 10^{-27} \, kg]$
D	Diameter	$[m]$
e	Electric Charge	$[Coulomb]$
g	Acceleration of gravity	$[m/s^2]$
P	Pressure	$[Pa], [bar]$
Q	Heat flow	$[kJ/h]$
Re	Reynold's number	$[-]$
T	Temperature	$[K], [ºC]$
t	Time	$[s], [h], [yr]$
V	Volume	$[m^3]$
v	Velocity	$[m/s]$

Abbreviations:

CVD	Chemical Vapor Deposition
DP	Differential Pressure
FB	Fluidized Bed
FBR	Fluidized Bed Reactor
FSR	Free Space Reactor
IFE	Institute for Energy Technology
REC	Renewable Energy Corporation
SS	Stainless steel
SEM	Scanning Electron Microscope
SMP	Samsung MEMC Polysilicon
TEM	Transmission Electron Microscope
TCS	TriChloroSilane
TUC	Telemark University College
XRD	X-Ray Diffraction

Part I

1. Introduction

Solar cells are an increasing consumer of polysilicon in the world market. Although the rapid expansion in world production capacity have presently made the silicon prices drop, the long term expectations are still growing in PV energy demand and thereby significant growth in polysilicon consumption can be expected in the future Liu (2012), Steeman (2012) and Bernreuter (2012).

1.1 The polysilicon value chain

The value chain from the quartz quarry to the finished modules is long and involves several stages see Fig 1.1. The quartz is harvested from a quarry, reduced to metallurgical grade silicon in a furnace, and then undergoes additional purification before it may be used as feedstock for solar applications. This additional purification is most commonly achieved in a hydro chlorination process where trichlorosilane (TCS) is produced. Further processing yields monosilane (silane) and both TCS and silane may be used as precursors in the subsequent decomposition process, Shriver and Atkins (2010).

This subsequent process involves heating the reactant to above the thermal decomposition temperature and thereby release the bound silicon. For these two gases this temperature is in the order of 350 - 480°C. The overall process is a bit more complex as there exist several intermediate reactions and species, and since pressure, temperature and concentration cause shifts in the reaction coefficient of these reactions. The actual operation temperature of reactors utilizing these gases is therefore hence in the range 650 – 850°C and 950 – 1150°C Herrick (1984).

A main difference between the two precursors is the aggressiveness of the reverse reactions as well as the nature of the intermediate species. For TCS, the reaction chamber contains concentrations of HCl that aggressively binds to insufficiency bound silicon. This etching process constantly removes loosely bound silicon. For silane based reactors there is no HCl present and the reverse reactions are far less aggressive. The result of this difference is a larger risk for undesirable decomposition in silane-based reactors. This type of decomposition may lead to production of silicon powder (fines) or even influence the quality of the finished product.

Historically, TCS has been favoured since this enables a fairly easy route to sufficient quality compared to silane based routes. The main challenges have been construction materials and process control. However, there are theoretical limits to how efficient TCS routes may become due to the presence of these reverse reactions. There is therefore an increased interest in silane-based routes.

This is where we are

Metallurgical Silicon → Purification → Wafering & cell process → Module
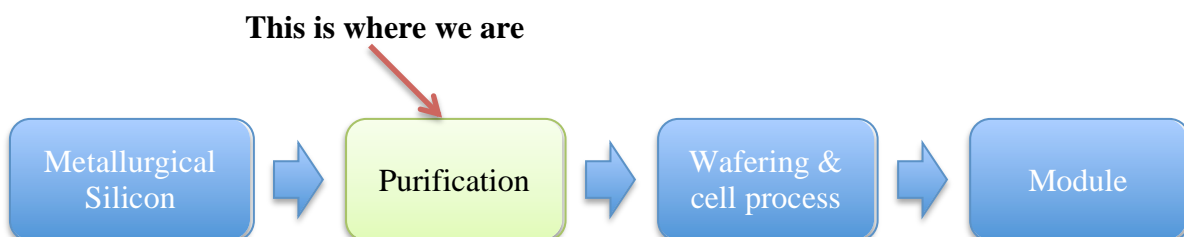
Figure 1.1: Solar Cell Value Chain

In a Siemens reactor the reactant gas is fed into a bell reactor containing heated silicon rods see Fig. 1.2. The reactant gas is heated to decomposition by the rods and deposits a layer of silicon on the rods while the excess gas is extracted. The reactions are temperature dependent and will not occur below finite thresholds. In order to prevent unwanted depositions on the wall, the rest of the reactor is thus cooled. The Siemens reactor is the most frequently used CVD reactor. The quality of the finished product is high at the expense of high-energy consumption and low gas utilization.

Figure 1.2: Siemens Reactor

Figure 1.3: Fluidized bed reactor

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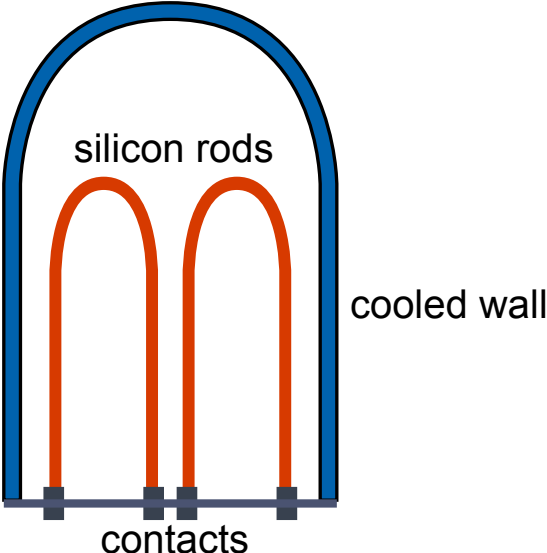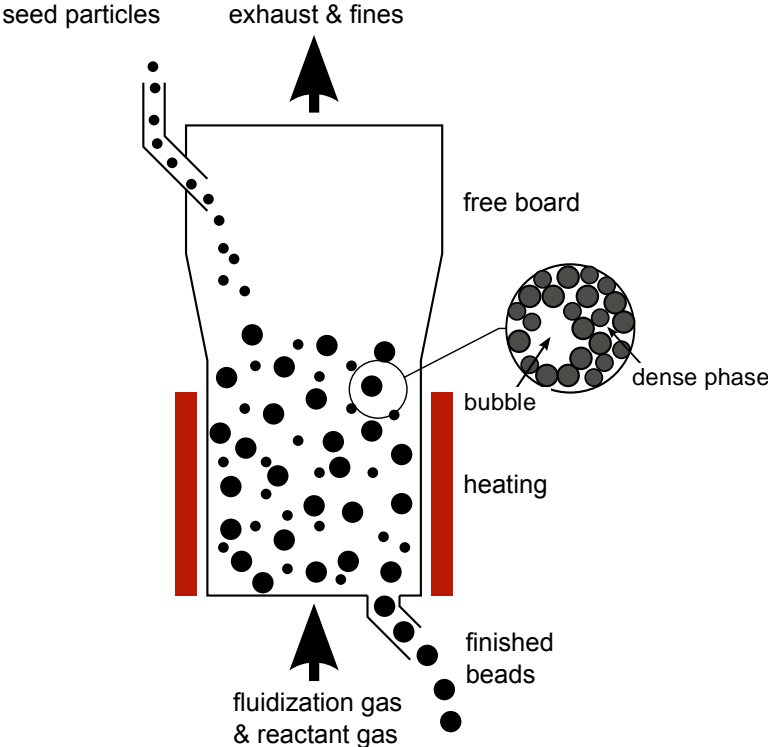In a fluidized bed a column of particles is kept fluidized by an ascending gas flow, see Fig 1.3. In the fluidized state, the bed of particles behaves like a liquid and may be easily agitated and heated. Many processes utilize this technology for different purposes; typical applications are processes involving reactions between solids and gases where large solid surface area is advantageous, Yang (2003).

For silicon production, a silicon containing reactant is introduced to the fluidized particle bed whereby the reactant is thermally decomposed and thereby releases silicon. The operation temperature is typically far below the melting point of silicon and the released material is therefore solid.

In order for a solar cell to work, one needs to have a very clean material and a low number of defects. When talking about impurities and defects, the challenge involves single atoms and missing atomic bonds, Nelson (2009). The process of refining is therefore demanding and this is one reason why the simple layout of the Siemens reactor has been favoured.

The fluidized bed inherently has a quite chaotic nature. The agitated particle bed and the constantly shifting voids or bubbles create a continuously changing environment. The decomposition itself is also quite complex as the silicon containing reactant; mainly trichlorosilane or monosilane does not simply release the silicon and continues as silicon depleted gas. The process involves several possible reactions whereof several reversible as well as a large number of interrelated intermediate species. These species are both in gas phase, in the form of solid dust, as well as surface species at the beads.

A third problem is fine formation due to homogeneous reaction in preference to deposition on feed particles, Odden (2005a). Finally the fluid bed reactor (which currently has the best potential for the silane process) involves complex interaction of hydrodynamics with kinetics and hence is difficult to scale up. The interested reader is referred to paper III and IV of this thesis.

Monosilane based fluidized bed reactors appear to give the lowest possible cost of operation over the established methods. There are, however, many challenges with porosity and impurity encapsulations that need to be solved if the method is to dominate commercially.

1.2 Background for the interest of fluidized bed production of silicon

The workhorse of today's industry is the Siemens reactor where either trichlorosilane (TCS) or silane is decomposed, and the silicon is deposited on heated rods. Several improvements have been made to the design resulting in a substantial reduction in energy consumption, Coso (2007). However, the need for maintaining large temperature differences between the deposition surfaces and the reactor wall, as well as the limited deposition surface area limit the theoretical reactant yield and lowest possible energy consumption. TCS has proven successful for these reactors, among several reasons because some reverse reactions will remove loosely bound solid silicon and thereby assure high quality of the deposited material.

The main motivation for developing the fluidized bed technology is to reduce the production cost of polysilicon. Both TCS and silane has been tested in these types of reactors earlier. However, only silane-based routes have proven successful enough to produce material for the commercial market so far. The main active companies are today Renewable Energy

Corporation (REC) and MEMC, Ege (2007), MEMC (2010), Osborne (2011), Ibrahim (2007). There are also many other large players presently and openly looking into FBR research, among them Wacker Chemie, GCL, Hanwha and Samsung MEMC Polysilicon (SMP).

A common presumption in the industry is that the silane based FBR technology holds the potential to be the next generation polysilicon production.

1.3 Prior experience in fluidized bed production of silicon

The industrial development of fluidized bed production of polysilicon has been long and several research groups have contributed over several decades. The aim of this project was to build expertise and push the research frontier of the polysilicon research. One first challenge was therefore to find this frontier. The history of this development is interesting as the industrial and the academical progress have been largely independent.

This situation has been due to the scale of the investments needed in order to resolve key issues. The investments have been too large for the academia to do without support from the industry, and the industry have lacked the interest in supporting independent research, as resolving these key issues is important in order to keep the distance to competitors. The result of this development is a large number of industrial patents and a number of research papers on topics academia believe to be important to the industry.

To summarize the design development history is challenging. However, the interested reader is referred to paper I and II of this thesis, which highlight key steps of progress through the last 50 years.

1.4 General Polysilicon market situation

The total world capacity for polysilicon is forecasted to be 385 000 tons in 2012, NPD Solarbuzz (Q3 2012). The capacity has increased significantly over the last years exceeding the demand and thereby forcing the prices below the cash cost of most suppliers. One main reason for the continued expansion in capacity regardless of the present market situation is the time it takes to build new facilities. Most of the capacity coming into the market in the coming years is the result of projects initiated in 2007 to 2008. The total available capacity is however, not the same as the capacity able to deliver material to the market at the present prices.

The short time expectations for the market are consolidation and reduction in the number of suppliers due to oversupply and low prices. The long-term expectation is still market growth, see Fig. 1.4. Since most companies experience prices below their cash cost, this is not only a race between the technologies but just as much a contest of financial ability.

Currently the only companies holding potential for acceptable margins in the current market is REC and MEMC with their silane based FBR processes. The companies have stated the possibility of a cash cost far lower than the benchmark Siemens technology. The two utilizes different routes for silane production and so far, the REC method of silane production from TCS seems to be advantageous in terms of cost. In the large picture, the overall energy

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consumption as well as the theoretical limits of competing technologies favour silane based FBRs, Jiao (2011), Herrick (1984).

The prices are currently changing very fast, but over the last months the prices has been between 16 and 20 $/Kg which is substantially lower than the cash cost of average Siemens based production facilities.

This situation has naturally lead to a renewed and increased interest in silane based fluidized bed processes and several new companies, both existing silicon producers and equipment manufacturers have entered the race and are working on developing this technology.
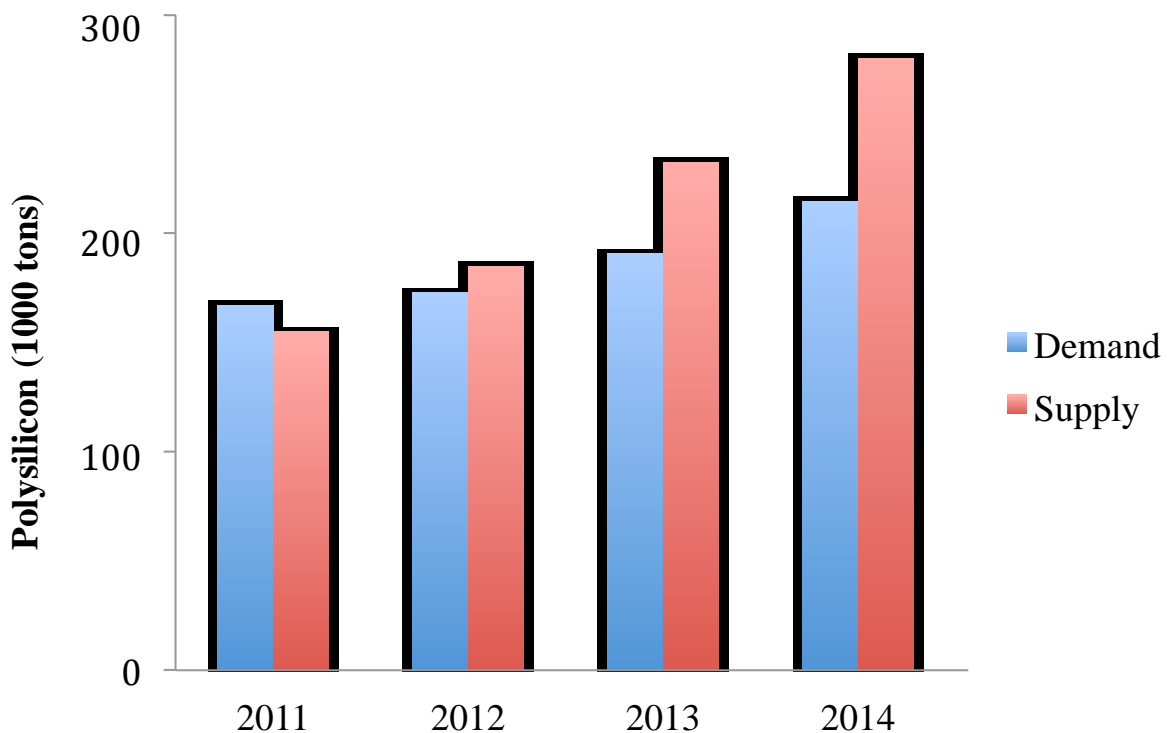

Figure 1.4: Development of polysilicon market, Solarbuzz (2012)

1.5 Fluidized bed market situation

Fluidized bed reactors hold the potential to become the dominating method for production of solar grade silicon. Large players in today's market like Renewable Energy Corporation (REC) and MEMC are producing increasing amounts of their material through FBR instead of Siemens reactors. The two have over 20 years history going back to Union Carbide Corporation and Ethyl. MEMC has currently entered a joint venture with Samsung Fine Chemicals forming the company SMP that is also planning silane-based production in South Korea. Other companies like Wacker have had substantial research programs on FBR based silicon feedstock production although Wacker has solely published TCS based results. Recently GCL has also announced the initiation of a FBR research program. GCL is also focusing on silane for their FBR and thereby joining MEMC and REC in using this precursor as opposed to TCS, NPD Solarbuzz (2012).

1.6 Project objectives

The main goal of the project was to design, build, operate and verify a state of the art fluidized bed for production of polysilicon. Further, the aim was to find favourable operation domains in order to promote growth of a good quality material, obtain a good reactant yield and suppress fines formation. In order to progress fast another objective was to identify critical operation and design parameters early based on literature. This task involved an extensive survey of proposed innovative solutions as well as earlier experimental and analytical efforts.

1.7 Main Contributions

1. A semi pilot size fluidized bed reactor for production of polysilicon through monosilane pyrolysis has been designed, built and operated.
2. The design process has resulted in a novel patent pending solution.
3. Two different process modes have been identified yielding porous and dense depositions.
4. It has also been proven possible to deposit a dense material over a layer of porous material and thereby prove that fine scavenging is possible and that such materials include porous regions, thereby verifying an already established presumption*.
5. Two different types of fines growth have been identified and accounted for. The two types of growth are homogeneous decomposition and the other is removal of loosely bound material from the surface of the fluidized beads.
6. Silane based fluidized bed material is associated with a specific type of growth yielding a periodic pattern of porous regions. The PhD project has been able to reproduce this type of growth in steady state in a hot wall reactor and thereby shown that this phenomenon is not specifically linked to the process in a FBR.
7. A review over the design development of polysilicon fluidized beds has been published.
8. A review of growth mechanisms, associated modelling and empirical research has also been published.
9. Four journal papers and four conference proceedings have been published as a result of this PhD project.

The candidate W. Filtvedt was the main author and contributor to all published articles and conference proceedings. He was also the first inventor to the filed patent application and has performed all the experiments, aided by others as specified in the preface of each paper in Part II.

1.8 Outline of the Thesis

The aim of this thesis was to design, build and operate a state of the art fluidized bed reactor for silicon production through monosilane pyrolysis. The use of silane, was motivated by the potential in terms of low decomposition temperature and possible yield. Further, a subsequent aim of the work was to optimize process parameters in order to tailor and control growth and deposition quality.

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*Investigations of monosilane based FBR material has shown rings of pores within the beads. These porous rings may be related to fine scavenging mechanisms Dahl (2009), Zbib (2012).

Since the field of research is old, it was considered important to map out what solutions and relationships had been explored before, and to try to extract the key features that had been proven important. The available material on designs and solutions was collected and systematically ordered, in order to map out the freedom to operate and how far the development frontier had progressed. This work is presented in paper I and II of this thesis.

Upon choosing operating parameters and process domain, it was considered important to understand the underlying decomposition and growth mechanisms. Investigating the decomposition and deposition is challenging as several interrelated factors contribute. To understand these underlying mechanisms and how they influence the process is crucial in order to bring the technology further. The available literature was investigated with the aim of extracting dominating mechanisms. The findings are presented in paper III and IV of this thesis.

Based on the discovered key design features, a pilot size FBR was designed and built. It was considered important how the inlet area was designed and operated. Much design work therefore went into how to optimize this in order to promote growth of high quality material and suppress fines formation and silane residuals in the exhaust. Basic CFD analysis aided the distributor design and the anticipated performance was verified prior to fluidization and decomposition experiments. The involved reactions are temperature dependent, and one important aspect of controlling the process is therefore to control the temperature distribution by managing the heat transfer. Initial verification involved mapping out the temperature distribution by means of thermal imaging. Background for the design and initial heat distribution tests are presented in paper V.

When testing the reactor, several interesting phenomena where explored. The core of the experimental work revolved around the active growth mechanisms within such reactors, and how to monitor, understand and ultimately control them. Different types of growth was attempted and achieved. It was also proven possible to produce different types of fines, reproduce results reported by others, as well as prove the ability to control some of these mechanisms. The initial findings are presented in paper VI.

One specific phenomenon investigated is the type of bead growth active within a silane FBR. Other groups have reported radially dispersed, porous lines within beads harvested from FBRs, Dahl (2009), Zbib (2012). The origin of these lines has not been fully understood, but it has been assumed that the characteristic features are related to the unsteady growth conditions within a FBR. However, in this project is has been proven possible to operate a steady state hot wall reactor, and find growth conditions at which similar patterns were formed. More research is needed in order to draw final conclusions, but being able to reproduce such patterns in steady state, may be one step on the way to understand the phenomenon. This experiment is presented in paper VII.

The last part of the work revolves around operation of the fluidized bed reactor and characterization of the produced material. Different growth regimes were identified and the ability to supress fines formation and promote growth on the fluidized beads was demonstrated. Different types of fines formation and their origin were also found. To deposit a dense layer over a layer of deposited fines and thereby capture the fines was also achieved. These findings are presented in paper VIII.

1.9 Publications

Paper I:

W. O. Filtvedt, A. Holt "Use of FBR technology for production of Silicon Feedstock" Proceedings of Silicon for the Chemical and Solar Industry X, Geiranger Norway, Department of Materials Science and Engineering, Norwegian University of Science and Technology. (2010) 275 – 280

The proceedings provide a comparative study of polysilicon production methods and why FBR production may have an advantage over alternative methods. Fundamental advantages and challenges of competing routes are discussed.

Paper II:

W. O. Filtvedt, M. Javidi, A. Holt, M. C. Melaaen, E. Marstein, H. Tathgar, P. A. Ramachandran, "Development of fluidized bed reactors for silicon production", Solar Energy Materials and Solar Cells 94 (2010) 1980 – 1995.

The article gives a summery of the proposed design solutions for FBR production of polysilicon through the last 50 years. Key challenges and main solution trends are identified. The article includes discussions on heat loss, fluidization regimes, fines formation, unwanted depositions, material quality and contamination. A number of groups and companies have been active over the years due to the cyclic nature of the polysilicon market. This history has led to a number of different solutions to the same challenges. Systemizing this background was regarded important as many quite related solutions have been developed independently over the years.

Paper III:

W. O. Filtvedt, A. Holt "Silane based CVD reactors, governing mechanisms and concepts" Proceedings of SolarCon China 2012, Shanghai, Symposium II: Silicon Materials Manufacturing, (2012) Article 6.

This article revolves around a discussion on silicon growth mechanisms active within a silane based CVD reactor. Further, the paper provides a discussion on how these mechanisms are influenced by the fluid mechanics of a FB reactor and how to deal with the inherent challenges. Much fundamental research has been performed on silane pyrolysis and characterization of powders and films produced under different process conditions. However, the experiments have often been performed at low pressures and concentrations, alternatively at scales quite far from the industry. When operating the FBR, it stands out that some of the growth mechanisms active in larger scales and at atmospheric pressures are not fully accounted for by the earlier experiments.

Paper IV:
W.O. Filtvedt, A. Holt, P.A. Ramachandran, M.C. Melaaen, "Chemical Vapor Deposition of Silicon from Silane: Review of Growth mechanisms and Modelling/Scale up of Fluidized Bed Reactors", Solar Energy Materials and Solar Cells 107 (2012) 188–200

The article contains a survey of established theory around silane decomposition and silicon growth within a CVD reactor. The article gives some insight to what experimental and analytical studies that have been performed earlier. The presentation further gives an overview of established modeling procedures and inherent challenges with scaling based on input from lab and pilot sized reactors. The paper concludes with a discussion on different reactors currently active in the market and how these meet the challenges of decomposition and growth.

Paper V:
W. O. Filtvedt, M. C. Melaaen, A. Holt, M. Javidi, B. R. Olaisen "Composite Distribution Solution for Minimizing Heat Loss in a Pyrolysis Reactor" International Journal of Chemical Reactor Engineering Vol 9, (2011) A84

The publication gives a presentation of the IFE FBR design. Thermal imaging and basic CFD modelling is used to verify and describe the potential of the solution. This solution limits the heat loss through the distribution plate without giving undesired depositions or insufficient temperatures in the bottom of the particle bed. The solution was patent pending at the time of thesis submission and the patent application is found as Appendix 1 of this thesis.

Paper VI:
W. O. Filtvedt, H. Klette, A. Holt "Process Optimization in Fluidized Beds for Silicon Production" Proceedings of Silicon for the Chemical and Solar Industry XI, Bergen Norway, Department of Materials Science and Engineering, Norwegian University of Science and Technology. (2012) 275 – 280

The proceedings include a presentation of initial experimental results from the early silicon deposition studies. SEM is used to inspect the deposition and a discussion on the process control and quality of the produced material. Silane was decomposed and a silicon layer was grown on the TCS based seeds.

Paper VII:
W. O. Filtvedt, A. Holt "Silane Based CVD Growth, Governing Mechanisms, Material and Concepts" Proceedings of EU PVSec 2012, Frankfurt Germany, (2012) 2.AV.4.44

The proceedings provides a presentation of an empirical study of growth on a hot wall in a through flow reactor. The experiment is performed in another silane pyrolysis reactor at IFE. The experiment was an attempt to reproduce a periodic pattern of pores known to be present in commercial silane based FBR material. The theory was that the periodic pattern is related to fundamental growth mechanisms within such reactors and not especially related to the nature of a FBR. It was possible to reproduce the pattern in steady state.

Paper VIII:
W. O. Filtvedt, T. Mongstad, A. Holt, M. C. Melaaen, H. Klette "Growing Silicon from SiH4 in a Fluidized Bed Reactor, Operation and Results" Accepted for publication by International Journal of Chemical Reactor Engineering (2012)

The article presents experimental results from several different runs of the FBR. Different growth regimes possible within a silane based FBR is accounted for and presented. Regimes leading to porous and dense material are presented. Further, a relationship among temperature, silane concentration and fluidization regime were found. There was no attempt to form a generalized model for the observed phenomenons. Two different sources of fines were found as well as process domains where both were supressed. The two types of fines identified was gas initiated fines and powder released from the surface of the silicon beads. The ability to grow a dense layer over a deposited porous layer was demonstrated and the nature of the captured material is presented.

2. Purification process

The starting point for production of polysilicon is metallurgical grade silicon. The precursor gases are produced through hydrochloronation of metallurgical silicon and subsequent refinement to either TCS ($SiHCl_3$) or silane (SiH_4). These reactants are subsequently thermally decomposed and elemental silicon is harvested. A main feature of the two routes is that they can produce a clean silicon containing gas. A clean precursor for the decomposition stage is refined from this gas. The challenge in the decomposition stage is to avoid contamination of the deposited material. Two routes are here presented, the Siemens reactor were resistance heated silicon rods are used for heating and decomposing the precursor, and the FBR where silicon beads are used to carry heat to the precursor gas for subsequent decomposition and deposition on the beads.

2.1 Precursors

TCS is produced by blowing hydrogen chloride through a fluidized bed of silicon particles at about 300°C, eq. 2.1. For an optimized system the fraction of TCS of the total produced gas, may be in the order of 85 – 90%. The rest will primarily be other chlorosilanes that have to be recycled, Shriver and Atkins (2010).

$$Si + 3\ HCl \rightarrow SiHCl_3 + H_2 \qquad\qquad (2.1)$$

There are several ways of processing TCS into silane, but one commonly used route is through a series of redistribution reactions and intermediate distillations. One such route is summarized in eq. 2.2 – 2.4. Since a major part of the processing involves altering the temperature in order to promote certain reactions and separate different gases, much work has been done over the years to limit the heat loss and maximise heat recovery.

$$2\ SiHCl_3 \rightarrow SiH_2Cl_2 + SiCl_4 \qquad\qquad (2.2)$$
$$2\ SiH_2Cl_2 \rightarrow SiHCl_3 + SiH_3Cl \qquad\qquad (2.3)$$
$$2\ SiH_3Cl \rightarrow SiH_4 + SiH_2Cl_2 \qquad\qquad (2.4)$$

In the first stage trichlorosilane $SiHCl_3$ is decomposed into dichlorosilane (SiH_2Cl_2) and silicon tetrachloride ($SiCl_4$), eq. 2.2. These two gases are separated by distillation since the boiling points of the two are 8°C and 57.65°C respectively. Dichlorosilane is then decomposed into trichlorosilane and monochlorosilane (SiH_3Cl) as shown in eq. 2.3. Subsequently the gases are separated through distillation since the boiling temperatures of the two are, 31.8°C and 22.8°C respectively. Lastly the monochlorosilane is decomposed into monosilane (SiH_4) and dichlorosilane before the last distillation as seen in eq. 2.4. The boiling points of the last two products are -112°C and 8°C respectively.

The primary concerns when producing the precursors are the purity of the product and the operation and capital cost of the process. These cost are linked to how efficient the overall process is in terms of energy consumption, cost of power, labour and capital. The challenge of purity is a broad term involving both the design of the individual steps, the purity and quality of the design materials as well as the stability of the feedstock. Of course interrelated challenges may occur, such as varying impurity levels of certain species in the feedstock may promote reactions with equipment surfaces and thereby indirectly lead to contamination, although the impurity level in the feedstock may be low.

2.2 Decomposition and deposition

Producing silicon from these precursors means heating them to above their decomposition temperature. The decomposition temperature of silane is about 420°C depending on pressure, for TCS the theoretical number is 468°C. These numbers are, however, not representative as the decomposition leads to a number of intermediate species that subsequently may both decompose or react with each other.

There are two fundamental challenges in regards to choice of operation temperature. For the TCS based Siemens reactor, a number of silicon rods are used as the deposition surface. A set of silicon filaments are placed under a cooled dome and heated to about 1100°C. The heat is supplied by passing a current through the silicon rods. The choice in temperature is partly a result of silicon's electrical conductivity properties that becomes favourable at these levels, and partly a result of present intermediate species in a TCS based reactor. When operating the reactor at these high temperatures, it is both possible to increase the yield since the operation temperature exceeds the decomposition temperature of produced higher order chlorosilanes. It also supresses chlorine encapsulations and thereby increases the quality of the produced material, Herrick (1984).

When moving from Siemens reactors to FBRs, it is possible to reduce the operating temperature since there is no need to control electrical conductivity of the silicon. The reactors are however still operated at temperatures in the range 850 - 1050°C due to the possibility of chlorine encapsulations at lower temperatures and to increase the yield.

Silane based reactors have two advantages over TCS based reactors. The first advantage is the possibility of increased yield, since the produced intermediate species have decomposition temperatures below the operation temperature of the reactor. It is thus possible to harvest more of the bound silicon in the precursor and thereby reduce need and scale of the recycling facility.
The second advantage is the process temperature, which is in the order 650 - 800°C. Thermal losses may therefore be reduced both as a result of lower heating of the through flow and lower temperature difference between the hot and cold surfaces.

Processing the precursors further to elemental silicon is the result of one of these two overall reactions Eq 2.5 and 2.7:

$$SiH_4 \rightarrow Si + H_2 \hspace{5cm} (2.5)$$

$$SiHCl_3 + 2\,H_2 \leftrightarrow Si + 3HCl \hspace{4cm} (2.6)$$

In the case of silane there are however about 114 possible intermediate reactions whereof several reversible, Frenklach et al. (1996). These intermediate reactions are sensitive to the concentration of different intermediate species and macroscopic properties such as temperature and pressure. When the silane molecule decomposes and produces a set of intermediate species, the local properties will determine what route the silicon atoms take on its way to elemental silicon. For all silane based reactors there are several challenges. The first being production of fine dust (fines) which is a broad term describing all forms of small particles that may be produced within such reactors. One contributor to such formations is

decomposition in gas phase, where solid silicon particles are formed from gas precursors without a solid deposition surface. A second contributor is inadequately bound depositions that are released from the beads post deposition.

Another challenge is undesirable depositions on surfaces other than the intended deposition surface. For all such pyrolysis reactors, this is a problem. The reactions leading to formation of solid species from gaseous precursors are temperature dependent. A main solution is therefore to keep all surfaces where deposition is not wanted, colder than the desired deposition surfaces. This is however not sufficient as silane based reactors tend to produce substantial amounts of fines that tend to build up at all surfaces including the cooled ones. The fines absorption of the radiate heat in such reactors is large thus leading to a challenge of undesired heating of surfaces one wants to keep cold.

The third challenge is inadequate quality of the finished product. The low quality may include porosity, amorphous encapsulations and impurities. The challenge of impurities is a combined and broad theme as this both includes crude and direct problems like design materials in the pyrolysis reactor, but also indirect challenges like porous and amorphous structures ability to form bonds to contaminants post production.

Several mechanisms come into play and determine the nature of the deposited material and whether production of fine dust, porous depositions or dense material is dominating. The interested reader is referred to paper III and IV of this thesis for more details.

2.3 Fluidized bed reactor

An alternative to the Siemens reactor is the fluidized bed reactor (FBR). In a FBR, the reactor vessel is filled with silicon particles Fig. 1.3. A fluidizing gas like hydrogen or nitrogen is injected at the bottom of the reactor to fluidize the particles. The definition of fluidizing the particles means the drag force on the individual particles balances the weight of the particle. In this state, the bed of particles behaves like a liquid and the continuous flow of gas keeps the bed in motion Yang et al. (2003). The particles are heated by some means to a temperature above the decomposition temperature and the reactant gas is inserted to the bed. Upon decomposition, the silicon is deposited on the particles thus making them grow. After some dwell time the particles have grown to a size suitable for extraction. The finished beads are then extracted and new small seed particles are either inserted to or produced within the bed.

For TCS based reactors, the reverse reactions can be aggressive, making the overall yield too low. The desired deposition surface in a FBR is the beads. Since the temperature and surface species of the beads varies in time, the silicon atoms will have varying bondage to the surface and may thus be more easily removed than in a Siemens reactor where the conditions at the deposition surfaces are more stable.

For silane based reactors the main challenge have been purity and to some degree porosity. There are also several intermediate and reverse mechanisms in silane-based reactors. A main difference from TCS is however that the intermediate species to a larger degree are solid and hence some may be captured. The solid intermediate species are in the form of clusters of hydrogen containing silicon. The clusters have dangling bonds. New dangling bonds are continuously produced as hydrogen is released. They may thus be scavenged and harvested by forming bonds to the surface of the silicon beads. The increase in yield comes with the cost of

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larger inhomogeneity. Even though the material is more inhomogeneous and may contain more impurities than what is achievable in a Siemens reactor, the material has proven to be competitive on the world market MEMC (2010), Jiao et al. (2011). The common FBR layout is to have injection of the fluidizing gas through a distribution plate at the bottom of the reactor. The reactant gas is either premixed with the fluidizing gas or injected diluted or undiluted through separate nozzles. The heating can be done in a number of ways at a number of locations through the bed, but the simplest way is to heat the wall of the bed directly by means of heating elements.

The volume above the bed higher than where the particles reach when getting ejected from bursting bubbles is called the freeboard. In industrial applications the freeboard often suffers from fines clogging. If reactant gas reaches the freeboard without being decomposed it is likely to produce fines because the temperature often is too low to produce crystalline structures although it is above the decomposition temperature. Several solutions exist to solve this challenge.

Other FBR problems are clogging of reactor internals because of undesired depositions, production of fine dust (fines) because of homogeneous decomposition and agglomeration due to insufficient agitation of the bed. Homogeneous decomposition is decomposition in gas phase while heterogeneous decomposition is decomposition at a depositing surface such as the silicon beads.

A number of different FBR designs have been proposed over the years. Several companies and research groups have performed research and proposed designs. Due to the cyclic nature of the polysilicon market, few research groups have been continuously active over long periods of time. This lack of continuity in combination with scarce availability of development reviews has resulted in a number of both similar and very different solutions to the same fundamental challenges. The interested reader is referred to paper I and II of this thesis for more details.

3. PhD project

The aim of the project was to build and operate a state of the art fluidized bed and in doing so, identify key challenges within the technology in order to map out where future research needs to be focused. Few research groups outside the industry have performed experimental research on this scale. It is believed important to do applied research on larger scales in order to understand the process and challenges within the industry. Ultimately both the quality, yield and fines formation are linked to the intermediate reactions which is again linked to the scale. It is therefore important to gain empirical insight on how to control the overall process under conditions similar to those used in the industry.

3.1 FBR design and experimental setup

Early in the project it was identified that the temperature of the deposition surface upon impact with the reactant is important in determining the nature of the produced material. There are several reasons for this correlation and the interested reader is referred to paper III and IV of this thesis for more details.

Several layouts and solutions have been proposed over the years. Since the market has been highly fluctuating, few research teams have been continuously active over a long time. The few programs that have been active are within industry and the results of the research are therefore not published. This situation has caused slow technology improvement rate and much parallel research. The most obvious indication for the situation is the large number of patents filed over the years. There also exist several incidents of seemingly reinvention of forgotten solutions. The interested reader is referred to paper II for more details on the design evolution over the years.

In a silane based CVD reactor, the deposition surface needs to attain a temperature of at least 650°C. However, at temperatures this high, the decomposition reactions are quite fast and when combined with the short distances present within a FBR, this results in a short reactant residence time. This short time results in a very small active volume of the reactor. Most of the reactions are happening close to the inlet of the precursor. To keep close control of this part of the bed is therefore important since this influences fines formation, the quality of the produced material as well as the fluidization regime.

3.2 The IFE FBR design

Since the importance of the inlet area was identified through literature surveys, the candidate started working on a design capable of decoupling the inlet temperature of the fluidization gas from the operation temperature in the precursor inlet zone. Of course there is no way to completely decouple these temperatures. The flow of gas will have mass and thereby exchange heat with the beads upon impact. However, the largest heat loss is through the surface of the distribution system, often a distribution plate. The surface of the distribution plate will exchange heat with the beads and if cold thus cool the beads.

The inlet temperature of the gas needs to be maintained below the point of decomposition for the precursor. Most designs therefore do this by cooling the distribution plate. This can give insufficient cooling of the plate and thereby clogging due to growth in the plate, alternatively too efficient cooling which affects the temperature of the bed close to the plate.

The IFE approach is to insulate the bottom surface of the reactor and thereby limit the thermal exchange. In order to maintain control of the inlet temperature of the gas, the gas was fed in needles through the insulated plate. The cross section and material of these needles needed to be dimensioned in order to have sufficient heat draining capacity without loosing too much heat as shown in Fig 3.1. Initial testing of the design is presented in paper V and experiments utilizing the solution are presented in paper VI and VIII. The solution was still patent pending when the thesis was submitted. The PCT patent application is found in Appendix 1.

3.2.1 Pre heating and heating

In order to define the temperature upon impact between the reactant and the deposition surface, the reactor was equipped with the possibility of reactant pre heating. Pre heating is here referred to heating the gas before insertion to the bed. For the disclosed solution the fluidization gas and the reactant are mixed before the pre heating. The gas temperature may never exceed the tube wall temperature, and the wall itself may never be allowed to be above the decomposition temperature of the gas. Thus, in order to keep the heat load sufficiently low, the pre heating of the inlet tubing was distributed over a length of 3 m in addition to the possibility of heating the wind box separately.

The fluidization column was also kept high due to the same argument. Both wall growth and fines formation are linked to the temperature of the wall. Keeping the wall temperature as close as possible to the bed temperature is therefore important. Since the minimum required energy input is given as a certain mass is inserted at a certain temperature by the fluidization and precursor gas, the only way of decreasing the wall temperature is by using a larger heat exchange area. The fluidization column was in most experiments kept at about 1.75m. With a diameter of 153mm this height is substantial, and especially since most of the reactions are fast and thus happening close to the bottom.

The system was built for monosilane pyrolysis and used a premix of silane with nitrogen, hydrogen or a mix of the two. Having the possibility of altering between diluents was motivated by several factors. The difference in viscosity and density of nitrogen and hydrogen yields different fluidization properties. Further, the inert properties of nitrogen at the given temperatures give a distinct difference in growth conditions. Hydrogen is the industrial alternative, because of its cost and how the overall recycle loop may be arranged. Also, hydrogen play a role in the intermediate reactions on the way from silane to silicon. Increasing the partial pressure of hydrogen will thus directly influence the intermediate reactions Slootman and Parent (1993). Nitrogen would however not be a viable alternative within the industry but is merely used to investigate the process.
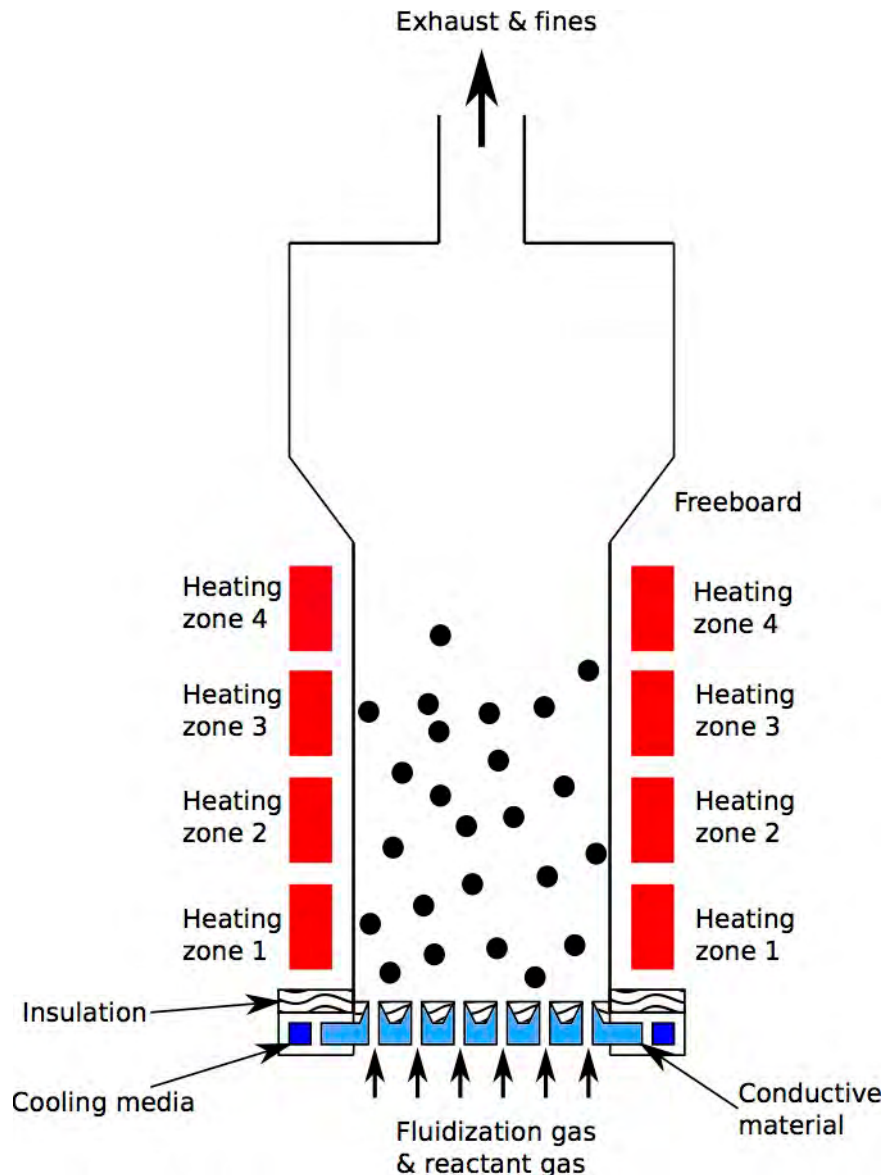
Figure 3.1: IFE fluidized bed reactor design

3.2.2 Instrumentation

The motivation for building the pilot size reactor was to retrieve data not obtainable in lab scale and if possible also beyond what is possible in industrial reactors. The reactor was therefore equipped with both temperature and pressure sensors directly into the bed. This solution is not an option in industrial applications as these sensors in most cases are bound to cause contamination.

The pressure sensors included both absolute sensors of various kinds; both for safety during operation and verification of vacuum during pump down before start up. The system was also equipped with differential pressure sensors (DP) in order to be able to track bubbles and qualitatively determine the state of fluidization. It should be noted that the ability to track bubbles requires only one bubble to be present between the sensors. This state typically only occurs if the bed is operated in slug flow, which is not the optimum operation domain to maximise output and minimize production of fines. However, the DP sensors may still give a

qualitative indication for state of fluidization even if several bubbles are present between them.

A quadruple mass spectrometer (MKS Vision 1000-C) was connected to the inlet and exhaust to analyze the purity of the reaction gases and to detect silane residuals in the exhaust. Mass spectrometry (MS) is an analytical technique that measures the mass-to-charge ratio of charged particles. It is used for determining masses of particles to determining the elemental composition of a sample or molecule. In the project MS setup, the pressure was reduced through a leaking valve in order to achieve a pressure of $1x10^{-3}$ bar, suitable for operation of the MS. The gas was ionized using a tungsten filament, and ionized species were directed into the quadruple MS.

Ionized SiH_4 exist in the form of Si^+, SiH^+, SiH_2^+ and SiH_3^+ ions. When ionized these species will form a characteristic distribution. This means that there will be a characteristic signature of peaks that may be separated from other present species. The interested reader is referred to paper VIII for more details.

4. Results

In this project a pilot size fluidized bed reactor for production of polysilicon by silane pyrolysis was designed, built and operated. Part of the design was patent pending upon submission of the thesis. An outline of the design is found in paper V of this thesis and the patent application is found in Appendix 1.

Two operation modes leading to two different types of silicon growth hence, porous and dense material have been established. Further, two different sources of fines production have been identified. The first being production of fines in gas phase and the second being release of loose material from the surface of the beads post deposition. These findings are presented in paper VI and VIII of this thesis.

It has proven possible to reproduce in steady state, a periodic porous pattern known to be present in silane based FBR material. These patterns were produced in a steady state flow through reactor. It has thus been established that the periodic patterns are not necessarily directly linked to the fluid mechanics of a FBR. The results are presented in paper VII of this thesis.

There exists a series of intermediate reactions and species in the monosilane to silicon process. The local temperature and pressure within the reactor will influence the production and annihilation of these species. An advantage over the use of trichlorosilane as precursor is that it has fewer reverse reactions and that the product distribution is shifted more heavily towards silicon. The overall yield of the mono-silane process is thus higher than that of the TCS process with lower recycle rate. The decomposition may start at temperatures as low as 350°C depending on pressure and a series of different stages may be active up to 610°C where the last bounded hydrogen will be released if the dwell time is long enough. The fines produced within the FBR may consist of amorphous silicon, silicon hydride, silicon-hydrogen complexes and even crystalline silicon, depending on operating conditions and the history of the individual particles constituting the fines. Several research groups have contributed to the present understanding of the decomposition and deposition process. A review of this development as well as a discussion on future research is presented in paper III and IV.

The design of the pyrolysis reactors currently utilized within the industry is the result of 50 years development. Several challenges have been identified and a large number of process solutions have been attempted. Due to the cyclic nature of the polysilicon market, the associated research has likewise been cyclic and very few research groups have been active over long periods of time. This situation has yielded several patents and different solutions to the same challenges. Since much material is available, but not systemized, it was regarded as an important contribution to present this evolution. The design development history is reviewed in paper I and II.

4.1 Reactor operation

One important result found in this project is the correlation between the state of fluidization, temperature, silane concentration and product quality. All these factors interplay and it is critical to map out the ideal operating domain for each specific layout. One complicating aspect is the growth of the beads. The growth influences the fluid mechanics and needs to be accounted for when designing and operating the system. Smaller beads give the possibility of utilizing lower superficital velocities with smaller bubbles and less fines formation. However, upon operating the system for some time, the average bead size increase yielding a necessary increase in fluidization flow. A strategy for bead extraction, sorting and reintroduction is therefore crucial in order to maintain a uniform product quality and process control.

Further, it was found that the best indication for the state of fluidization was the combined input from the differential pressure and temperature sensors. The DP sensors indicate the scale of the bubbles and where in the bed they are initiated. Typically the top of the bed will be fluidized first, upon going to higher velocities, the initiation point will be forced down until it reaches the distribution plate. However, the temperature sensors provide direct view of the efficiency of the mass transfer within the bed. Upon increasing the mixing of the bed, the temperature uniformity increases. By investigating the difference between individual zones, one gets a qualitative view of where mass transfer is occurring and if certain parts of the bed are stagnating. One may also use the temperature profile at the wall to aid this investigation. Large temperature differences at the wall generate large temperature differences in the bed that the mass transfer will have to overcome. The operation and associated product of the reactor is presented in paper VI and VIII of this thesis.

4.2 Product quality

Three aspects are generally considered when defining product quality. These are purity, crystallinity and porosity. For fluidized bed material, the fines production as percentage of the total silicon production indicates of the quality of the process.

4.2.1 Purity

Product purity depends on many diverse factors and involves process design, construction materials, product handling as well as feedstock stability. These have not been central to this project, as the aims of this project has been understanding of the fundamental decomposition and growth mechanisms, and not primarily design of a commercial system. However, some insight was gained through the execution of the project.

A central topic in silicon FBR design is how to construct the fluidization vessel. Silicon is a hard material and the abrasive wear on the reactor wall and internals is substantial. Since this wear contributes with possible contaminants, the design material of the wall is important. It should be noted that depending on operating conditions, there might be substantial depositions on the reactor wall. Several patents therefore exists on how to intentionally grow, maintain and remove protective silicon layers on the wall in order to separate the wall from the silicon beads and thereby minimize contamination. Further, it should be noted that these processes are challenging to control. There may therefore in any regards be situations where a part of the wall is exposed to the wear of the beads. In this situation, at least two points should be considered. What contaminants are present in the wall and what is the likeliness of them being removed by the abrasive wear? Some materials end up as favourable candidates including

quartz, silicon carbide and silicon nitride. The production route for the design material would be equally important especially in defining the homogeneity and possible contaminants. Production techniques vulnerable to wear as well as cross contamination from other products produced with the same equipment may lead to varying and unpredictable contamination.

Should one succeed in maintaining a protective silicon layer on the wall, there are still challenges with the high mobility of certain contaminants in silicon at the operating temperatures of such a reactor.

Little empirical research has been performed on impurities in this project. The main focus of the project was to monitor and control the process in order to build competence on reactor operation and silicon growth. In order to retrieve a sufficiently clear understanding of the internals of the reactor during operation there was a need for a substantial number of sensors. This large number of metallic sensors within the bed naturally prevented the ideal conditions for minimizing contamination. There was therefore not a main concern to minimize contamination from other sources. All experiments where performed within a stainless steel vessel without liner. The literature survey did however give some insight on how to proceed if one aims at minimizing contamination. These findings are presented in paper II of this thesis.

4.2.2 Crystallinity and Porosity

Crystallinity follows automatically by operating the reactor at high enough temperature. This temperature is theoretically about 610°C. However, the decomposition sequence involves a large number of intermediate reactions and species.

If the process is first optimized for high fines production in order to deposit a layer of fines on the beads and subsequently optimized for dense depositions, the first deposited fines will be captured inside the beads. In this project it was demonstrated that the fines capturing will result in pores within the beads. Earlier investigations by others have found pores within silane based FBR material, but it is now established that such pores may come from fines capturing.

The surface of these pores includes material originating from fines and it is found that this surface may be amorphous even though the bulk material is crystalline Zbib (2012). To control the production of fines and how they are scavenged will therefore both influence the porosity of the produced beads, as well the amorphous fraction of the beads since the internal surface of the pores may be amorphous due to the fines scavenging.

Production of dense and porous material within a FBR is presented in paper VI and VIII of this thesis. Fines capturing is presented in paper VIII.

Further, it has proven possible to reproduce a periodic porous pattern known to be present in silane based FBR material. The periodic deposition was achieved in a steady state flow through reactor. The motivation for this exercise was to investigate if the phenomenon was directly linked to fluid flow in a FBR or linked to the fundamental growth conditions during silane pyrolysis in a hydrogen rich atmosphere at these pressures and temperatures. The attempt was successful in achieving the pattern. However, full understanding of the underlying mechanisms is not established and thus leaves rooms for further research. The experiment promoting porous cyclic growth in steady state is presented in paper VII.

4.3 Fines formation

There are two main types of silicon growth within a silane pyrolysis reactor. The two are homogeneous decomposition also known as gas phase nucleation and growth, the other is heterogeneous growth at a surface. In a FBR the desired deposition surface is the silicon beads. The overall situation is more complex and involves a series of intermediate gaseous and solid species as well as reactive surface species. However, the simplification of two main types of growth may have some advantages. As a general approach, one may regard the competition between the two as a probability investigation of the two outcomes linked with a probability of the decomposition itself, Hsu et al. (1987).

If there is a silane molecule present and the temperature is high enough to achieve decomposition, the probability of either of the two outcomes will be linked to the distance or mean free path between the silane molecule and its reactive neighbour compared to the mean free path to a solid surface. The simplification has obvious shortcomings due to the number of possible intermediate species, but the model correlates well to this projects findings.

There exist at least two strategies to achieve heterogeneous deposition based on this theory, either decreasing the mean free path to the beads or increasing the mean free path between the reactive species. Decreasing the distance between the beads is most efficiently done by reducing the mean bubble size or alternatively by utilizing complex designs where the reactant gas is introduced to parts of the reactor where the bubble size is known to be smaller.

Fines capture includes the production of surface reactive species that interact with other intermediate species. The mechanisms are not sufficiently investigated to develop precise models and more experiments on amorphous silicon encapsulation and intermediate species interaction are necessary to elucidate the underlying mechanisms and aid further process development. Hydrogen is released from amorphous silicon at 610°C upon going from amorphous to crystalline structure, Odden II (2005). The structure transaction is not clearly visible in SEM studies, but may be identified by X-ray diffraction or TEM. It is probable that crystalline fines will be harder to encapsulate than amorphous fines due to the lack of dangling bonds and thus a definite reduction in sticking coefficient. The necessity of not passing this transition point is crucial if the design aims at enhancing fines scavenging.

In this project at least two sources of fines production were identified and accounted for. These were gas phase decomposition and the release of loosely bound silicon from the surface of the silicon beads. Further, the gas phase production of fines was correlated with the concentration of silane in the feed gas as well as the fluidization velocity. Increasing the concentration of silane, the temperature or the fluidization velocity leads to increased fines production. The findings are presented in paper VI and VIII of this thesis.

5. Conclusion and further work

5.1 Conclusion

Several attempts have been explored in the pursuit of replacing silicon as the backbone of the photovoltaic industry. The process has been going on for as long as the market has existed. However, so far silicon has proven the most competitive and efficient route despite all obvious challenges and shortcomings, Cucchiella (2012). Improving this technology further is therefore important, as there are currently no convincing short-term alternatives. This project has been directly focused at lowering the cost of polysilicon by investigating the challenges of the most promising alternative to TCS based Siemens proposed so far.

5.1.1 Project

The aim of the project has been to build a state of the art FBR for production of polysilicon and to optimize process parameters according to known challenges. FBR production of polysilicon as a concept is as old as the Siemens reactor, however FBR production has always been the promising alternative but not the dominating route. One aim of the work has therefore been to explore the obstacles that prevent rapid transition to FBR production. Through this project polysilicon has been produced and favourable process domains have been identified. Two different types of process modes have been proven to yield porous and dense growth. The ability to grow dense material by silane pyrolysis in a FBR has not been published by others and is one important step in understanding the underlying growth mechanisms. The process design proposed in this project is patent pending. Two review articles presenting the development of the technology and advances in process understanding over the last five decades was published.

5.1.2 Methods

The core of the contribution is contrained in the experimental data retrieved from an operative FBR designed and built through this project. Much work has been performed in regards to safety and monitoring. The involved gases are highly flammable and silane self ignites in air at room temperature. Attention to safety is therefor crucial in order to prevent accidents.

The project has resulted in an operative reactor capable of producing a material exceeding the density and homogeneity presently available at the open marked. In this regards, the project has been successful. However, it should be noted that the project has only focused on density, yield and crystallinity. There has not been any attempt to optimize for purity which is one of the most important aspect for the industry.

Pressure, temperature monitoring and thermal imaging as well as Mass Spectrometry SEM, Optical microscopy and XRD have been used to understand the process and characterize the produced material.

Further, a set of experiments was performed in a free space reactor in order to investigate the origin of periodic porous regions known to be present in FB material. The experiment was performed at steady state flow through a hot pipe reactor. The cross-section of the deposition was then investigated by optical microscopy, SEM and XRD.

The literature and patent surveys performed have been crucial in order to aid the design and operation of the reactor. Having a good overview of prior related research has facilitated a narrow search for favourable operation domains and provided a deeper understanding when running the reactor and characterizing the produced material.

5.1.3 Contributions

The PhD project has resulted in an operative fluidized bed, capable of producing a dense and homogeneous product. Through the project, deposition of fines with subsequent deposition of dense material has been demonstrated. This type of phenomenon yields pores known to be present in monosilane based FBR material. Two different types of fines are also demonstrated; one originating from nucleation and growth in gas phase and the other being released loose surface formations from the beads post deposition.

Further, a periodic pattern known to appear in FBR material has been produced in a steady state in a hot wall reactor. This result provides new insights in decoupling the phenomenon from silane based FBR material. The project has also resulted in four journal articles and four conference proceedings.

5.2 Suggestions for further work

There are several different aspects that should be investigated in the coming years. First and foremost, the governing decomposition and growth mechanisms are not fully understood, especially when going to atmospheric and elevated pressures. High concentration and higher-pressure operation may be desirable as this may enable higher throughput and lower operating cost for the industry. However, going to higher pressures and concentrations seems to yield different growth conditions that are not yet sufficiently studied. Also, going to higher pressures necessitates more costly reactor designs that may make the overall cost picture less favourable.

Cyclic porous growth is identified but not fully understood. It is believed important to investigate this phenomenon further in order to avoid this problem in industrial applications and maybe even use it to control the process. If the cyclic growth is related to some physical phenomenon giving attractive forces between the fines and the surface species of the beads under specific conditions, these conditions may be provoked to actively enhance the growth and thus increase production.

More research needs to be focused on fines formation and and the classification of fines. Further, it is important to establish what types of fines are suitable for scavenging, how to promote scavenging and how the actual scavenging mechanisms work. The concept of defining fines, as a one-dimensional quantity is misleading as fines contains a broad selection of highly different species, Caussat (1998).

Further, the project findings suggest the formation and scavenging mechanisms to be linked and part of the same fundamental process. A deeper understanding of these processes and identification of critical parameters is crucial in bringing this technology further.

In order to run continuously, a strategy for bead extraction, sorting and reintroduction needs to be explored. Several patents reveal an interest in the topic from the industry. However, little research has been performed by academia on how to control the sorting and seeding processes. An inherent challenge with the silicon FBRs is the possibility of a quite broad size

distribution. Having this wide distribution makes the fluid mechanics and process control demanding. This is, however, important as the fluid mechanics directly influences the yield, fines formation and product quality.

A challenge with earlier open research has been too little cooperation with the industry. An interesting area of research would be to do more applied research on operative industrial systems. This type of applied research would both directly aid the reactor development, but also shed light on new research topics closer to the actual industrial challenges.

6. References

Allen R. H. and Boone J. E., " Process for preparing polysilicon with diminished hydrogen content by using a fluidized bed with a two-step heating process" US Pat 5.242.671 (1993)

Bernreuter J., "The polysilicon market - Perspectives on Demand, Supply and Production Technologies" Silicon for the Chemical and Solar Industry Vol 11, pp 281 - 284 (2012)

B. Caussat, M. Hérmati, J. P. Couderc,"Local modeling of mass transfer with chemical reactions in a gas-solid fluidized bed. Application to the chemical vapor deposition of silicon from silanes" Powder technology 101, pp 43 – 55 (1998)

Coso G., Tobì I. as, Canizo C., Luque A., "Temperature homogeneity of polysilicon rods in a Siemens reactor" Journal of Crystal Growth 299, pp 165–170 (2007)

Cucchiella F., D'Adamo I., " Estimation of the energetic and environmental impacts of a roof-mounted building-integrated photovoltaic systems" Renewable and Sustainable Energy Reviews Vol 16, No 7, pp 5245–5259 (2012)

Dahl M. M., Bellou A., Bahr D. F., Norton M. G. and Osborne E. W., "Microstructure and grain growth of polycrystalline silicon in fluidized bed reactors "Journal of Crystal Growth 311, pp1496 - 1500 (2009)

Ege P. E., Hansen J., Allen L. C., "Silicon spout-fluidized bed", Assigned to REC Silicon, WO 2007.012027 (2007)

Frenklach M., Ting L., Wang H., Rabinowitz M. J., "Silicon particle formation in pyrolysis of silane and disilane", Israel Journal of Chemistry 36, pp 293–303. (1996)

Herrick C. S. and Woodruff D. W., "The Homogeneous Nucleation of Condensed Silicon in the Gaseous Si-H-Cl System" J. Electrochem. Soc.: Solid-state Science and Technology, pp 2417 - 2422 (1984)

Hsu G., Rohatgi N., Houseman J., "Silicon Particle Growth in a Fluidized-Bed Reactor" AIChE Journal Vol. 33, No. 5, pp 785 - 791 (1987)

Ibrahim J., Ivey M. J., Truong T. D., "High purity granular silicon and method of manufacturing the same", Assigned to MEMC, EP 1 833 759 B1 (2007)

Jiao Y., Salce A., Ben W., Jiang F., Ji X., Morey E., Lynch D., "Siemens and Siemens-like Processes for Producing Photovoltaics: Energy Payback Time and Lifetime Carbon Emissions" The Minerals, Metals and Materials Soc. JOM Vol. 63 No. 1 (2011)

Liu Y., Liu Y., "The Industrial research about China Solar PV Based on the Price of Polysilicon" Advanced Materials Research Vol. 383-390, pp 7043-7048 (2012)

MEMC Inc, "Building on the Past, Ready for the Future: A Fiftieth Anniversary Celebration of MEMC Electronic Materials, Inc", Vol. 55–56, pp. 38–40, MEMC electronic materials www.memc.com. (2011)

Nelson J., "The Physics of Solar Cells", Imperial College Press, 57, Shelton Street, Covent Garden, London WC2H 9HE, (2009)

NPD Solarbuzz Q3'2012 "Polysilicon and Wafer Supply Chain Quarterly Report" www.Solarbuzz.com (2012)

Odden J.O., Egeberg P.K., Kjekshus A. "From monosilane to crystalline silicon, Part I: Decomposition of monosilane at 690 - 830K and initial pressures 0.1 - 6.6MPa in a free-space reactor" Solar Energy Materials and Solar Cells 86 pp165 - 176 (2005)

Odden J.O., Egeberg P.K., Kjekshus A., "From monosilane to crystalline silicon. Part III. Characterization of amorphous, hydrogen-containing silicon products" Journal of Non-Crystalline Solids 351, pp 1317 - 1327 , (2005)

Osborne W. W., Spangler M. V., Allen l. C., Geertsen R. J., Ege P. E., Stupin W. J., Zeininger G., "Silicon fluid bed reactor", Assigned to REC, US 8.075.692 B2 (2011)

Shriver D. F. and Atkins P. W., "Inorganic Chemistry (5th Edition)". W. H. Freeman and Company, New York, 358. pp 645 (2010)

Slootman F., Parent J.-C., "Homogeneous gas-phase nucleation in silane pyrolysis", Journal of Aerosol Science 25 (1), pp 15–21. (1993)

Steeman R., Yonga J., Mjøsb Ø., Song A.,"Integrating the Value Chain: The Impact of Silicon Quality on Cell Performance" Energy Procedia Volume 15, pp 20 - 29 (2012)

Yang W.-C. "Handbook of fluidization and fluid-particle systems" Marcel Dekker Inc. 270 Madison Ave. NY 10016 (2003)

Zbib M. B., Dahl M. M., Sahaym U., Norton M. G., Osborne E. W. and Bahr D. F., "Characterization of granular silicon, powders, and agglomerates from a fluidized bed reactor" Journal of Mater Science 47, pp 2583-2590 (2012)

Part II

Paper I

W. O. Filtvedt, A. Holt

Use of FBR technology for production of Silicon Feedstock

Proceedings of Silicon for the Chemical and Solar Industry X, Geiranger
Norway, Department of Materials Science and Engineering, Norwegian
University of Science and Technology. pp 275 – 280 (2010)

W. Filtvedt was the main author and contributor to the publication. A. Holt was
the supervisor of the candidate and co-author of the publication.

Use of FBR technology for production
of Silicon Feedstock

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Abstract

About 40% of the energy consumed producing a grid connected solar energy system based on crystalline silion solar cells, is used to produce the silicon feedstock [13]. Reducing the energy consumption in this step is therefore crucial in order to minimize the energy payback time of installed capacity. The development of FBR for the production of poly silicon is here reviewed. Through the last half century several research groups and companies have contributed to the development of such reactors to a point where the method is competitive on the terms given in today's marked. Most work within the field of research has been done by the industry and this has resulted in few articles and a substantial amount of patents on the topic. This proceedings aims to give a short summary of the development, on what concepts have been investigated, what challenges arose and where the development stands today.

Introduction

Market situation

The world's energy demand is ever increasing and there is a growing interest in finding alternative renewable energy sources. The concept of Photo Voltaic (PV) cells is over a century old. But the increasing energy prices in combination with more cost efficient production methods and higher efficiencies already makes PV competitive in several countries and regions today. Over 88% of today's PV cells contain silicon [12]. Being one of the most abundant elements on earth, the accessibility of the raw material is in most aspects unlimited. The processing is however complicated and energy consuming as the most efficient cell concepts require a contamination of selected impurity species as low as ppb level. These highest purity levels are today obtainable by going through gas and chemical vapour deposition (CVD). New metallurgical routes have also shown promising results. Elkem Solar is one company utilizing a unique route yielding competitive cell efficiencies at low production cost.

Silicon based solar cells are expected to play a major role in the utilization of solar energy and the market for poly-silicon is expected to

grow rapidly in the next five years. The projected worldwide capacity in 2012 is predicted to be about 200,000 Mt./year and individual plant capacity is expected to be of the order of 10,000 Mt./year, if not larger [2], [1] Correspondingly, the share of power generation from PV is expected to increase and is already of the order of 3.8 GW installed base in Germany. The target cost of production is set to around $20-25 per kg [1].

Silicon CVD

In the early days of silicon CVD several gases were explored for the purpose, but in today's reactors monosilane SiH_4 (silane) and trichlorosilane $SiHCl_3$ (TCS) are the ones frequently used. Upon being heated to the decomposition temperature, the gases undergo the

$$SiH_4 \rightarrow Si + 2H_2 \tag{1}$$

$$SiHCl_3 \rightarrow Si + 3HCl \tag{2}$$

The decomposition temperature for silane is about 420°C [3]. However at this temperature the kinetic energy of the individual silicon atoms is too low to form crystalline structures. Low temperature atmospheric pressure decomposition will therefore cause amorphous structures to form [4]. Silane based CVD reactors are therefore often operated at temperatures in the range 650°C to 800°C. Some designs utilize after treatment of the beads at even higher temperatures to assure a crystalline structure.

The decomposition temperature of TCS is about 468°C [3]. The CVD reactors utilizing TCS are however often operated at higher temperatures because amorphous structures might cause chlorine encapsulations. These chlorine encapsulations will cause defects and reduce the quality of the material. Typical temperature range for TCS reactors is 850 - 1100°C.

The Siemens reactor

In a Siemens reactor the reactant gas is fed into a bell reactor containing heated silicon rods. The reactant gas is heated to decomposition by the rod and deposits a layer of silicon on the rods while the excess gas is extracted. In order to prevent unwanted depositions on the wall the rest of the reactor is cooled.

The Siemens reactor is the most frequently used CVD reactor. The quality of the finished product is high on the expense of high energy consumption and low gas utilization. The basic idea behind the Siemens reactor is the same as the Bell patent of 1946 where silicon bound in a silane is thermally decomposed by a hot surface, whereby the silicon is released and deposited onto that surface. Fundamentally the heat and silicon comes from each side of the deposition surface.

There are a number of ways to produce the heat, the most commonly utilized method is to heat doped silicon rods by resistant heating. Other methods include using silicon nitride coated graphite elements as the heating element. This method eases the temperature control, but introduces an additional purifying step after the deposition to remove the nitride.
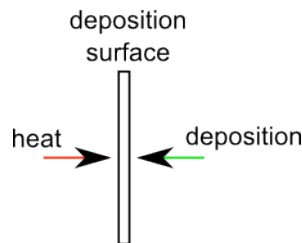
Figure 1: The Siemens reactor, heat is injected from the back of the deposition surface

The Fluidized bed reactor

In a FBR, the reactor vessel is filled with silicon particles Fig. 2 A fluidizing gas like hydrogen is injected at the bottom of the reactor to fluidize the particles. Fluidizing the particles means the drag force on the individual particles is on the same scale as the weight of the particle. In this state the bed of particles behaves like a liquid and the continuous flow of gas keeps the bed in continuous motion. The particles are heated by some means to a temperature above the decomposition temperature

and the reactant gas is inserted to the bed. Upon decomposition the silicon is deposited onto the particles thus making them grow. After some dwelling time the particles have grown to a size suitable for extraction. The finished beads are then extracted and new small seed particles are either inserted to or produced within the bed.

Fluidized bed reactors hold the potential to become the dominating CVD reactor for production of solar grade silicon. Large players in today's market like Renewable Energy Corporation (REC) are producing increasing amounts of their material through FBR instead of Siemens reactors. Other companies like Wäcker and MEMC have also had substantial research programs on FBR based silicon feedstock production.
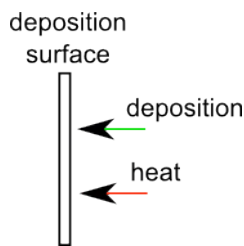
Figure 2: The FBR reactor, heat and depositions are both injected from the outside of the beads

One common FBR layout is to have injection of the fluidizing gas through a distribution plate at the bottom of the reactor. The reactant gas is either premixed with the fluidizing gas or injected diluted or undiluted through separate nozzles. The heating can be done in a number of ways at a number of locations through the bed, but the simplest way is to heat the wall of the bed directly by means of heating elements.

The volume above the bed which is higher than what the particles reaches when getting ejected from bursting bubbles is called the freeboard. The freeboard often suffers from fines clogging. If reactant gas reaches the freeboard without being decomposed it is likely to produce fines because the temperature is too low to produce crystalline structures although it is above the decomposition temperature.

The fundamental difference from the Siemens method is that there is no way to produce the heat within the beads. Several research groups have looked into producing the heat within the beads by different types of fields, but this is not easily done without additional heat sources. This means that both heat and depositions comes from the same side of the deposition surface. To achieve a thermodynamically advantage to the

Siemens method these process need to happen at different space and time locations.

There are basically two main ideas to achieve this desired effect. Either first heat the beads and then transport them to a location within the bed where they are subjected to a silicon containing reactant gas, whereby the decomposition and deposition is utilized. Wäcker chemie and Kim et al. of Korea Institute of Chemical Technology have both solely published designs based on this idea.

The other idea is to decompose and deposit at lower temperatures and then transport the beads to a high temperature zone for annealing and crystallization. This method is extensively utilized by ASIMI, now REC Silicon, in their published designs as well as MEMC.

Challenges

Fines formation

The FBR has several advantages to the Siemens method. If one zooms in on the actual thermal and fluid mechanical mechanisms that govern the decomposition and deposition one sees that there are two opposing mechanisms fighting each other. The heat travels through the gas to heat up the individual silane molecules. As the molecules get heated to a level of decomposition the flow direction and velocity is crucial to make the silicon atom get in contact with a silicon surface before it bonds to another free silicon atom resulting in the production of fines. One advantage of the Siemens method is that the thermal and fluid mechanical zones may be defined and monitored in a very controlled manner.

The problem is however that you either have to choose to have a large high temperature zone outside the rods which yields high utilization of the gas but less of the decomposed silicon atoms reach the hot silicon surface before combining with other silicon atoms, thus yields higher fines production.

The other solution is to confine the high temperature zone to a small region around the rods by massive outside cooling. This is the method used in the Siemens reactors today. Through low heating, intense cooling and a substantial fluid velocity the gas utilization is quite low in the order of 30%, but the amount of fines is very low.

If the same exercise is made in a FBR one notices that the scale of the problem is quite different. As long as bubbles are small most of the free silicon atoms fuse to silicon particles and the amount of fines is very low. A problem of the FBR is that the flow is quite chaotic and the temperatures and velocities in the decomposing and depositing part of the reactor varies greatly over time. This means that the structure of the finished product varies and if care is not taken some structures will cause hydrogen entrainment [5].

The main mode for silane decomposition is by two pathways as discussed by Lai [6] One is the homogeneous pathway and the other is the heterogeneous pathway and Lai indicated that the homogeneous pathway is responsible for the fine formation. In their model, SiH_4 decomposes in the gas phase to form Si vapor. It may be noted that the vapor pressure of Si is low but is included in the model. Once the Si vapor concentration exceeds the supersaturation value, the Si vapor nucleates into Si nuclei which then coagulates and coalesce into fine particles. The fines can also be captured by the seed particles. This is sometimes known as the scavenging mechanism, Lai adopted this mechanism and coupled it with a phenomenological model for fluid beds.

Unwanted depositions on internals

A general challenge of all silicon FBR reactors is undesired depositions on the reactor internals. The problem is the fundamental transport mechanisms governing in a FBR process see Fig 2. Since both heat and mass transport is happening from the same side of the deposition surface, the heat has to be transferred to the beads by some means without getting in contact with the reactant gas.

In general there are three methods being utilized to minimize undesired depositions. The first is to avoid contact between a hot wall and reactant gas. Both Wäcker, MEMC and CalTech has proposed injecting a protective gas layer over the hot surface to avoid contact between the wall and the reactant gas.

The second is to actively remove depositions by etching. Both REC Silicon, Kim et al. and MEMC has proposed different ways to utilize this method. N. M. Hwang looked into this method in 1999 and by his findings it should be quite possible to utilize simultaneous deposition and etching in the same reactor volume [7]. This solution was later incorporated in S. M. Lords design of 2002 [8].

The third method is utilizing a fundamental challenge of all FBR designs. Because of the high temperature of the bed compared to the relatively low melting point of the silicon beads, the bed behaves sticky

[8] and inhabits a violent nature. In combination with the hardness of silicon this yields high abrasive wear on the internals of the reactor. By controlling the flow of the bed, one may use this wear to control the thickness of the wall depositions. This method is both utilized in CalTech's design of 1984 [9], Union carbide corporation's design of 1989 [10] and ASIMI now REC Silicon's design of 1995 [11].

Summary

The most promising FBR design currently is the ASIMI now REC Silicon layout. The basic idea is to do the deposition semi cold, This means a temperature above the decomposition temperature, but below ideal crystallization temperature. After the deposition the beads are brough to a hotter part of the reactor for post deposition annealing. MEMC is also using this design, although they are also dividing their reactor into radial zones of different reactant gas concentration.

The other main solution is preheating the beads in a hot part of the reactor and then transport them to a cold part of the bed. The reactant gas is then injected to the colder part of the bed meeting the hot beads. After the deposition, the beads go back to the hot part and the cycle continues. Wäcker and KRICT have both utilized this method.

A more extensive review article on the topic is submitted for publication.

References

1. M. Javidi, and P. Ramachandran, *Developments in Polysilicon for PV Applications* , Photovoltaic Summit Europe, Rome Italy (2009)

2. Gerald Parkinson, *Polysilicon Business Shines Brightly*, Chem. Eng. Progress, Vol **104** No 8 (2008) pp 8-11

3. Stephen P. Walch and Christopher E. Dateo, *Thermal decomposition pathways and rates for Silane, Chlorosilane, Dichlorosilane and Trichlorosilane*, Journal of physical chemistry, Vol **105**, (2001) pp 2015-2022

4. W. A. P. Claasen and J. Bloem, *The nucleation of CVD silicon on SiO_2 and Si_3N_4 substrates*, J. Electrochemical Soc **Vol 127** Issue 1, (1980) pp 194-202

5. Larry M. Coleman and William Tambo, Assigned to Union Carbide Corporation, *Waste treatment in silicon production operation,* US Pat 4.519.999 (1985).

6. Shih-Ming Lai, *Fluidized bed pyrolysis of silane*, Washington University (Saint Louis, Mo.). Thesis Chemical Engineering, (1987).

7. Nong M. Hwang, *Deposition and simultaneously etching of Si in the CVD process: apporach by the charged cluster model*, Journal of Crystal Growth, **Vol 205**, (1999) pp 59 – 63

8. Stephen M. Lord, *Machine for production of granular silicon* US Pat 2002.0.081250 (2002).

9. G. C. Hsu et al. Assigned to California Institute of Technology, *Fluidized bed silicon deposition from silane* US Pat 4.444.811 (1984)

10. Sirdhar K. Iya, Assigned to Union Carbide Corporation, *Reactor for fluidized bed silane decomposition* US Pat 4.818.495 (1989)

11. Stephen M. Lord and Robert J. Milligan, Assigned to Advanced Silicon Materials inc, *Method for Silicon deposition* US Pat 5.798.137 (1995)

12. Photon International, March 2010.

13. Alsema, E.A, de Wilde-Scholten, M.J. And Fthenakis V., *Environmental Impacts of PV Electric Generation – A critical comparison of Energy Supply options* 21st European Photovoltaic Solar Energy Confererence, p 3201-3207, (2006)

Paper II

W. O. Filtvedt, M. Javidi, A. Holt, M. C. Melaaen, E. Marstein,
H. Tathgar, P. A. Ramachandran

Development of fluidized bed reactors for silicon production

W. Filtvedt was the main author and contributor of the publication. A. Holt and
M.C Melaaen were the supervisors of the candidate and co-authors of the paper.
M. Javidi was the project manager at the time of the paper and has together with
P. A. Ramachandran contributed especially to chapter 4.2 & 4.3. H. Tathgar and
E. Marstein were co-authors of the paper.

Paper III

W. O. Filtvedt, A. Holt

Silane based CVD reactors, governing mechanisms and concepts

Proceedings of SolarCon China 2012, Shanghai, Symposium II: Silicon Materials Manufacturing, (2012) Article 6.

W. Filtvedt was the main author and contributor to the publication. A. Holt was the supervisor of the candidate and co-author of the publication.

Silane based CVD reactors, governing mechanisms and concepts

W. O. Filtvedt and A. Holt

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The reactions and mechanisms governing in a silane based CVD reactor for polysilicon production are complex and the end material depends on several interrelated factors. Different mechanisms come to play in a Siemens, fluidized bed or free space reactor. Understanding of these mechanisms is important in order to map out the limitations of competing technologies and to forecast future reactor concepts. The decomposition of the silane molecule undergoes a series of intermediate stages before forming the final product. The reactant concentration, heat rate, pressure and heat capacity of the diluent will influence these intermediate stages and play an important role in the formation of amorphous or crystalline structures.

Reactions

In the early days of silicon CVD several gases were explored for production of polysilicon, but in today's reactors monosilane SiH_4 (silane) and trichlorosilane $SiHCl_3$ (TCS) are the ones frequently used. Upon being heated to the decomposition temperature, the gases undergo the following reactions:

$$SiH_4 \rightarrow Si + 2\ H_2 \qquad\qquad [1]$$

$$SiHCl_3 + H_2 \rightarrow Si + 3\ HCl \qquad\qquad [2]$$
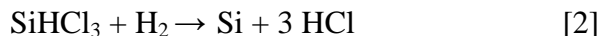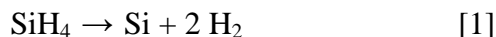
The decomposition temperature for silane is about 420°C (1). However at this temperature the kinetic energy of the individual silicon atoms is too low to form crystalline structures. Low temperature atmospheric pressure decomposition will therefore cause amorphous structures to form (2). Silane based CVD reactors are therefore often operated at temperatures in the range 650°C to 800°C. Some designs utilize after treatment of the beads at even higher temperatures to assure a crystalline structure.
The decomposition temperature of TCS is about 468°C (1). There exists however several intermediate gaseous species with higher decomposition temperature and reversible reactions with reaction rate inversely related to the temperature. The CVD reactors utilizing TCS are therefore often operated at higher temperatures to improve yield and because amorphous structures might cause chlorine encapsulations. These chlorine encapsulations will cause defects and reduce the quality of the material. Typical temperature range for TCS reactors 850 - 1100°C.

Decomposition reaction sequences

The earliest studies of silane pyrolysis (3) assumed a straight forward decomposition of the silane molecule into silicon and hydrogen according to eq. (1) However, later studies (4) introduced an intermediate stage in accordance with eq (3). The disilane molecule was to be a required intermediate stage between monosilane and silicon.

$$2 \ SiH_4 \rightarrow \ Si_2H_6 + \ H_2 \qquad\qquad [3]$$

The actual chain of events seems however to be more complex and more in depth work has been done on the matter by Purnell & Walsh (5). The general idea is that there is a complex set of reactions whereof some reversible that ends up with hydrogenated silicon, that is silicon that contains some hydrogen, a mix of silicon-hydrogen complexes and silicon of varying morphology. Purnell & Walsh concluded that the reaction described in eq. 4 would be the most likely first step. However, Robertson, Hils and Gallagher did several low pressure experiments and pro- posed that the decomposition process is surface initiated (6). They are however open to the reaction described in eq. 5 but then initiated from a surface in the CVD chamber. Ring et al. (7) did several isotope labelling studies and also indicated that the reaction described in eq. 5 could be more likely. The problem of large disilane production was however acknowledged and accounted for with additional reactions.

The apparent difference in opinion was later resolved through a number of different experiments and papers (8, 9, 10) and the chain reaction initiated by the reaction described in eq. 4 is now considered to be the most probable. Although surface initiated chain reactions are important for low pressure CVD, they cannot be dominating for higher pressures and especially when going to higher concentrations.

$$SiH_4 \rightarrow SiH_2 + H_2 \ (4)$$
$$SiH_4 \rightarrow Si_2H_3 + H \ (5)$$
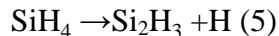
Further modelling was performed by Coltrin and Breiland et al.(11, 12). They proposed the initial reaction eq. 4 followed by the reactions described in eq. 6 - 8 and later the model grew even further incorporating thermal diffusion (13, 14).

$$SiH_2 + SiH_4 \rightarrow Si_2H_4 + H_2 \ (6)$$
$$Si_2H_4 \rightarrow Si_2H_2 + H_2 \ (7)$$
$$Si_2H_2 \rightarrow Si_2 + H_2 \ (8)$$
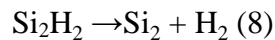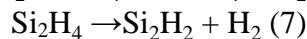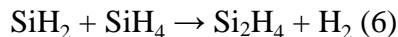
Another proposal was that Si_2 in gas phase served as a precursor for gas phase nucleation of silicon. This was founded on the identification of Si_2 in gas phase above a heated surface by laser excited florescence (9). The production of SiH_2 during monosilane

pyrolysis was verified by O'Brien and Atkinson (15) and they concluded this to be an important intermediate step.

The decomposition of monosilane is complex and the carrier gas may play an important role in the reverse reactions. A clear indication for this phenomenon is the work by Slootman & Parent (16) where a change in dilution shifted the critical concentration to temperature ratio.

Deposition

When the monosilane molecule decomposes, a chain reaction is initiated. The chain reaction is complicated and will depend on silane concentration, temperature, pressure, temperature of confining surfaces and the gradient of these variables. At lower pressures there is a distinct tendency to heterogeneous deposition and it may be indicators that the decomposition is surface initiated. Several investigations have been performed on the properties of a deposited film under different conditions (17, 18, 19). For atmospheric pressure, the deposited silicon will contain hydrogen and be amorphous up to a

temperature of $605°$ C (18, 20 - 25). The amount of hydrogen and the temperature at which it is possible to release it, will depend on operating conditions.

If the temperature is sufficiently high, the depositions will be crystalline (26). Whereas for lower temperatures the structure will depend on the operating conditions.

Herrick & Woodruff studied the difference between SiH_4 and $SiHCl_3$ and found that reverse mechanisms suppressed fines formation for trichlorosilane at the operating temperatures of a silicon CVD reactor whereas fines formation for a monosilane based reactor would be substantial (27). The results yielded that trichlorosilane would produce a more shiny and pure material although the yield would be lower for lower temperatures. For higher temperatures such as several Siemens layouts, the reactor reaches the decomposition temperature of many of the intermediate species and so increases the yield. This theory is in good agreement with the substantial amount of experimental data produced by others.

The number of produced particles will mostly depend on the temperature, but also concentration, pressure and type of dilution will play a role. It may seem that the hydrogen concentration directly influences the chain reaction. Frenklach et al. studied the production of particles produced homogeneously by laser scattering analysis (28). Their findings were that the production of new particles as a function of temperature reached an

apparent maximum at $877°$ C. The authors acknowledge the difficult task of explaining the decay in particle formation as the temperature is increased further. Their explanation is rather that the size of the particles as the temperature is further increased invokes different optical properties and will thus be read differently by the laser scattering method used.

In their modelling they made use of 117 elementary reactions and 42 chemical species. Wilke et al. also supported the two step mechanism from silane to silylene to silicon (29). Their aim was to describe silicon deposition on wafers in a hot wall reactor.

Alam & Flagan of Caltech developed Free Space and Fluidized Bed technology over several years and came a long way in defining the particle growth mechanisms (30, 31). A central topic in their research is the production and annihilation of intermediate species

and how mean free path to a particle surface in combination with these species determined the balance between production of fines, annihilation of fines and heterogeneous growth on fines.

$$\bar{d} = \left(\frac{6C\alpha_R}{\varphi\rho_p N_0} + d_0 \right)^{\frac{1}{3}} \qquad (11)$$

The mean particle diameter d is proposed according to eq. 11. C is the molar concentration of the reactant species responsible for the particle growth, α_R is the volume of condensed-phase material produced per mole of reactant gas, ρ_P is the particle density, and d_0 and N_0 are the initial particle diameter and number concentration, respectively. Growth is this limited by the amount of vapor available per particle. Unconstrained nucleation of low-vapor pressure species leads to very high number concentrations. The theory indicates two major fundamentals, i) the initial number of formed particles will influence the end size distribution since a large number of particles will all compete for the same remaining vapor and thereby limit subsequent particle growth. ii) To grow large silicon particles, it is necessary to limit the amount of condensable vapor in the reactor. Their solution is to let the same particles pass through a chamber of conditions that permits scavenging of condensable species but suppresses formation of new particles.

Alams theory continues and aims at describing how to maximise particle growth and suppress formation of new particles. The work continued later with Wu & Flagan (32) who concentrated on finding the critical concentration at which particle formation was suppressed. According to their work this development was abrupt and changed drastically at specified concentration / temperature relationships.

Reactor concepts

Various designs and alternations have been proposed through the years and the reader interested in FBR design is referred to the review of Filtvedt et al. (33) for a broader insight to the development history. This chapter will go through some highlights and aims to link the different designs to the various mechanisms active in a Silicon CVD reactor.

<u>FBR designs</u>

In a FBR, the reactor vessel is filled with silicon particles see Fig. 1. A fluidizing gas like hydrogen or helium is injected at the bottom of the reactor to fluidize the particles. Fluidizing the particles means the drag force on the individual particles is on the same scale as the weight of the particle. In this state, the bed of particles behaves like a liquid. When the gas flow is increased even further bubbles are formed and this keeps the particle bed in continuous motion. The particles are heated by some means to a temperature above the decomposition temperature and the reactant gas is inserted to the bed. Upon decomposition the silicon is deposited on the particles thus making them grow. After some dwelling time, the particles have grown to a size suitable for extraction. The finished beads are then extracted and new small seed particles are either inserted to or produced within the bed.
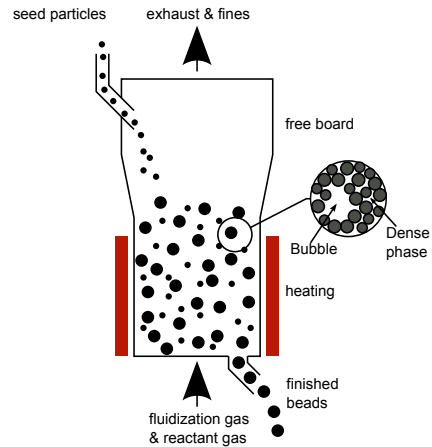
Figure 1. The fluidized bed reactor

Early FBR designs were closely linked to reactors built for catalytic cracking. One of the early topics was generating the seed particles. The seed particles naturally needs to be as pure as the finished product and this might be challenging if conventional crushing techniques are applied.

There are generally two established approaches to the solution. Either produce seeds from a part of the produced material or to produce the seeds directly from the reactant gas. A version of the first solution was proposed by S. Iya of Union Carbide Corporation who suggested the use of a high velocity jet to produce seed particles within the reactor (34). The problem of the solution was that this high velocity may produce large bubbles which will increase the mean free path to a solid nucleation site when the silane molecule reaches thermal decomposition (35, 36). This will in turn yield higher production of fines as well as the long high temperature dwelling time will increase the probability of producing amorphous silicon complexes which is harder to capture.

A version of the alternative design was proposed by Hsu et al. (37) which suggested producing fines within a separate reactor and introducing them to a FBR after some growth. One of the benefits of the solution is that the particles produced in a FSR tends to be spherical or semi spherical and the use of spherical seeds will enhance the probability of ending up with a spherical finished product. One challenge with the method is to grow the seeds in such a way that they consist of crystalline silicon of low porosity.

The problem of fines generation is known to be related to a combination of mean free path to a solid nucleation site, the concentration of reactant gas and the temperature. Within a FBR, increasing the mean free path is the same as increasing the virtual velocity and thus the mean bubble diameter. Gautreaux et al. (1988) (38) acknowledged this relation and proposed running their FBR in two modes. A high velocity fines generating mode and a low velocity fines capturing mode. The solution was taken further by Lord et al. of ASIMI which proposed a conical reactor in order to have the two modes at the same time (38, 39)

The Siemens Reactor

In a Siemens reactor, the reactant gas is fed into a bell reactor containing heated silicon rods (Fig. 2). The reactant gas is heated to decomposition by the rod and deposits a layer of silicon on the rods while the excess gas is extracted. In order to prevent unwanted depositions on the wall, the rest of the reactor is cooled.

The reactor was developed by Siemens during the 1950s and a number of patents were taken out on various alternations and operation modes of the layout. Originally the proposed reactant was TCS, but today also monosilane is frequently utilized.

The Siemens reactor is the most frequently used CVD reactor (40). The quality of the finished product is high at the expense of high energy consumption and low reactant gas utilization.
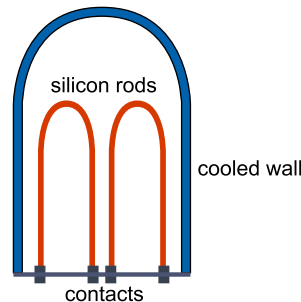
Figure 2. The Siemens reactor

The production of intermediate species and the surface growth on the rod is easier controlled since the temperature of the deposition surface is closely controlled compared to competing reactor concepts.

The crystal structure, porosity and purity of the silicon have proven to be more even than the material produced in fluidized bed or free space reactors.

The energy consumption has been decreased over the last years mainly through two strategies: i) Increasing the number of rods in the reactor and thereby limit the fraction of hot deposition surface which is directly interchanging thermal irradiation with the cold wall. ii) Coat the surface of the reactor wall with a liner of higher reflectance than the original quartz to limit absorbance of thermal irradiation.

Both strategies have proven somewhat successful, but the production of fines in a monosilane based siemens reactor will cause a layer of amorphous silicon powder on the inside of the bell jar and thus limit the effect of a reflective layer. For TCS based reactors however, the intermediate species will first and foremost be gaseous and not serve to produce such a powder layer.

Conclusion

Todays methods for polysilicon production is inadequate for future requirements to power consumption without compromising with purity. There exists several strategies to lower the power consumption both for Siemens and Fluidized bed reactors.

Today the lowest power consumption is achieved in monosilane based FBRs. However, maintaining high and stabile purity has proven challenging for all players active with this technology. The main challenge in a FBR is twofold, controlling the properties of the deposition surface namely the temperature and other properties of the beads. The other challenge is to control the decomposition sequence in such a way that unwanted intermediate species is avoided and/or managed and that the deposited silicon is homogeneous throughout the bead.

The Siemens reactors main challenge is power consumption. Controlling the deposition surface and decomposition sequence has proven possible and many of todays players are able to achieve high and stabile purity. The power consumption of the Siemens reactor is both connected directly to the reactor itself and the inherent temperature differences. It is also connected to the reactant yield, which is limited by reactant diffusion to the deposition surfaces. The rest of the reactant has to be recycled, also resulting in high power consumption.

Future concepts will have to either decrease the distance the reactant molecule has to travel to a deposition surface, fluidized bed reactors may be one such solution although the purity control has to be improved. Another strategy will be to increase the total deposition surface through scaling. Siemens may be one possible route, but there are obvious challenges with operation as the batch sizes increases.

Polysilicon production will continue to be interesting and important in the coming years and success in this process step is crucial in order to reduce the energy payback time for silicon based solar cells.

Acknowledgments

References

1. S.P. Walch, C.E. Dateo, *J. Phys. Chem.*, **105** pp 2015–2022 (2001)
2. W.A.P. Claasen, J. Bloem, *J. Electrochem. Soc.* **127** (1) 194–202, (1980)
3. T. R. Hogness, Thomas L. Wilson, Warren C. Johnson *J. Am. Chem. Soc.* **58**. pp 108-112 (1936)
4. K. Stokland, *Det Kongelige Norske Videnskapelige Selskaps skrifter* **3** (1948)
5. J. H. Purnell, R. Walsh, *Proc. Roy. Soc. Ser. A*. **293**, 543 (1966)
6. Robertson, D. Hils, A. Gallagher *Chem. Phys. Let.* Vol. 103. Num. 5 (1984)
7. M. A. Ring, et al. J. *Am. Chem. Soc.* 92. 16. pp 4845- 4848 (1970)
8. M. A. Ring, H. E. O'Neal Proc. of the Flat Plate Solar Array Project Workshop on the Science of Silicon, Material Preparation, DOE/JPL, 1012-81, pp. 63-75 (1983)
9. Pauline Ho, William G. Breiland *App. Physics Letters*, Vol 44, No1, (1984)
10. Howard Purnell, Robin Walsh *Chem. Physics Letters*, Vol 110, No 3, pp 330 - 334 (1984)
11. Michael E. Coltrin, Robert J. Kee, James A. Miller *J. Electrochem Soc*. Vol 131, No. 2 pp 425 - 434 (1984)
12. William G. Breiland, Michael E. Coltrin, Pauline Ho, *J. Appl. Phys*. 59 (9), pp3267- 3273 (1986)
13. Michael E. Coltrin, Robert J. Kee, James A. Miller *Ann. Rev. Phys. Chem*. 38: pp109-40 (1987)
14. Michael E. Coltrin, Robert J. Kee, Greg H. Evans *J. Elec- trochem. Soc*. Vol 136, No. 3, pp 819- 829 (1989)
15. J.J. O'Brien and & G.H. Atkinson *J. Phys. Chem*. 92, pp 5782- 5787 (1988)
16. Frank Slootman & Jean-Claude Parent. *J. Aerosol Sci*. Vol 25, No 1. pp15-21 (1994)
17. C. C. Mai, T. S. Whitehouse, R. C. Thomas, D. R. Goldstein, *J. Electrochem Soc*. Vol 118, No. 2 pp 331 - 334 (1971)
18. T. I. Kamins, T. R. Cass, *Thin Solid Films*, 16 pp 147-165 (1973)
19. A. M. Beers, H.T.J.M. Hintzen, H.G. Schaeken, J. Bloem CVD, *J. of Crystal Growth* 64 pp 563 - 571, (1983)
20. A A Onischuk, V N Panfilov *Russ. Chemical Reviews* 70 (4) pp321-332 (2001)
21. Eddy Walther Hansen, Arne Kjekshus, Jan Ove Odden *Journal of Non-Crystalline Solids* 353 pp 2734- 2743 (2007)
22. J.O. Odden, P.K. Egeberg, A. Kjekshus *Solar Energy Materials & Solar Cells* 86 pp165176 (2005)
23. J.O. Odden, P.K. Egeberg, A. Kjekshus *J. of Non- Crystalline Solids* 351 pp13171327 , (2005)
24. Michael Frenklach, Larry Ting, Hai Wang, Martin J. Rabinowitz *Israel J. of Chem.* Vol 36 pp. 293- 303, (1996)
25. T. E. Wilke, K. A Turner, C. G. Takoudis *Chemical engineering Science*, Vol 41. No 4, pp 643-650, (1986)

26. M. K. Alam, R. C. Flagan *Aerosol Sci. And Tech*. 5: 237-248 (1986)
27. Carlyle S. Herrick & David W. Woodruff *J. Electrochem. Soc.: Solid-state Science and Technology*, pp2417-2422 (1984)
28. M. K. Alam, R. C. Flagan Assignee Caltech US Pat 4.642.227 (1987)
29. Jin Jwang Wu, Richard C. Flagan *J. Appl. Phys*. 61 (4), (1987)
30. W.O. Filtvedt, M. Javidi, A. Holt, M.C. Melaaen, E. Marstein, H. Tathgar, P.A. Ramachandran *Solar Energy Materials & Solar Cells* 94 pp1980 - 1995 (2010)
31. Sridhar K. Iya, Assigned to UCC, US Pat 4.424.199, (1984).
32. G. Hsu, R. Hogle, N. Rohatgi, A. Morrison A. *J. Electrochem. Soc.: Solid-State Science and Technology*, pp660-663 (1984)
33. G. Hsu, A. Morrison, N. Rohatgi, R. Lutwack, T. MacConnell *IEEE Photovoltaic Specialist Conference* (7 Kissimee) (1984)
34. George C. Hsu, Harry Levin, Richard A. Hogle, Ananda Praturi, Ralph Lutwack Assignee Caltech US Pat 4.444.811 (1984)
35. Marcelian F. Gautreaux and Robert H. Allen, Assigned to Ethyl Corporation,. US Pat 4.784.840, (1988).
36. Stephen M. Lord and Robert J. Milligan, Assigned ASIMI. US Pat 5.798.137, (1995).
37. Stephen M. Lord and Robert J. Milligan, Assigned to ASIMI, US Pat 5.810.934, (1998).
38. T. Kojima, T. Kimura, M. Matsukata *Chem. Engineering Sci*. Vol 45, No 8. pp2527- 2534 (1990)

Paper IV

W.O. Filtvedt, A. Holt, P.A. Ramachandran, M.C. Melaaen

Chemical Vapor Deposition of Silicon from Silane: Review of Growth mechanisms and Modeling/Scaleup of Fluidized Bed Reactors

W. Filtvedt was the main author and contributor to the publication. A. Holt and M. C. Melaaen were the supervisors of the candidate and co-authors of the paper. P. A. Ramachandran was a co-author and has especially contributed to chapter 7 of the paper.

Paper V

W. O. Filtvedt, M. C. Melaaen, A. Holt, M. Javidi, B. R. Olaisen

Composite Distribution Solution for Minimizing Heat Loss in a Pyrolysis Reactor

W. Filtvedt was the main author and contributor to the paper and has also performed the experimental and modeling work. M. C. Melaaen and A. Holt were the supervisors of the candidate and co-authors of the papers. M. Javidi was the project manager at the time of the publication and co-author of the paper. B. R. Olaisen was a co-author of the paper.

Composite Distribution Solution for Minimizing Heat Loss in a Pyrolysis Reactor

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Composite Distribution Solution for Minimizing Heat Loss in a Pyrolysis Reactor*

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Abstract

The article presents a novel design for a distribution plate. The solution is suitable for a reactor vessel where a reactant gas needs to be maintained at a different temperature from the reaction chamber in order to avoid unwanted occurrences, such as clogging of the distribution plate. A normal procedure involves cooling of the distribution plate which is reported to either increase heat loss substantially or yield insufficient temperature in parts of the reaction chamber. The problem is especially important for reactors where the difference in reactant inlet temperature and desired reaction temperature is large. The investigated design utilized materials of very different thermal conductivity to only cool specific parts of the distribution arrangement and thereby minimize heat loss. Our system is a distribution plate for use in a fluidized bed reactor for silane pyrolysis. However, the solution is general and may be utilized in many types of vessels and chemical reactors.

KEYWORDS: polysilicon, fluidized bed, distribution plate, heat loss

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1 Introduction

1.1 Background

The worlds energy demand is ever increasing and there is a growing interest in finding alternative renewable energy sources. The concept of photovoltaic (PV) cells is over a century old. But the increasing energy prices in combination with more cost effective production methods and higher efficiencies already makes PV competitive in several countries and regions today. Over 95% of todays PV cells contain silicon. Being one of the most abundant elements on earth, the accessibility of the raw material is in most aspects unlimited. The processing is however complicated and energy consuming as the most efficient cell concepts require a contamination of selected impurity species as low as ppb level (Jenny Nelson 2009). These purity levels are today only obtainable by going through gas and chemical vapour deposition (CVD).

Silicon based PV cells are expected to play a major role in the utilization of solar energy and the market for polysilicon is expected to continue to grow rapidly in the next five years. The projected worldwide capacity in 2012 is predicted to be about 200,000 Mt./year and individual plant capacity is expected to be of the order of 10,000 Mt./year, if not larger (Gerald Parkinson 2008), (M. Javidi & P. Ramachandran 2009). Correspondingly, the share of power generation from PV is expected to increase and is already of the order of 3.8 GW in Germany. The target cost of silicon production is set around $20-25 per kg (M. Javidi et al. 2009).

1.2 Application

Fluidized Bed Reactors (FBR) have been widely used for many different applications. The fundamental function of a FBR is to fluidize solid particles by an ascending gas flow of high enough velocity. In a silicon CVD FBR, a thermally decomposable silicon compound is introduced and decomposed through heating. The two commonly used reactants are silane and trichlorosilane. Silane is utilized by Rec silicon and MEMC while trichlorosilane is utilized by Wäcker chemie. For many other FBR applications, one tend to insert the reaction gas diluted in the fluidization gas and inserted both through a common distribution plate at the bottom of the reactor volume. This layout has been explored for silicon CVD to some extent. Both Hsu. et al of Caltech (G. Hsu, N. Rohatgi , J. Houseman

1987), Iya of Union Carbide Corporation (Sirdhar K. Iya 1987) and Yoon et al. of KRICT (P. Yoon and Y. Song 1988) have all explored introducing a premixed fluidization gas and tried to avoid clogging through cooling of the distribution plate. However, the layouts being used commercially today is mostly based on different principles.

1.3   Fundamental problem

Silane decomposes at $420\,°C$ (S. P. Walch & C. E. Dateo 2001), even though clogging is reported to be a problem at even lower temperatures (Hsu, et. al 1987), (S. K. Iya 1987), (P. Yoon et al. 1988). To assure a crystalline silicon structure, the beads need to be exposed to temperatures above $710\,°C$ (S. M. Lord & R. J. Milligan 1995). This temperature may either be applied at the time of deposition or alternatively later through annealing. The fundamental problem is therefore that one needs to keep the temperature low at the point of reactant gas insertion while keeping the temperature high in other areas of the reactor in order to assure correct crystal structure

If one tries to solve this problem directly by intense cooling and heating at subsequent locations this leads to severe thermal losses. This is especially the case if the bottom of the reactor is kept cold while the top is heated since the heat is then continuously removed.

1.4   Earlier solutions

A number of different reactor layouts have been proposed for FBR silicon production. The interested reader is referred to the work of Filtvedt et al. (Filtvedt et al. 2010). The first FBR reactors for silicon production were all based on premixed fluidization and reactant gas (Harry W. Ling 1961), (H.S.N Setty et al. 1974), (S. K. Iya 1987), (Robert H. Allen 1988). However, because of the challenges with either clogging or severe heat-loss in the bottom of the reactor, the new designs of the 90s and 00 where mostly based on different types of separate reactant and fluidization gas inlets. New challenges using undiluted reactant gas involved increased fines production and impuriy incapsulations.

One promising two inlet design is heating and fluidizing the bottom and introducing the reactant gas to the upper part of the reactor like Kim et al. (Kim et al 1994). Alternatively running the reactor semi continuously like S. M. Lord (Stephen M. Lord 2002) where high temperature and reactant gas are applied alternately in time. Other solutions include

inserting the reactant gas through a central nozzle while fluidizing the bed through a peripheral distribution plate as proposed by Kulkarni et al. of MEMC (Kulkarni et al. 2009).

A modern premix design is applying the heat within the reactor by an infrared light source through a spout jet like Lord et al. (Lord et al. 1995) this solution is the one being utilized for the largest production volumes today. The solution includes depositing at lower temperatures, and then anneal the deposited layer to form a crystalline structure. A number of publications have been made on the design over the last years including recrystallization of beads of Dahl et al. (Dahl et al. 2009) and modelling of bed behavior Piña et al. (Pina et al. 2006). The publications don't claim to be the actual process being utilized for commercial production. A challenge with the solution is the bubble size which is bigger within a spout than a bubbelig bed and it is found that an increase in bubble size is correlated to an increase in fines formation.

The earlier bubbeling bed designs based on premixed reactant and fluidization gas have utilized fluidizing through a homogeneous perforated distribution plate. The problem is therefore quite straight forward; the reactant gas decomposes at a certain temperature and the reactor needs a certain temperature to assure correct crystallization. Both these temperatures needs to be maintained. The thermal losses are then only depending on the internal heat transport mechanisms as described by Gunn and Hilal (D. J. Gunn & N. Hilal 1996) among others.

The silicon CVD FBR reactor is somewhat unusual in the sense that the required inlet conditions of the reactant gas is so far from the required reactor operational temperatures. Several researchers has acknowledged this difference and called out for unique designs to help aid the problem.

Other research groups to investigate the distribution plate clogging problem include Lackey et al. (Walter J. Lackey, Jr. & John D. Sease 1975) who proposed a thick distribution plate with thinner regions for letting the distribution gas through. The solution is not especially made for silicon production, but the goal is nevertheless to avoid depositions from decomposition of the fluidization gas.

2 Grid design

Many researchers on silicon FBRs report high quality beads when keeping the bed in bubbling regime (Hsu, et. al 1987), (S. K. Iya 1987), (P. Yoon

et al. 1988), (Lord et al. 1995). In order to keep the bed in this regime, the process needs to be continuously monitored and controlled. The beads continuously grow in the reactor and since the bubbling regime offers limited mixing of the bed, there is need to have control of the average bead size as well as the bead size distribution through the bed. The largest beads tends to move downwards to where the deposition is largest (Lord et al. 1995). This mechanism might spiral down and eventually kill the bed. Several methods may be utilized to aid the problem, but continuous bead removal from the bottom of the bed and reintroduction of the smallest beads at the top is a well known solution.

In order to achieve a good gas distribution over the whole bottom of the bed, several different distributor designs are possible. This involves using a distributor plate or cone alternatively to utilize a tube construction at the bottom of the bed, often referred to as a sparger grid. Sparger grids may be especially desirable in large beds where the preferred injection direction might be horizontal or downward.

Due to contamination problems, sparger grids are not especially desirable in silicon FBRs. Most designs either utilizes a distributor plate of some sort, alternatively a spout layout. Established design equations proposes this relationship when designing a distributor plate; the pitch L_h in Fig 1 depends on the hole density N_d according to equation 4. The hole density is given in number of holes per unit area. (Karri et al 2001)

PARAMETERS

C_d	0.746	= discharge coefficient
d_h	1x10^{-3}	= grid hole diameter, m
g	9.81	= gravitational acceleration, m/s^2
K	0.3	= grid pressure-drop coefficient, upward gas entry
L_B	0.15	= operating bed depth, m
N	66	= number of grid holes
N_d	3499	= number of hole density, holes/m^2
ρ_B	1190	= operating bed density, kg/m^3
$\rho_{g,b}$	0.14729	= density of gas at bed operating conditions kg/m^3

$$\Delta P_{grid} = K g \rho_B L_B \tag{1}$$

$$U_h = C_d \sqrt{\frac{2\Delta P_{grid}}{\rho_{g,h}}} \qquad (2)$$

$$Q = N \frac{\pi d_h^2}{4} U_h \qquad (3)$$

$$L_h = \frac{1}{\sqrt{N_d}} \qquad (4)$$

RESULTS

L_h	0.0169	= grid hole pitch, m
U_h	62.9	= velocity of the gas through the grid hole, m/s
Q	3.26 x 10^{-3}	= total volume flux through grid, m^3/s
ΔP_{grid}	525	= pressure drop across grid, Pascal

Based on these equations one realizes that for normal size reactors, the pitch between the distributor holes may be several orders higher than the hole diameter. This simple concept yields the possibility of building up a composite distribution plate. One may cool certain areas and insulate certain other parts of the plate. Starting from this standpoint one may already reduce the total thermal losses by only cooling a certain area around each hole and not the entire distributor. By exploring different geometry options of different materials, we where able to reduce the theoretical thermal losses even further.

Our reactor had ID 155mm and possible bed height of 500mm. A number of different operation conditions is possible in the bed but to meet the range of possibilities the grid consisted of 66 holes with a diameter of 1mm. Square pitch was chosen for the pattern see Fig 1. As one may see the viritual velocity through the bed at the outlet of the distribution plate is for this setup 0.185 m/s.

3 New design

The design was based on the fundamental textbook equations reported by Karri et al. (Karri et al 2001) among others. Based on the number and length of the holes, the design was taken further in the commercial CAD
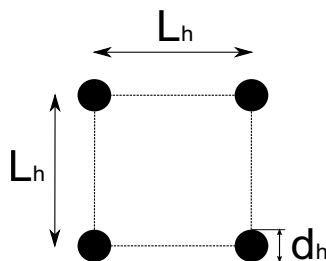
Figure 1: Hole pattern in distribution plate, square pitch

program Solid Works. The basis for the layout was how to assure low enough temperature in the thermal boundary layers of the individual holes in combination with minimizing the heat loss from the reactor volume. The chosen design was a highly conductive plate at the base with a number of pins enclosing each hole through the insulation see Fig 2. The pins finished in a conical shape in order to reduce the amount of heat transfer into the pins. A practical problem was the sum of contributions from each pin from the center of the plate to the wall. Because of this effect the temperature in the center of the plate would be significantly higher than by the wall as shown in Fig 2.

Another obvious challenge with the design is the length and diameter of the individual pin. This problem is also dependent on the type of material in the baseplate and the pins. One desirable solution is to use an anisotropic material with different k-value in each direction for the pins and for the baseplate. Different types of composite carbon materials may be desirable for such applications and especially combinations of different composite carbon materials.

However, for the chosen design, isotropic materials were used. The base plate and the pins were made from one piece of aluminium. Because the plate was inserted between two cooled flanges, the aluminium had to sustain several installations. Because of this, the chosen aluminium alloy was Al 6082. For insulation a commercial available high temperature compact wool was used. The k-value for this material was 0.08 W/mK.

To predict the temperature distribution in the different regions of the baseplate a solid CFD model was tested in Fluent. Since the plate has two symmetry planes only one quarter of the plate needed to be modelled. The model was quite simple. The top of the plate was subjected to a constant temperature of 600 °C while the side of the base plate was main-
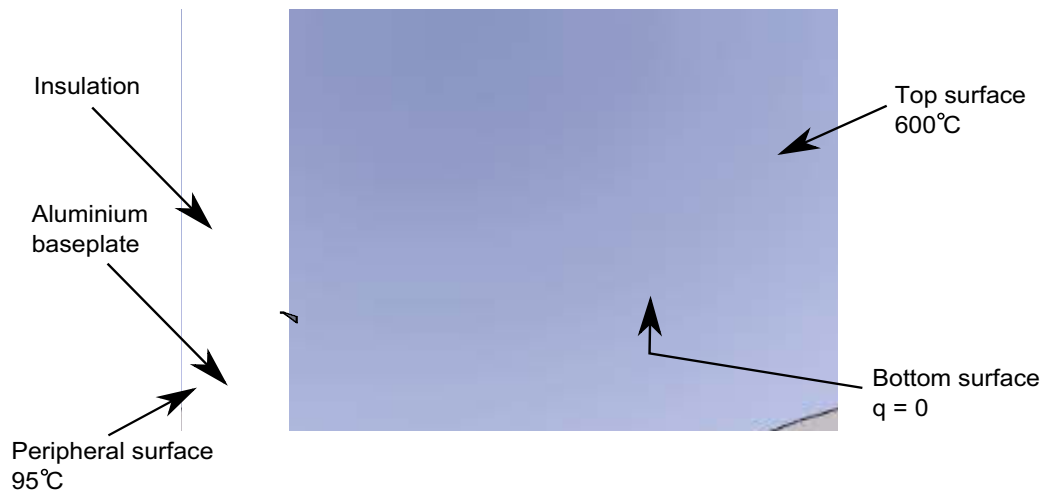
Figure 2: Distribusjonsplate design

tained at $100\,°C$. The bottom of the baseplate is facing the windbox and the entering gas. Because the windbox is kept at a temperature close to the bottom baseplate temperature and since the entering gas has limited heat capacity the chosen boundary condition is anisotropic. The chosen mesh was T-grid will average cell length of 0.5mm. From these simulations we found that the temperature rise from the side to the center of the baseplate was around $25\,°C$ as can bee seen in Fig 3, the scale has $25\,°C$ steps.

The silicon FBR through silane pyrolysis is most commonly performed in bubbling regime. For the one familiar with the art of FBR engineering the bed height, hole pattern and minimum fluidization velocities are easily obtainable through textbook examples. However, the problem is somewhat out of the ordinary because of the large volume expansion given from the raise in temperature in the first few centimeters of the reactor (Lord et al. 1995). The problem arises because of the large difference between decomposition and ideal crystallization temperature. This problem is usually avoided by reference in the conditions at the inlet of the reactor and sufficient fluidization conditions here makes sufficient fluidization of the whole bed (Lord et al. 1995), (Kim et al. 1994). This means that one takes reference in the properties of the incoming gas and use the inlet velocity as the virtual velocity through the whole bed although the large volume expansion increases the virtual velocity substantially during the first few cm of the bed.

9.00e+02
8.75e+02
8.50e+02
8.25e+02
8.00e+02
7.75e+02
7.50e+02
7.25e+02
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6.75e+02
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5.75e+02
5.50e+02
5.25e+02
5.00e+02
4.75e+02
4.50e+02
4.25e+02
4.00e+02

Contours of Static Temperature (k)

Dec 10, 2010
ANSYS FLUENT 12.0 (3d, pbns, lam)
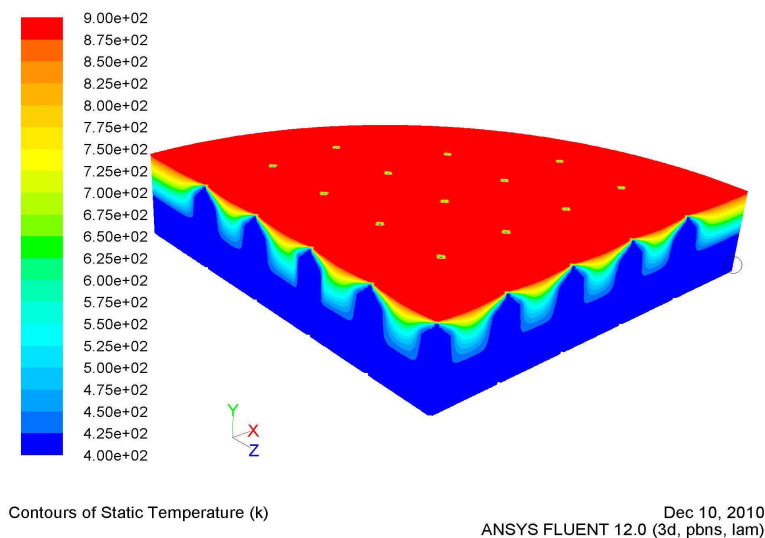
Figure 3: Temperature analysis distribution plate

4   Experimental testing

4.1   Experimental setup

The distribution plate was installed between two cooled flanges at the bottom of a fluidized bed. The two flanges had individual cooling systems and where cooled by boiling water at about $95\,^{\circ}$C, see Fig 4. The instrumentation involved temperature probes at each side of the plate. For these initial runs the plate was tested without gas flow and beads, this made it possible to gain access to both the windbox and the reactor internals.

One could therefore do thermography imaging of the distribution plate from both sides. There were also Termo couple probes 10 mm outside each side of the plate to monitor the surface temperature realtime. All four zones had individual temperature sensors see Fig 4. The heating of the bed was done by irradiative heating elements from outside the reactor wall.
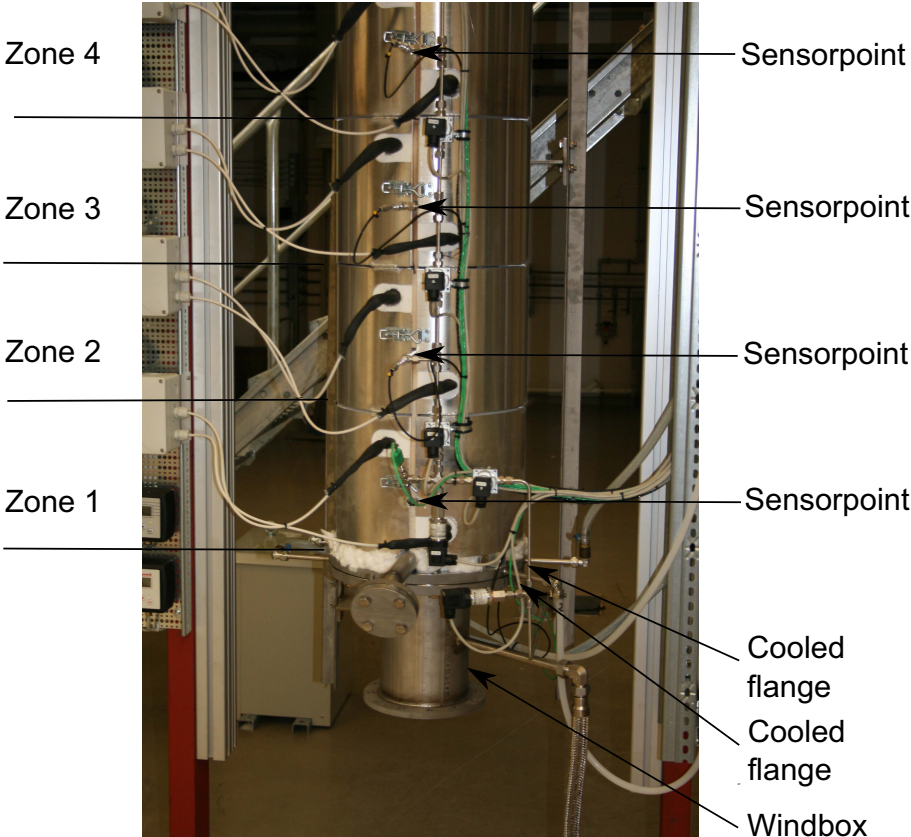
Figure 4: Experimental setup
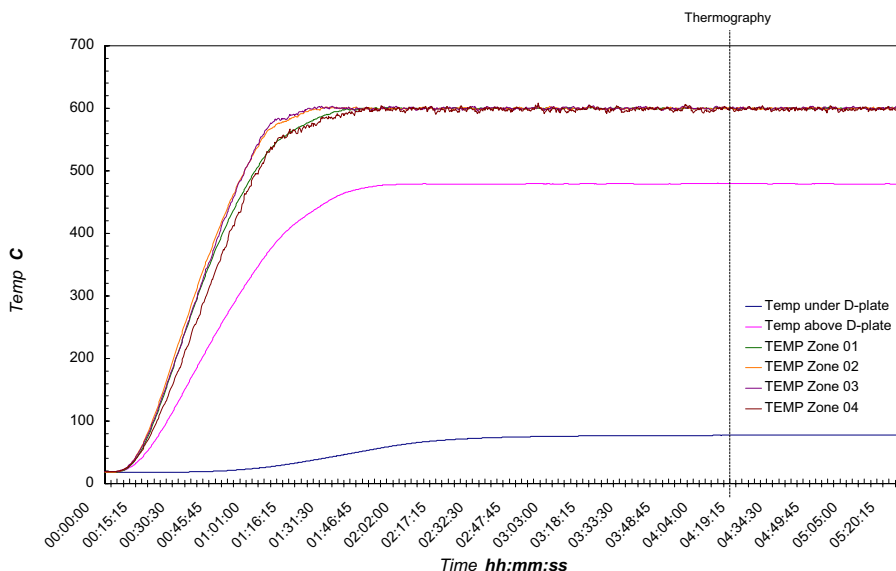
Figure 5: Temperature development

4.2   Results

4.2.1   The individual setups

The heating and cooling system was tested under a number of different configurations to test different heating and cooling loads over the plate. For the initial run the plate was intensively cooled and kept below 15 °C while the temperature above the plate was risen to 178 °C. This initial run was problematic since the thermal losses around the plate was quite severe in addition to insufficient temperatures in the lower regions of the reactor volume.

To aid the problem the flange cooling was reduced for the second run, the inlet temperature of the cooling media was 10 °C while the outlet temperature was 44 °C. This setup resulted in a temperature of 278 °C while the temperature below the plate was about 35 °C. The success in this run was the quite substantial temperature difference on each side of the distribution plate. The problem was however the still insufficient temperatures in the reactor volume in addition to the large temperature difference around the cooling flange.

The third next subsequent and last run was done with water at boiling temperature. The inletflow was reduced to a bare minimum such that the whole cooling flange reservoir reached boiling. At the outlet, the first section was made from a 1,5m vertical section which overflow when the water level got too high. This setup yielded a close to constant temperature around the flange and the extracted heat was removed through evaporation. By using this setup, the temperature just below the baseplate hold a constant temperature of about $78\,^{\circ}\mathrm{C}$ as can be seen in figure 5 while the temperature 10 mm above the distribution plate reached $423\,^{\circ}\mathrm{C}$. The temperature in zone 1 rose to $600\,^{\circ}\mathrm{C}$ sensor placement may be seen in Fig 4.

4.2.2 Heat distribution

The reactor was heated from room temperature to operation temperature of $600\,^{\circ}\mathrm{C}$. When all zones reached operating temperature and the temperature over and under the distribution plate reached steady state, the temperature distributions were investigated by thermography measurements as shown in Fig 6.

The CFD model had predicted the heat temperature distribution over the bottom of the baseplate to be close to uniform from the center to the border see Fig 3. The temperature difference through the plate from the bottom to the top was challenging to measure during the tests, but from the CFD analysis this was predicted to be close to constant.

When analysing the bottom of the distribution plate a thermography picture was taken from underneath the wind box see Fig 6. The black shadow in the picture is the gas feed line which is below and colder than the plate. As one may clearly see from the picture, the temperature distribution is close to constant over the plate thus making the results consistent with the CFD findings.

The reactor is equipped with an inspection glass at the top of the reactor, making it possible to investigate with optical instruments. To map the temperature distribution over the top of the plate, a thermography picture was taken from the top of the reactor as seen in Fig 7.
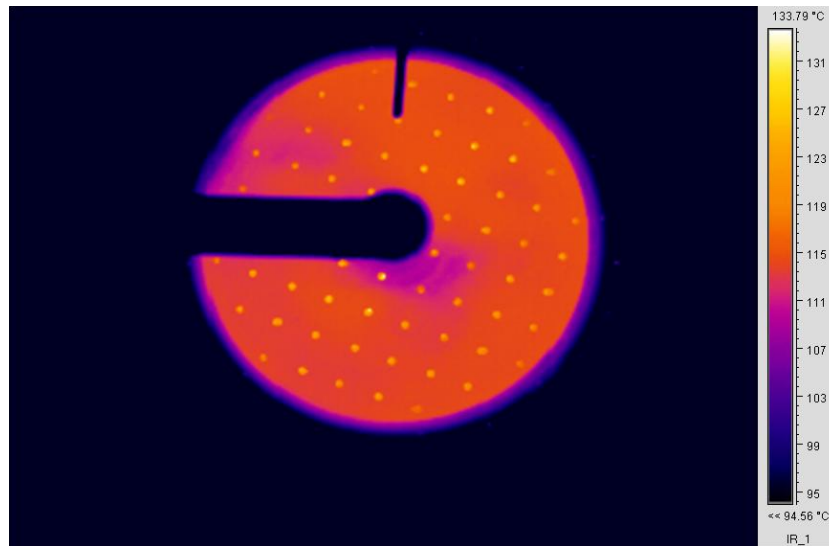
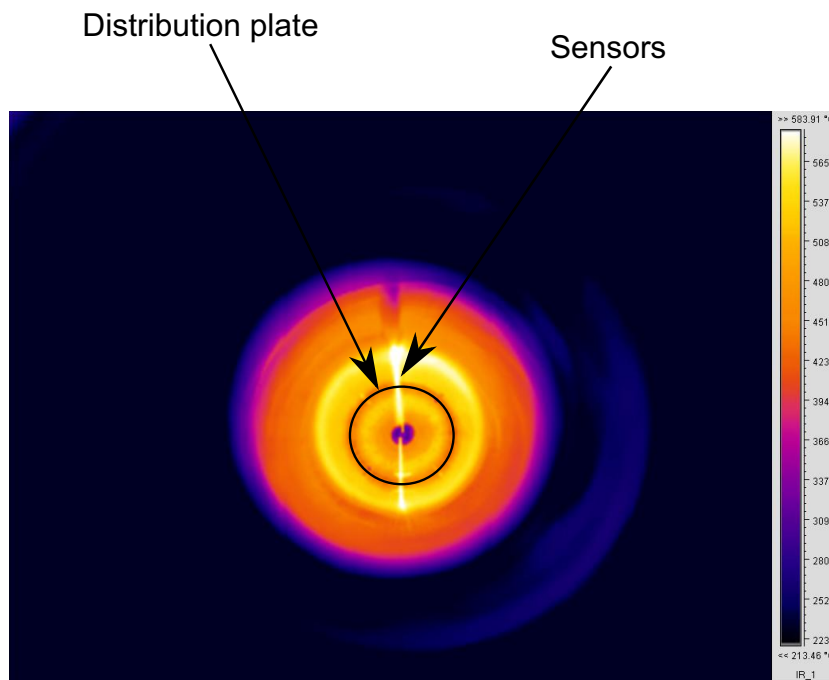Figure 6: Thermography picture from the bottom of the plate

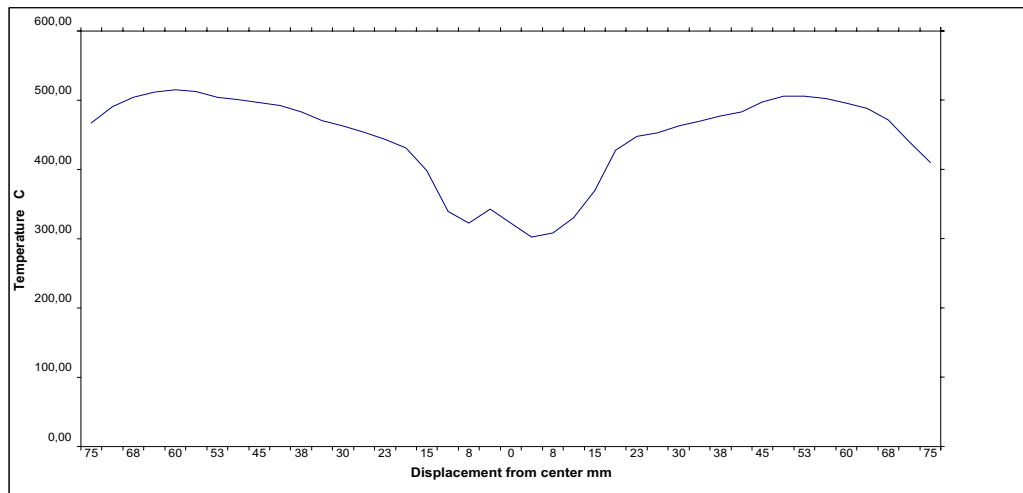Figure 7: Thermography picture from the top of the plate

Figure 8: Temperature distribution over the top of the plate, extracted from the thermography raw data

Since the reactor is over 2.5 m tall, the distance to the plate in combinations with the limitations of the camera yields a picture low on details compared to the picture taken from the bottom. Nevertheless, it is clear that the temperature of the distribution plate is lower than the measuring probe just above the distribution plate see Fig 5. This is possible because the gas flow is shut off and thus that the heat transport mechanisms from the plate to the overlying gas is limited. It should in this regards also be noted that the heat transport from the wall to the inside of the reactor is limited since the reactor is lacking particles. When both these mechanisms are operational, one may expect the heat transport to be more efficient and thus a more even temperature distribution than when running the reactor empty. Another feature is that the temperature is low by the wall then going up to a maximum about 30mm from the wall and gradually decreasing until the center of the plate. There seems to be a step in temperature in a 15mm radius around the center of the plate, see Fig 8.

This effect is not fully investigated. However, it might not be physical, but a result of reflection or other optical effects. When doing the initial runs, the bottom of the windbox was untreated and thus shiny. This resulted in a much too low observed temperature as well as the hole pattern from the distribution plate was reflected onto the inner wall of the box, showing a periodic pattern of light coloured spots, thus indicating

higher temperature at these spots. The inside of the box was thus coated with a high temperature, black paint in order to control these effects. This resulted in Fig 6 which was in good coherence with probe measurements.

The head-load over the distribution plate is expected to be more uniform when the reactor is filled with beads.

5   CFD model

All runs were done without particles and fluidization gas. There was therefore interest in finding how the temperature would be transferred through the insulation, into the aluminium and further into the flow. The motivation for the exercise was not to model the complete picture, but merely to investigate the heating of the flow.

The commercial software Fluent was used to model the heat transfer. The problem was defined by a finite temperature on each side of the plate and the thermal properties of the materials involved. The fluid mechanical and thermal properties of the fluid was calculated by the commercial software Ergun. The grid was produced in Gambit with a triangular mesh in the solid region and a quadric mesh in the fluid region. The motivation for this difference was the sharp corners of the solid regions which yielded a triangular mesh while the fluid region could be meshed with a quadric mesh for better precision. The interfaces separating the regions were however meshed first in order to define boundary regions and assure a good cell to cell transport of properties. A typical cell size of 2.8×10^{-5} mm^2 was used for both solid and fluid regions see Fig 10.

The Reynold number of the problem was in the order of 1.5×10^3 and the CFD analysis was thus performed without a turbulence model. To assure no loss of precision and since the case was in the transitional region, some runs were done with a k-ϵ model. There was minimal difference with or without the turbulence model and the presented run was thus made without a turbulence model.

Physical properties, gas mixture 100 °C

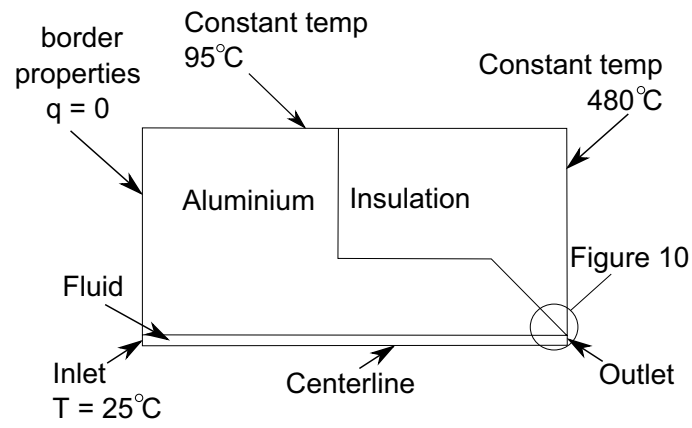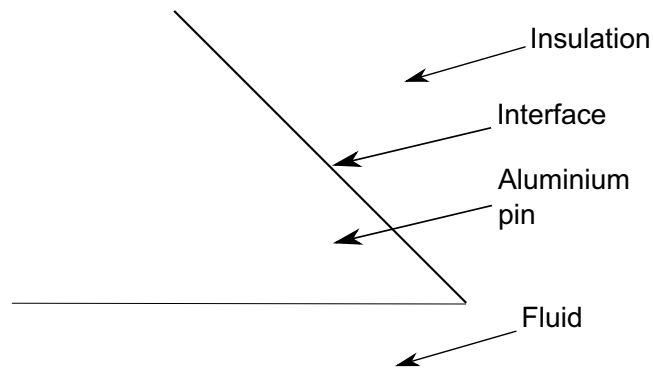|	
Density	$= 0.244$ kg/m^3
Thermal Conductivity	$= 0.17571$ W/mK
Specific heat	$= 11962.98$ J/Kg K
Molecular weight	$= 8.03048$ g/mol
Viscosity	$= 1.231 \times 10^{-5}$ Pa S

Figure 9: The case
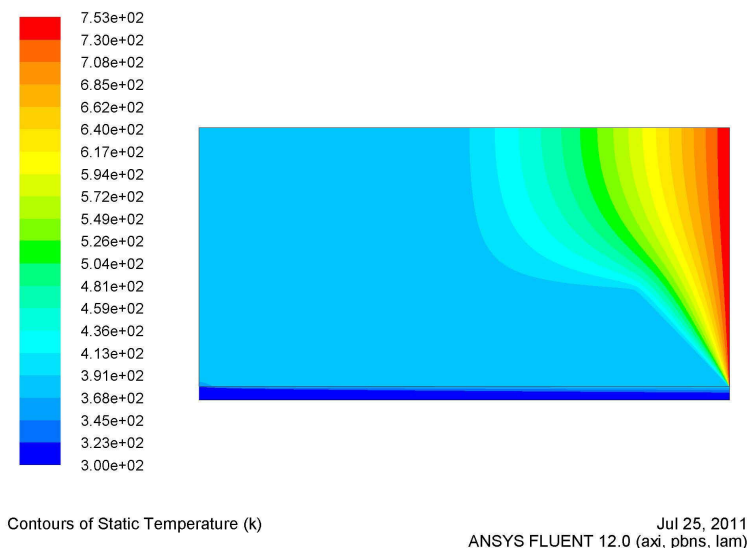

Figure 10: Part of the mesh, section from Fig. 9

Figure 11: CFD analysis on the distribution plate

The presented design was based on the layout described in Fig 2. This layout minimized the thermal losses and it was possible to keep the reaction gas heating to a minimum. If one took reference in keeping the edge of the baseplate at 95 °C, it was quite easy to keep the entire base sufficiently cold if the design had a sufficient transverse crossection.

As one would expect, there was a thermal boundary layer by the tube wall which grew slowly depending on the velocity. At 80 m/s through a 1mm dia tube the thermal boundary layer would occupy about 30% of the tube radius at the exit, see Fig 11. From these results it is quite clear that the baseplate needs to be maintained below the decomposition temperature in order to avoid decomposition and possible clogging. Another conclusion one might draw from this is that the gas entering the reactor will have quite low temperature if one choose not to heat either the wind box or the supply line. There is therefore important to keep a good mixing of the bottom bed, to keep an efficient heat transfer from the wall to the reactant gas.

6 Conclusion

Using a composite distribution plate consisting of materials with different heat conduction properties was very successful. Earlier researchers have reported problems with too high temperatures in the distribution plate and insufficient cooling when utilizing only flange cooling. Although the experiments done in this article have been executed in a limited manner, there is still sufficient results to draw a conclusion on the applicability of the method. The distribution plate was capable of sustaining a large temperature difference on each side. This gives that the thermal losses over the distribution plate was limited although the wall temperature of the individual holes in the plate was kept sufficiently low.

More empirical results are needed in order to find a design suitable for full scale use. Especially the execution of the individual pins and perhaps a varying pin design over the plate should be investigated. Other designs might include several materials or even gradually varying materials to improve performance.

Another desirable execution would be to utilize materials of anisotropic thermal properties. Such layouts would have a better chance of succeeding when the design process is aided by extensive use of CFD analysis.

One should note that the exercises in this articles have limitations. There are several mechanisms relating to fines generation that needs to be investigated further in order to map out other challenges that might occur. Being able to introduce the reactant gas cold and heating it to decomposition temperature rapidly after insertion, might not be desirable because of other mechanisms that these tests have not been able to discover. The team wishes to continue the research with several tests with different reactant gas concentrations, flow rates and particle sizes in order to study the applicability further. These tests will be aided by CFD modelling in order to increase the cost effectiveness of the research.

References

Robert H. Allen, 1988, Assigned to Ethyl Corporation, "Fluid bed reactor and process". US Pat 4.748.052,

M. M. Dahl, A. Bellou, D. F. Bahr, M. G. Norton and E. W. Osborne, 2009 "Microstructure and grain growth of polycrystalline silicon in fluidized bed reactors" Journal of Crystal Growth 311, 1496 - 1500

W.O. Filtvedt, M. Javidi, A. Holt, M.C. Melaaen, E. Marstein, H. Tathgar, P.A. Ramachandran, 2010, "Development of fluidized bed reactors for silicon production" Solar Energy Materials and Solar Cells 94 pp 1980 - 1995,

Gerald Parkinson, "Polysilicon Business Shines Brightly", 2008, Chem. Eng. Progress, Vol 104 No 8 pp 8-11,

D. J. Gunn and N. Hilal, 1996, "Heat transfer from vertical inserts in gas-fluidized beds". International Journal of Heat and Mass Transfer, Vol. 39, No. 16, pp. 3357-3365,.

G. Hsu, N. Rohatgi , J. Houseman, 1987, "Silicon Particle Growth in a Fluidized-Bed Reactor", AICHE Journal, Vol. 33, No. 5, 784-791,

Sirdhar K. Iya, 1987, Assign Union Carbide Corporation "Zone heating for fluidized bed silane pyrolysis", US Pat. 4.684.513 , .

M. Javidi, and P. Ramachandran, 2009, "Developments in Polysilicon for PV Applications". Photovoltaic Summit Europe, Rome Italy

Hee Y. Kim, Young M. Song, Jong Y. Jeon, Dae H. Kwon, Kang M. Lee, Jae S. Lee, Dong S. Park, 1994. Assigned to Korea Research Institute of Chemical Technology, "Heating of fluidized bed reactor by microwaves". US Pat 5.374.413,

Milind S. Kulkarni , Steven I. Kimbel, Jameel Ibrahim, Vithal Revankar, 2009, Assigned to MEMC Electronic materials Inc, "Fluidized bed reactor systems and methods for reducing the deposition of silicon on reactor walls" US Pat 2009.0.324479 A1,

Walter J. Lackey, Jr. & John D. Sease, 1975, *Means for effecting fluidization in pyrolytic carbon coating processes.* The Unitied States of America as represented byt the United States Energy and Research and Development US Pat 3.889.631

Harry W. Ling, 1961, Assign to E. I. du Pont de Nemours and Co , "Production of Silicon". US Pat 3.012.861,

S. M. Lord, R. J. Milligan, 1995, Assigned to Advanced Silicon Materials inc, "Method for Silicon deposition". US Pat 5.798.137,

Stephen M. Lord, 2002, "Machine for production of granular silicon". US Pat 2002.0.081250,

Jenny Nelson, "The physics of solar cells", 2009, Imperial College Press 57 Shelton Street Covent Garden London

Juliana Piña, Veronica Bucal ay Noem Susana, Schbibz Paul Ege, Hugo Ignacio de Lasa, 2006, "Modeling a Silicon CVD Spouted Bed Pilot Plant Reactor" International Journal of Chemical Reactor Engineering Vol. 4, Article A9

H.S.N Setty, Carl L. Yaws, Bobby Ray Martin, Daniel Joseph Wrangler, 1974, Assigned to Texas Instruments Inc, "Method for operating a quartz FBR for the production of Silicon" US Pat 3.963.838,

Stephen P. Walch and Christopher E. Dateo, 2001, "Thermal decomposition pathways and Rates for Silane Chlorosilane, Dichlorosilane and Trichlorosilane", J. Phys. Chem. A. 105, 2015-2022

W. C. Yang, 2001 "Handbook of Fluidization and FluidParticle Systems". Marcel Dekker Inc., 270 Madison Ave., New York, 10016, Karri et al. pp 155- 170

Poong Yoon and Youngmok Song, 1988, Assign Korea Research Institute of Chemical Technology "Fluidized bed reactor with microwave heating system for preparing high-purity polycrystalline silicon", US Pat. 4.786.477

Paper VI

W. O. Filtvedt, H. Klette, A. Holt

Process Optimization in Fluidized Beds for Silicon Production

W. O. Filtvedt was the main author and contributor to the publication and has also performed the experimental work presented. H. Klette was the project manager at the time of the paper, responsible during operation of the FBR and co-author of the paper. A. Holt was the supervisor of the candidate and co-author of the paper.

Process Optimization in Fluidized Beds for Silicon Production

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Abstract

For an installed silicon based solar cell panel, about 40% of the energy costs involved in the production of the panels can be attributed to the production of the silicon feedstock itself (poly production and crystal growth) [1]. . Hence reducing the energy consumption in these steps is crucial in order to minimize the energy payback time of installed capacity. For the first step, viz., the poly production, the most promising cost reduction alternative is the fluidized bed reactors (FBR) using silane as a precursor.

Decomposition of monosilane is a complex process involving several intermediate stages and the local operation properties will influence these reactions and ultimately determine the product quality and yield of the process gas. Especially heat distribution and how the process gas is heated has proven important.

A central problem in FBR layouts is therefore heat management and balance. The research team has designed, built and operated a FB reactor and produced silicon from monosilane based on a novel layout minimizing heat loss and fines production. The layout is based on a high bed compared to other FB applications in order to minimize the heat-load over the chamber surface in combination with a novel gas distribution solution.

The goal of the design was to have a steep temperature increase in the first volume the process gas passes without having large heat losses. The reason for having this steep increase is to assure the deposition temperature to be high since this temperature has direct influence on the formation of intermediate gaseous and surface species and thereby ultimately the quality. The design was successful in achieving this result. Another problem in FBR design is production of fines. There was production of fines during the experiment and especially when going to higher concentrations of silane in the feed gas. The production of fines is complex and more work is needed in order to gain deeper knowledge of these mechanisms and how to control them.

The pyrolysis of monosilane is an exotherm reaction. However, the team experienced difficulties of keeping the temperature sufficiently high in the inlet area when going to higher concentrations. Allthough conclusions to the origin of these challenges are demanding, some possibilities are explored.

Silicon CVD

In the early days of silicon CVD, several gases were explored for the purpose, but in today's reactors monosilane SiH4 (silane) and trichlorosilane SiHCl3 (TCS) are the ones frequently used. Upon being heated to the decomposition temperature, the gases undergo the following reactions:

$$SiH_4 \rightarrow Si + 2H_2 \qquad (1)$$

$$SiHCl_3 + H_2 \rightarrow Si + 3HCl \qquad (2)$$

The decomposition temperature for silane is about 420°C [2]. However at this temperature the kinetic energy of the individual silicon atoms is too low to form crystalline structures. Low temperature atmospheric pressure decomposition will therefore cause amorphous structures to form [3]. Silane based CVD reactors are therefore often operated at temperatures in the range 650°C to 800°C. Some designs utilize after treatment of the beads at even higher temperatures to assure a crystalline structure. For the interested reader it may be noted that the decomposition temperature is pressure dependent and may be higher at elevated pressures [4].

The decomposition temperature of TCS is about 468°C [2]. The CVD reactors utilizing TCS are however often operated at higher temperatures because amorphous structures might cause chlorine encapsulations. These chlorine encapsulations will cause defects and reduce the quality of the material. Typical temperature range for TCS reactors is 850 - 1100°C.

Fluidized bed reactors

In a FBR, the reactor vessel is filled with silicon particles (see Fig. 1). A fluidizing gas like hydrogen or helium is injected at the bottom of the reactor to fluidize the particles. Fluidizing the particles means the drag force on the individual particles is on the same scale as the weight of the particle. In this state the bed of particles behaves like a liquid and an increase in gas flow will form bubbles and the continuous flow of gas will keep the bed in continuous motion.

The particles are heated by some means to a temperature above the decomposition temperature and the reactant gas is inserted to the bed. Upon decomposition the silicon is deposited on the particles thus making them grow. After some dwelling time the particles have grown to a size suitable for extraction. The finished beads are then extracted and new small seed particles are either inserted to or produced within the bed.
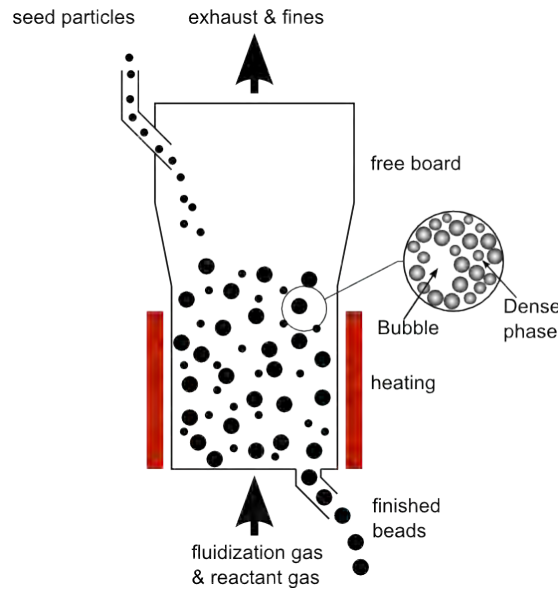
Figure 1: Schematic fluidized bed reactor

Fluidized bed reactors hold the potential to become the dominating CVD reactor for production of solar grade silicon. Large players in today's market like Renewable Energy Corporation (REC) and MEMC are producing increasing amounts of their material through FBR instead of Siemens reactors . Other companies like Wacker have also had substantial research programs on FBR based silicon feedstock production.

The common FBR layout is to have injection of the fluidizing gas through a distribution plate at the bottom of the reactor (see Fig 1). The reactant gas is either premixed with the fluidizing gas or injected diluted or undiluted through separate nozzles. The heating can be done in a number of ways at a number of locations through the bed, but the simplest way is to heat the wall of the bed directly by means of heating elements.

The volume above the bed, which is above the height the particles reaches when getting ejected from bursting bubbles is called the freeboard. The freeboard often suffers from fines clogging. If reactant gas reaches the freeboard without being decomposed it is likely to produce fines because the temperature is too low to produce crystalline structures although it is above the decomposition temperature.

Obvious problems are clogging of reactor internals because of undesired depositions and production of fine dust (fines) because of homogeneous decomposition and agglomeration due to insufficient agitation of the bed. Homogeneous decomposition is decomposition in gas phase while heterogeneous decomposition is decomposition at a depositing surface such as the silicon beads.

There are a number of ways to arrange and design a fluidized bed for silicon production through silane pyrolysis [5]. The main problems in FBR design is inadequate product quality, production of fines and unwanted depositions on the interior of the reactor.

A central question in FBR design is the deposition temperature. In a Siemens reactor this is more precisely defined since the deposition is happening on an electrical heating element, which happens to be of silicon. In a FBR the immediate history of the bead

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upon impact with the reactant gas and other local properties will determine the deposition temperature.

In order to assure a crystalline deposition a good engineering deposition temperature is set to be 650°C. A theoretical foundation for this temperature may be found in a series of decomposition experiments, which more precisely defines the transition temperature to 610°C [6], a good review of the known literature in this regards is done by Onischuk et al. [7]. Although the temperature needed to assure high degree of crystalinity and low hydrogen content is set to 610°C, this does not mean that it is impossible to alter the properties after the deposition. Post deposition high temperature annealing is possible and has been proven to diminish the hydrogen if performed correctly [8].

Since the decomposition temperature is around 420°C and the deposition needs to happen around 650°C there are inherent problems of clogging, insufficient deposition temperature or high thermal losses. The Ife design aims at comprehending these challenges and solve the deposition temperature without meeting the classical problems.

The IFE Fluidized bed design

The aim of the IFE design is to acquire a high deposition temperature without having large heat losses and without getting clogging of the reactant distribution system. A similar layout to our system have been proposed earlier although without some key elements we find important. The overall idea is to have a high bed height to diameter ratio in order to reduce the heatload necessary over the walls. This overall idea is both proposed by Lord et al. at ASIMI now Rec Silicon and Hsu et al. earlier [6, 9].

Lord meets the problem of deposition temperature by adding irradiative heat in the center of the bed within a mixed spout in addition to wall heating. The problem is here the production of fines since a spout will have very low particle density and therefore more homogeneous nucleation and fines production.

Hsu et al. addresses the problem by cooling the distribution system. Different solutions are suggested, but they either suffer from clogging or inadequate temperatures in the deposition region of the bed.

The new solution is to keep the reactant gas at correct temperature all the way into the bed and at the same time insulate the bed from the premix chamber in order to reduce thermal losses as much as possible. A preliminary heat distribution study of the solution was published in 2011, then without testing of fluidization and decomposition of silane [10].

In more detail, the distribution plate consists of two different materials of different thermal conductivity (see Fig 2). The bottom part of the plate is made from a highly conductive material while the uppermost part is made from an insulating material. The thermal conductivity of the bottom part is in the order of 220W/mK while the uppermost part is about 0,08 W/mK, depending on the local temperature.

Fluidization and design features

The system is built for monosilane pyrolysis. A present way the design is used is by premixing the silane with either nitrogen or hydrogen alternatively a mix. Having the possibility of these two diluents is motivated by the difference in viscosity and density of the two gases as well as the inert properties of nitrogen at the given temperatures. Hydrogen is the industrial alternative because of cost and how the overall recycle loop may be arranged. Hydrogen has however proven to play a role in the intermediate reactions on the way from silane to silicon [4, 7, 11, 12]. It is therefore interesting to have the possibility to alter the diluent from between experiments.

The system is also equipped with the possibility of preheating. Since the decomposition is known to start around 420°C or even lower, it is crucial to keep the temperature sufficiently low during in-feed in order to prevent clogging. The gas feed may however be as high as 200Nl/m which yields extensive heat draining if the in-feed gas needs to be elevated from room temperature. During system start-up it proved important to use the preheat in order to keep a good mix of the whole column which is crucial in order to keep the heat load sufficiently low in each zone.

A rapid volume expansion of the gas upon entering the bed will contribute to good mixing in the whole bed and facilitate the design with the possibility of a steep gas-temperature increase in zone 1 (see Fig 2). Due to this it may be interesting to also use non-preheated gas in order to make use of this effect.

The reactor is equipped with temperature sensors for each zone 250mm apart, both wall temperature and centre bed temperature. High sampling frequency differential pressure sensors are set up between each zone to track and characterize bubbles. The distribution plate is also equipped with temperature sensors on each side. One side is touching the backside of the plate thus indicating the plate temperature. The reactor side is monitored with a sensor 25mm above the plate.
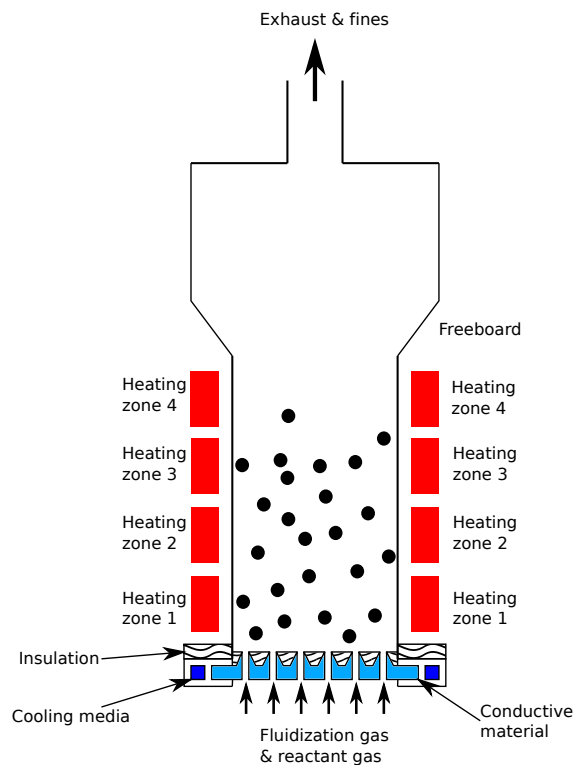
Figure 2: The IFE fluidized bed design

Distribution solution performance

The goal of the design is to be able to precisely define the inlet gas temperature and the bead temperature in order to define the decomposition sequence and thereby the growth.

A crucial feature of the solution is to decouple the inlet gas temperature and composition from the bead temperature in zone 1 and the heat loss.

By insulating the distribution plate, the top of the plate will naturally be hotter. Furthermore since the CVD growth rate is temperature dependent this may cause a problem. However, the top of the distribution plate also suffers from substantial wear from the fluidized particles. There is therefore not necessarily advantageous to prevent all formation of protective silicon layers.

In order to map out the bed expansion at different superficial gas velocities, the distance from the top of the freeboard to the top of the bed was measured with a commercial laser distance meter. The bed was mixed by high virtual velocity between each measuring set. The whole experiment was conducted 3 times to limit the measuring error.

The superficial gas velocity is defined as the total volume flux divided by the total cross section area of the reactor. It is an indication of the fluidization state of the bed, but the viscosity and density of the gas as well as the density and size distribution of the particles will also contribute to the picture. The findings were that the bed height got lower by higher superficial gas velocity, (see Fig 3) The trend changed around 0,13 m/s when visual fluidization at the top in the form of small bursting bubbles began. Upon

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increasing the velocity further, the fluidization got more intense and both the average height and standard deviation increased.
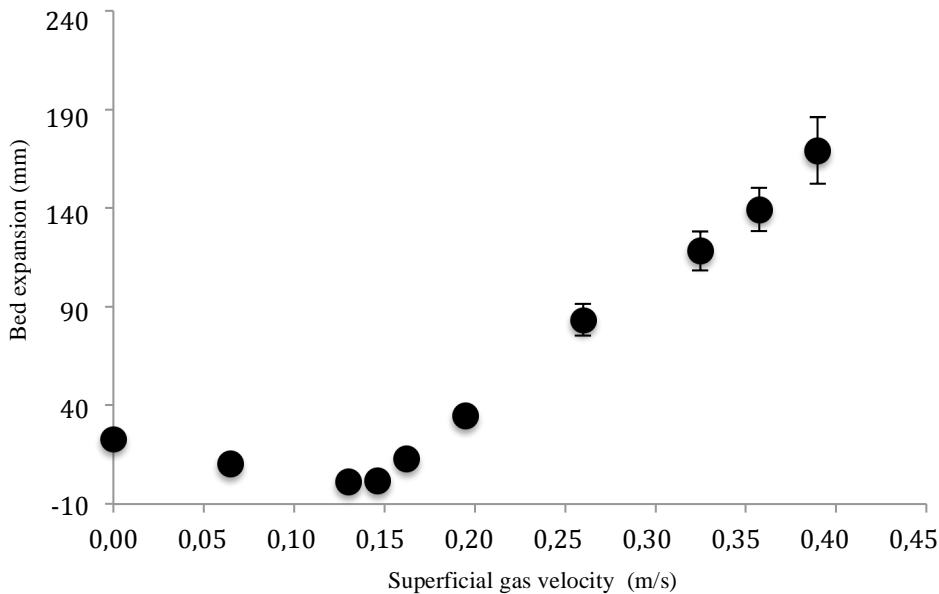
Figure 3: Bed expansion during nitrogen fluidization, bed temperature 700°C

There was indentified a series of fluidization states in which different portions of the total column took place in the mixing. Upon reaching steady state, the preheating could be turned off and we still maintained the same temperature and standard deviation in each zone. This required a fairly good mix of the bed and a superficial gas velocity of 0,31 m/s. The inlet temperature was 40°C and the temperature 25mm above the distribution plate was 650°C.

Silicon growth

The system was equipped with a Mass Spectrometer (MS) and with the possibility of sampling from either the feeding line to the FBR or the exhaust line. The feeding sampling was used to calibrate the MS between the different run conditions.

The motivation for installing the MS was both to keep track of the complete decomposition but also to see traces of incomplete decomposition and formation of intermediate species such as higher order silanes and silicon-hydrogen complexes. The resolution is limited but one may identify trends depending on temperature distribution and fluidization velocity. For the experiment presented here, the process temperatures are so high that traces of intermediate species were unexpected.

Seed material

The seed material was fractioned from commercial TCS FBR material on the market. The size distribution was 500 – 1000 µm (see Fig 4). A number of fluidizing experiments without deposition was performed prior to this experiment. The particles had therefore a quite clean and polished surface. No additional chemical cleaning was performed prior to the deposition.
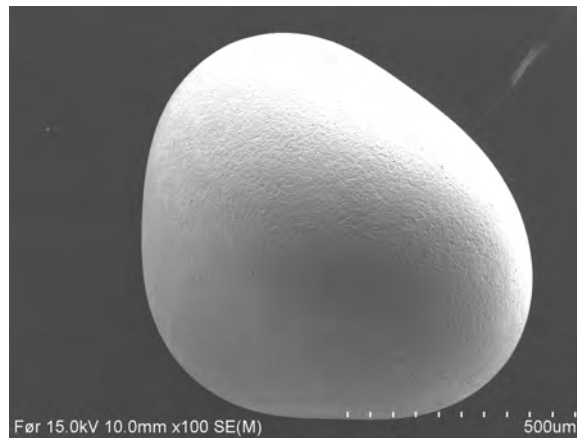
Figure 4: SEM image of seed particle

The CVD experiment

The deposition temperature as well as the involved gas and solid velocities and concentration of the involved species are crucial elements in determining the type of growth and ultimately the product quality [5, 6, 7, 11].

The deposition experiment was performed in nitrogen. Hydrogen is known to take place in some of the intermediate reactions and will thus influence the process differently from nitrogen. Hydrogen experiments will be presented in separate publications.

The start up of the experiment runs was done with an inlet fluidization velocity of 0,12m/s and a distribution plate temperature of 55°C. The temperature 25mm above the distribution plate was 665°C and the temperature in the center of zone 1 was 697°C.

The initial silane concentration was gradually increased to 1,8% during the first half hour. The MS was calibrated by the infeed and used to check the outfeed. There was complete decomposition and no visual pressure buildup in the filter. The inspection glass at the top of the reactor was checked and there was no sign of fines or decrease in sight.

The concentration of 1,8% was kept for another half hour and the reactor was inspected again, without any visual effect. The filter was continuously monitored without significant pressure build up.

After the initial testing the concentration was gradually increased to 4% during the first half hour. No significant changes were observed until reaching 4%. Upon reaching 4% the bottom of the bed seemed to cease fluidizing. The temperature above the distribution plate dropped 200°C in 3 minutes while the temperature in zone one stayed

the same. The reactor was now inspected but the inspection glass at the top of the reactor was completely covered with dust. There was pressure buildup in the filter, but a flush back system is used to keep this clean.

The fluidization velocity was then increased to 0,156m/s and the temperature above the distribution plate rose to 650°C. The temperature of the other zones followed inversely as the temperature above the distribution plate increased. When the temperature increased above the distribution plate the temperatures in the upper zones dropped and the heating elements gave more power to compensate.

After this initial testing the concentration was gradually increased to 8% during the next hour. Two phenomenon were observed. The time between each filter pressure buildup got shorter every time the concentration increased. The standard deviation of the temperature above the distribution plate increased as a function of the silane concentration (See figure 5). The silane was turned of after the experiment and the standard deviation returned to 16 after about 3 minutes.
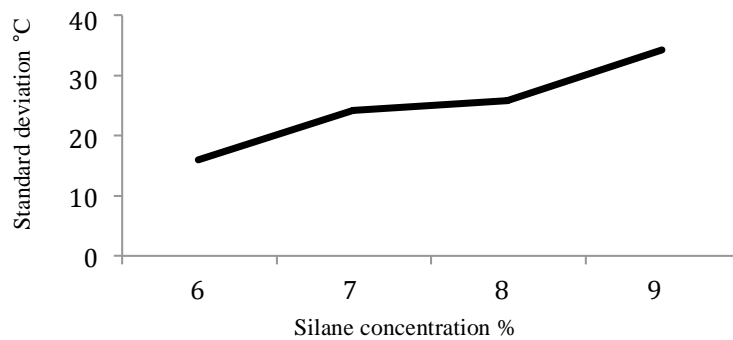
Figure 5: CVD growth of silicon form silane

The deposition

There was grown layers of silicon on the particles (see Figure 6 & 7), but the new layers appeared to be more porous than the seed particles. The growth also seems to support the earlier presumption of a combination of fines scavenging and direct growth although more research is needed in order to draw a final conclusion.

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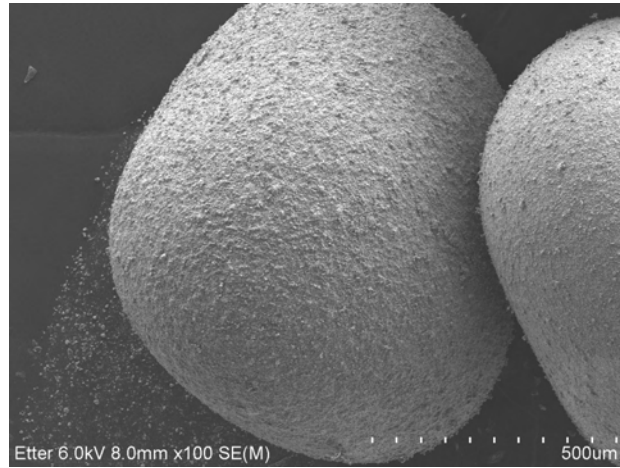
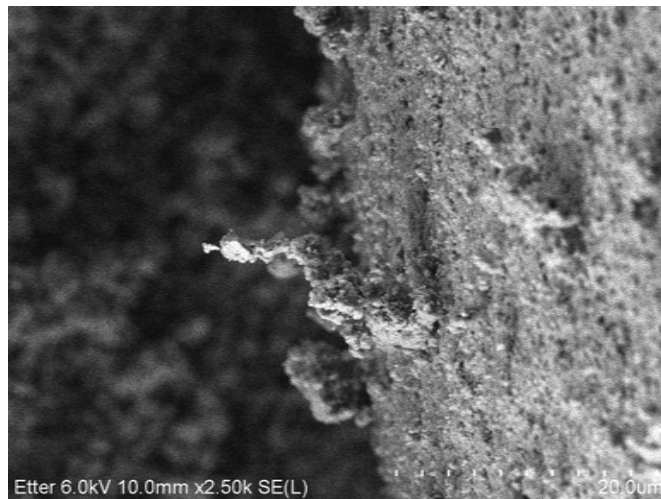**Figure 6**: Deposited layer on seed particle

Figure 7: Surface of deposited layer on seed particle

Discussion

The deposition experiment presented in this paper is initial and limited. The team was able to grow silicon on the seed particles, operate the reactor and maintain fluidization throughout the experiment.

When the silane concentration was increased the fines production got higher. There was also substantially more difficult to keep the bottom part of the bed fluidized and thereby heated when going to higher concentrations. The difficulties ceased when turning off the silane and the temperature distribution and stability returned to the levels experienced at lower concentrations.

There are a number of possible explanations to why the temperature in the bottom of the bed got lower when going to higher concentrations. Silane pyrolysis is an exothermal reaction and an increase in heat draining upon expanding the reactions is therefore not plausible. Another indication pointing away from this conclusion is the inverse relation between the bottom temperature and the temperature of the upper zones.

The effect has been seen before in lab scale experiments [12]. It has however not been verified that the effect is purely concentration dependent and that the effects cease when turning off the silane. It is known that there exist a series of intermediate gaseous and solid species [7, 11]. The production and annihilation of these species is concentration and temperature dependent. One possible explanation could be the production of adhesive surface species at certain temperature and concentration combinations and that these adhesive effects will influence the particle to particle frictional forces and thereby the fluidization properties.

There may be indications that increasing the silane concentration will lead to increase in fines production and influence the growth an quality of the deposition. The concentration is naturally directly linked to the production capacity of the system, it may therefore be seen as a controversy between quality and yield at one hand and capacity at the other. One way to come about this problem would be to use a number of silane inlets at various locations in the fluidization column. Several patents exist that point towards this solution [5].

Conclusion

More experiments are needed to conclude on some of the findings discovered. There seems to be a distinct relation between the silane concentration and the fluidization properties of the particles at the flow and temperatures investigated. The particles appear harder to fluidize when going to higher silane concentrations, especially in the lower regions of the bed. This is in accordance with earlier findings of others and the known production of intermediate gaseous, solid and surface species, but more experiments are needed before a final conclusion may be drawn.

The experiment was performed with small concentration of silane at the beginning going to increasing amounts until the ceasing of the experiment. There was a distinct increase in fines production upon going to higher concentrations.

Acknowledgment

References

1. M. Javidi, P. Ramachandran, Developments in Polysilicon for PV Applications, Photovoltaic Summit Europe, Rome, Italy, 2009.

2. Stephen P. Walch and Christopher E. Dateo, *Thermal decomposition pathways and rates for Silane, Chlorosilane, Dichlorosilane and Trichlorosilane*. Journal of physical chemistry, Vol **105**, (2001) pp 2015-2022 .

3. W. A. P. Claasen and J. Bloem, *The nucleation of CVD silicon on SiO2 and Si3N4 substrates*. J. Electrochemical Soc Vol **127** Issue 1, (1980) pp 194-202.

4. J.O. Odden, P.K. Egeberg, A. Kjekshus *Thermal Decomposition of Pressurized Monosilane*. DOI 10.1002/kin.20164, (2006)

5. W.O. Filtvedt, M. Javidi, A. Holt, M.C. Melaaen, E. Marstein, H. Tathgar, P.A. Ramachandran *Development of fluidized bed reactors for silicon production*. Solar Energy Materials & Solar Cells **94** pp19801995 (2010)

6. Stephen M. Lord and Robert J. Milligan, Assigned to Advanced Silicon Materials inc, *Method for Silicon deposition*. US Pat 5.798.137, (1995)

7. A A Onischuk, V N Panfilov *Mechanism of thermal decomposition of silanes*. Russian Chemical Reviews **70** (4) pp321-332 (2001)

8. Robert H. Allen and James E. Boone, Assigned to Ethyl Corporation, *Process for preparing polysilicon with diminished hydrogen content by using a fluidized bed with a two-step heating process*. US Pat 5.242.671, (1993).

9. George Hsu, Naresh Rohatgi, John Houseman *Silicon Particle Growth in a Fluidized-Bed Reactor* AIChE Journal Vol. **33**, No. 5, 784 – 791 (1987)

10. W. O. Filtvedt, M. Melaaen, A. Holt, M. Javidi, B. R. Olaisen *Composite Distribution Solution for Minimizing Heat Loss in a Pyrolysis Reactor* Int. J. Chem. R. Eng. **Vol. 9** Article A84, (2011)

11. W. O. Filtvedt, A. Holt, P. A. Ramachandran, M. C. Melaaen *Chemical Vapor Deposition of Silicon from Silane: Review of Growth mechanisms and Modeling/Scaleup of Fluidized Bed Reactors* Submitted to Solar Energy Materials & Solar Cells 2012

12. B. Caussat, M. Hemati, J. P. Couderc, *Silicon Deposition From Silane Or Disilane In A Fluid1ze.D Bed-Part I: Experimental Study* Chemical engineering Sci, . Vol. **50**, No. 22, pp. 3615-3624,

Paper VII

W. O. Filtvedt, A. Holt

Silane Based CVD Growth, Governing Mechanisms,
Material and Concepts

W. O. Filtvedt was the main author and contributor to the publication and has
also performed the experimental work presented. A. Holt was the supervisor of
the candidate and co-author of the paper.

SILANE BASED CVD GROWTH, GOVERNING MECHANISMS, MATERIAL AND CONCEPTS

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ABSTRACT: The reactions and mechanisms governing in a monosilane based CVD reactor for polysilicon production depends on several interrelated factors. The decomposition of the silane molecule undergoes a series of intermediate stages before forming the final product. The reactant concentration, heat rate, pressure and heat capacity of the diluent will influence the intermediate reactions and play an important role in the formation of amorphous or crystalline structures. Others have reported the occurrence of radial dispersed lines throughout silane based fludized bed beads [1, 2]. The team has been able to reproduce a pattern that appears similar to these patterns in steady state. The procedure included building and operating a lab reactor for the purpose of depositing silicon on a hot wall. SEM, Optical microscopy and X-ray diffraction have been used to characterize the depositions.
Keywords: Silicon Feedstock

1 BACKGROUND

The production of polysilicon for a Crystalline Silicon based solar cell requires about 40% of the total energy budget of the finished module, depending on the specific process. In order to reduce the energy payback time of installed PV capacity, attention is needed on this process step. Todays workhorse is utilization of trichlorosilane in the Siemens reactor. Monosilane based Fluidized bed reactors have proven to be a much more energy efficient process [3]. However, the FBR material is more inhomogeneous and may be inadequate for certain high efficiency cells. The requirement of understanding the processes, limitations and advantages of competing reactor concepts is important to forecast and aid future development.

Several investigations exist with regards to both silane pyrolysis and deposition [5]. A favored method has been low pressure operation and epitaxial growth. The operation domain present in an industrial FBR is however quite different and recent characterization articles have identified periodic deposition effects that are not present in the earlier investigations [1, 2]. This investigation has been able to reproduce these effects under controlled conditions and may be one step further in the understanding of these effects and how to control them in order to increase product uniformity.

2 THEORY

2.2 Decomposition of silane

In the early days of silicon CVD, several gases were explored for the purpose, but in today's reactors monosilane SiH4 (silane) and trichlorosilane SiHCl3 (TCS) are the ones frequently used. Upon being heated to the decomposition temperature, the gases undergo the following reactions:

$$SiH_4 \rightarrow Si + 2H_2 \qquad (1)$$
$$SiHCl_3 + H_2 \rightarrow Si + 3HCl \qquad (2)$$

The silane decomposition sequence initiation is about 420°C.

However at this temperature, pressure and the present hydrogen concentration, the silicon will form amorphous structures with dispersed hydrogen.

Silane based CVD reactors are therefore often operated at temperatures in the range 650°C to 800°C. Some designs utilize after treatment of the beads at even higher temperatures to assure a crystalline structure.

The decomposition temperature of TCS is about 468°C [4, 5]. The CVD reactors utilizing TCS are however often operated at higher temperatures because amorphous structures might cause chlorine encapsulations. These chlorine encapsulations will cause defects and reduce the quality of the material. Also, there are several reverse reactions complicating the picture even further [3]. Typical temperature range for TCS reactors is 850 - 1100°C.

2.2 Characteristic deposition pattern in silane FBR material

In literature it is known, that material produced by decomposition of monosilane in a FBR, may contain a characteristic periodic pattern of pores [1,2]

The common theory about the origin of this pattern has been the unsteady conditions of a FBR and that the various deposition types comes from deposition at various local conditions at the time and point of deposition.

This theory is interesting and may be correct. However, silane pyrolysis contains a set of reactions moving from the simple silane molecule through a number of intermediate species, into hydrogen containing silicon. Hydrogen may be removed from the material, but depending on the structure, this process may require high temperature and long time [6].

When performing this process within a FBR, both the kinetics and the fluid mechanical aspects need to be considered. This paper presents an alternative route to what is seemingly the same type of growth and structure. However, the route demonstrated, is performed in steady state, and thereby pointing away from a theory based on the dynamics of a FBR.

3 METHOD

3.1 The experimental rig

IFE is operating several reactors for silicon production through silane pyrolysis. In this project a labscale reactor with a wide parameter range for hot wall depositions have been built (see figure 1). The motivation

for the layout was to give a wide parameter range for concentration, temperature and pressure, in order to resemble the deposition conditions in various FBR designs. The radius of the deposition pipe is 50 mm. the material of the pipe was stainless steel, AISI316.

Various conditions have been examined. However, for this paper, we will focus on a set of conditions that gave rise to a pattern known in literature from fluidized bed material [1, 2].
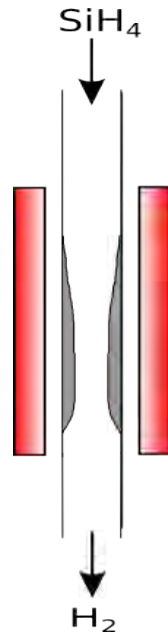

Figure 1: Hot wall deposition reactor

3.2 The experimental method

Silane diluted in hydrogen was fed into the pipe reactor at 0.7 bars absolute pressure. The infeed gas was fed in at room temperature. The deposition wall was kept at a temperature of 600°C. The concentration of the silane gas was 80 Vol % in hydrogen.

The total flowrate was 5 nl/min. The conditions were kept steady for 3 hrs, before the reactor was cooled down and the deposition harvested. The whole experiment was performed 3 times with negligible deviations of results between each run.

4 RESULTS

4.1 Fines

A Substantial amount of fines was produced during the experiments. There were minor changes between the runs, but this difference is believed to be associated with a varying degree of powder buildup in other parts of the pipe system prior to the fines filter.

The amounts of fines, as collected from the filter varied between 15 and 25% of the amount of silicon fed into the reactor.

When investigating the fines for crystallinity it came out as amorphous. However, if increasing the temperature to 650°C the fines came out as crystalline according to an XRD analysis (see figure 2). These results are in good agreement with results published by other groups [7, 8] as well as transition point disclosed in the literature [8].

However, a sample taken from the deposited wall material showed a crystalline signature even though the deposition surface had not been above 600°C. This is not

in conflict with findings reported by others, since other factors is known to take part in determining the nature of the deposited material. The transition from amorphous to crystalline is determined to be 610°C for post production treatment of fines [7, 8].
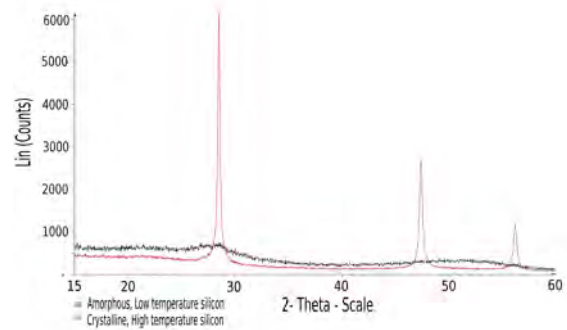

Figure 2: XRD analysis of harvested fines

4.2 Deposited silicon

The deposited silicon was partly covered with fines. However, the deposited material itself appeared dense and shiny. When investigating the material with an optical microscope, several lines parallel to the deposition surface appeared (see figure 3). The lines were not perfectly aligned with the wall, as there were irregular macroscopic waves. However, locally the pattern appeared regular and similar to what has been reported from FBR material earlier. The polishing lines prove challenging to remove, seemingly due to release of loose particles from the edge of the sample during polishing. The samples were treated by standard means with casting, polishing and etching.
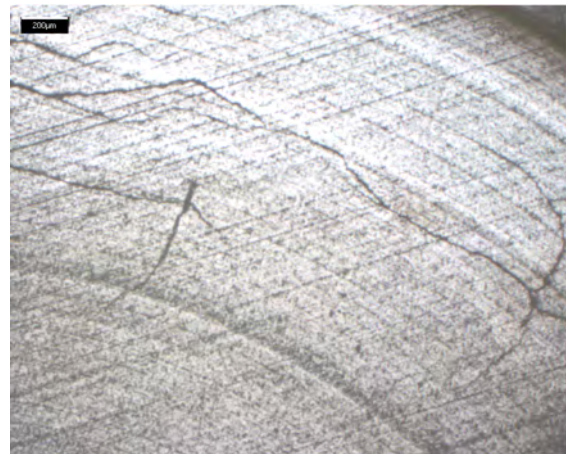

Figure 3: Radially distributed lines

When investigating the actual pores, they also appeared similar to what has been reported earlier (see figure 4).
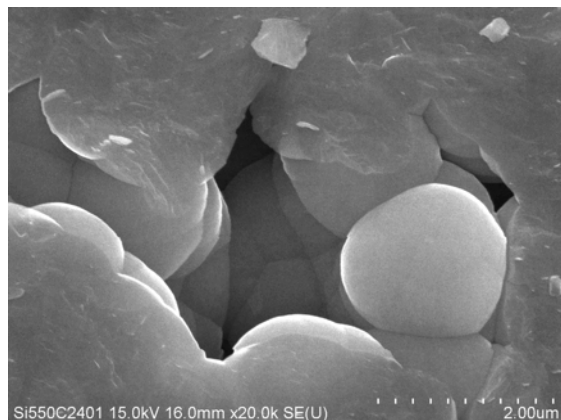

Figure 4: SEM image of pore

5   DISCUSSION

In order to determine what mechanisms are governing the decomposition within a FBR, one needs to consider both the kinetic and fluid mechanical aspects. The process involves several intermediate species and reactions that are both dependent on macroscopic properties such as temperature, pressure and concentration of reactants, but also other intermediate species.

What may be concluded is that both fines formation and wall growth has been achieved in the reactor. There seems to be an inherent periodicity in the wall growth even though the process has been under steady state. This may indicate a process where different intermediate gaseous and solid species interact in a way promoting cyclic growth. A second theory attempt could be an interrelated correlation between surface species and intermediate species passing the surface.

A less ambiguous attempt could be a simple covering of the surface by fines, and that this covering increased the active surface and thereby the scavenging ability of the surface towards intermediate gaseous species. This enhanced scavenging ability would, if present, reduce the local concentration of intermediate gaseous species and thereby limit nucleation and particle formation.

6   CONCLUSION

The data material presented is too scarce to be able to draw any universal conclusions. What has been demonstrated is the ability to grow a crystalline material at a temperature where the retrieved fines is amorphous. In doing so, the team has also been able to produce a periodic pattern, seemingly close to what has been identified in silane based FBR material earlier.

The findings are important as they may point towards new areas to search for solutions in improving silane based FBR design. Operating the pyrolysis under high concentrations and higher pressures seems to promote other mechanisms than those dominating at low pressures.

In order to aid further development in the industry, it is therefore important to increase the research on industry-close conditions.

Much is still unknown in large scale silane pyrolysis and more research is important in order to improve this field further.

6   REFERENCES

[1] M. M. Dahl, A. Bellou, D. F. Bahr, M.G. Norton, E.W.Osborne, Microstructureand grain growth of polycrystalline silicon in fluidized bed reactors, Journal of Crystal Growth 311 (2009) 1496–1500.

[2] M. B. Zbib, M. M. Dahl, U. Sahaym, M. G. Norton, E. W. Osborne and D. F. Bahr, Characterization of granular silicon, powders, and agglomerates from a fluidized bed reactor. J Mater Sci 47, (2012), 2583-2590

[3] C. S. Herrick, D. W. Woodruff, The Homogeneous Nucleation of Condensed Silicon in the Gaseous Si-H-Cl System, J. Electrochem. Soc.: Solid-state Science and Technology, (1984), 2417-2422

[4] S. P. Walch, C. E. Dateo, Thermal decomposition pathways and rates for silane, chlorosilane, dichlorosilane and trichlorosilane, Journal of Physical Chemistry 105 (2001) 2015–2022

[5] W.O. Filtvedt, A. Holt, P.A. Ramachandran, M.C. Melaaen, Chemical Vapor Deposition of Silicon from Silane: Review of Growth mechanisms and Modeling/Scaleup of Fluidized Bed Reactors, Submitted to Solar Energy Materials and Solar Cells (2012)

[6] Robert H. Allen, James E. Boone, Process for preparing polysilicon with diminished hydrogen content by using a fluidized bed with a two-step heating process, Assigned to Ethyl Corporation, US Pat 5.242.671. (1993)

[7] J. O. Odden, P. K. Egeberg, A. Kjekshus, From monosilane to crystalline silicon. Part III. Characterization of amorphous, hydrogen containing silicon products, Journal of Non-Crystalline Solids 351 (2005) 1317–1327.

[8] A. A. Onischuk, V. P. Strunin, M. A. Ushakova, V. N. Panfilov, On the path ways of aerosol formation by thermal decomposition of silane, Journal of Aerosol Science 28 (2) (1997) 207–222.

[9] W. O. Filtvedt, M. Javidi, A. Holt, M. C. Melaaen, E. Marstein, H. Tathgar, P. A. Ramachandran, Development of fluidized bed reactors for silicon production, Solar Energy Materials & Solar Cells 94 (2010) 1980 – 1995.

Appendix I

W. O. Filtvedt, A. Holt

Gas Distribution Arrangement for a Fluidized Bed

W. Filtvedt was the first inventor of the presented patent. A. Holt was the
supervisor of the candidate and second inventor of the patent.

(54) Title: GAS DISTRIBUTION ARRANGEMENT FOR A FLUIDIZED BED

FIG. 1

(57) Abstract: The invention concerns a gas distribution arrangement, a device for handling a chemical reaction comprising such a gas distribution arrangement and a method of providing a chemical reaction chamber with a gas. The distribution arrangement com - prises a distribution plate (16) for separating a chemical reaction chamber (14) from a gas inlet area (12) and having a first side (20) arranged to face the chemical reaction chamber and a second side(18) arranged to face the gas inlet area and comprising a set of through holes stretching between the first and the second side, where the first side of the plate comprises a first material surrounding the holes and having a first thermal conductivity, and the plate also comprises a second material forming a base structure also sur - rounding the holes and having a second thermal conductivity.

GAS DISTRIBUTION ARRANGEMENT FOR A FLUIDIZED BED

TECHNICAL FIELD

5 The invention relates to reactors for chemical
processes such as fluidized bed reactors. More
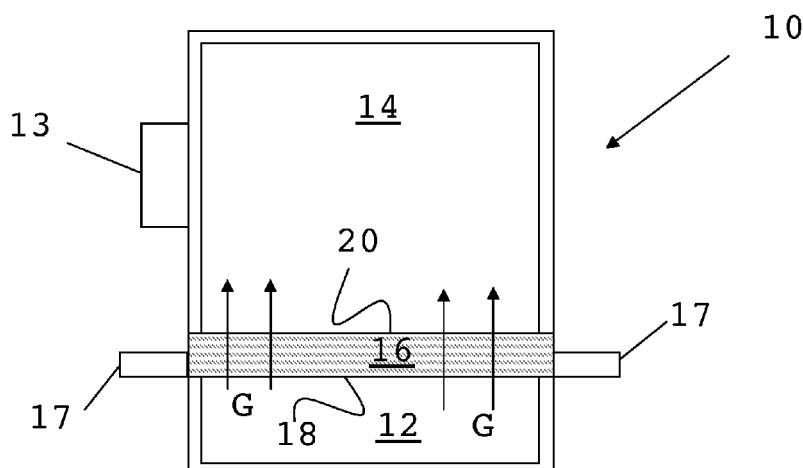particularly, the invention relates to a gas
distribution arrangement, a device for handling a
chemical reaction comprising such a gas distribution
10 arrangement and a method of providing a chemical
reaction chamber with a gas.

BACKGROUND

15 In some chemical reactions it is of interest to let a
gas enter a chemical reaction chamber via a
distribution plate, where the function of the
distribution plate is to ensure a uniform supply of the
gas to the chemical reaction chamber.
20

One type of chemical reaction chamber where the use of
such a distribution plate is needed is the Fluidized
Bed Reactor. Fluidized Bed Reactors are for instance
described by W.O. Fildvedt et al in "Development of
25 fluidized bed reactors for silicon production", Solar
Energy Materials and Solar Cells, Volume 94, Issue 12,
December 2010.

Here a gas is transported to the chamber from a gas
30 inlet area, often denoted Windbox, via a distribution
plate.

One known distribution plate is described in US
3,889,631.

In certain chemical reactions encouraged in Fluidized
5 Bed Reactors (FBR), the chamber is held at a high
temperature while the gas inlet area has a lower
temperature. As the gas enters the high-temperature
chamber of the FBR, the gas will decompose and be
deposited. This type of chemical process is attractive
10 to use when for instance producing polysilicon from
silanes in gas form.

However, it is important in this case that this
decomposition does not take place until the gas reaches
15 the chamber, because the gas may start to decompose
within the distribution plate and clog it, which will
negatively influence the chemical process. This may be
solved through cooling the distribution plate. However,
if this is done heat may be lost from the chamber
20 through the distribution plate.

There is therefore a need for improvement in relation
to distribution plates.

25 SUMMARY

The invention is therefore directed towards solving at
least some of the above mentioned problems associated
with distribution plates.
30

One object of the invention is thus to solve one or
more of the above mentioned problems.

This object is according to a first aspect of the
invention achieved through a gas distribution
arrangement comprising distribution plate for
5 separating a chemical reaction chamber from a gas inlet
area and having a first side arranged to face the
chemical reaction chamber and a second side arranged to
face the gas inlet area, the distribution plate
comprising a set of throughholes stretching between the
10 first and the second side, wherein:
the first side of the plate comprises a first material
surrounding the holes and having a first thermal
conductivity, and
the plate also comprises a second material forming a
15 base structure also surrounding the holes and having a
second thermal conductivity.

In a preferred embodiment of the present invention the
gas distribution arrangement is for the production of
20 silicon and more preferably for the production of
polysilicon from silanes and/or chlorosilanes in gas
form.

Preferably, the gas distribution arrangement is for a
25 fluidizing bed reactor in a chemical reaction chamber.

It should be appreciated that embodiments and aspects
of the invention are suitable or adaptable for other
types of chemical reaction chambers and/or fluidizing
30 bed reactors.

This object is according to a second aspect of the
invention achieved through a device for handling a
chemical reaction comprising:
a chemical reaction chamber,
5 a gas inlet area, and
a distribution plate for separating the chemical
reaction chamber from the gas inlet area, where the
distribution plate is a distribution plate as defined
in the first aspect of the invention.
10
This object is according to a third aspect of the
invention achieved through a method of providing a
chemical reaction chamber with a gas comprising the
steps of:
15 providing the gas G at a first temperature T1 in a gas
inlet area,
heating the reaction chamber to a second temperature
T2,
preventing heat of the reaction chamber from reaching
20 the gas inlet area using a first side of a distribution
plate, which first side is made of a first material
having a first thermal conductivity, and
transporting the gas from the gas inlet area through
holes in the distribution plate to the reaction
25 chamber, while cooling the holes using a base structure
of the distribution plate, which base structure is of a
second material having a second thermal conductivity
and also surrounds the holes.

30 The invention according to these aspects has a number
of advantages. The invention avoids clogging of the
distribution plate. It also improves the ability of the

chemical reaction chamber to retain a desired
temperature, which reduces the energy consumption of
the chemical reaction chamber. Another advantage of the
invention is that the net heat transport through the
5 distribution plate is reduced. A further advantage is
that a high temperature gradient is sustained over the
distribution plate thereby enabling more advantageous
process parameters.

10 The dependent claims are concerned with advantageous
variations of the invention.

It should be appreciated that one or more of the
invention embodiments and aspects may also comprise
15 one, or a combination of, the elements described herein
with reference to the drawings.

It should be emphasized that the term
"comprises/comprising" when used in this specification
20 is taken to specify the presence of stated features,
integers, steps or components, but does not preclude
the presence or addition of one or more other features,
integers, steps, components or groups thereof.

25 BRIEF DESCRIPTION OF THE DRAWINGS

The invention will now be described in more detail in
relation to the enclosed drawings, in which:
fig. 1 schematically shows a device for handling a
30 chemical reaction comprising a reaction chamber being
separated from a gas inlet area by a distribution
plate,

fig. 2 shows a view from above of the distribution
plate,
fig. 3 shows a cross-sectional view of the distribution
plate in fig. 3 according to a first embodiment,
5 fig. 4 schematically shows a first variation of the
walls of a hole in a distribution plate according to a
second embodiment,
fig. 5 schematically shows a second variation of the
walls of a hole in a distribution plate according to a
10 third embodiment,
fig. 6 schematically shows a third variation of the
walls of a hole in a distribution plate according to a
fourth embodiment,
fig. 7 shows a flow chart of a number of method steps
15 being performed in a method of providing a chemical
reaction chamber with a gas,
fig. 8 schematically shows a hole according to another
variation of a distribution plate comprising a further
material layer,
20 fig. 9 shows a graph of the temperature inside the
chemical reaction chamber and at the first and second
sides of the distribution plate, and
figs. 10 and 11 schematically show a further variation
of the device for handling a chemical reaction
25 comprising an additional layer located adjacent the
first side of the distribution plate according to a
further embodiment.

DETAILED DESCRIPTION

30

In the following description, for purposes of
explanation and not limitation, specific details are

set forth such as particular architectures, interfaces,
techniques, etc. in order to provide a thorough
understanding of the invention. However, it will be
apparent to those skilled in the art that the invention
5 may be practiced in other embodiments that depart from
these specific details. In other instances, detailed
descriptions of well-known devices and methods are
omitted so as not to obscure the description of the
invention with unnecessary detail.
10
The invention is generally directed towards
improvements of distribution plates used in chemical
reaction chambers such as in Fluidized Bed Reactors.

15 A device for handling a chemical reaction is
schematically shown in fig. 1. This exemplifying device
10 is here a Fluidized Bed Reactor. However, it should
be realized that the invention is not limited to this
type of reactor, but may be used also with other types
20 of reactors for other types of chemical processes. The
invention may more particularly be used in any type of
pyrolysis reactor or other temperature dependent
reactor where reduction of heat loss is essential.

25 In the device 10 there is a reactor chamber 14, which
is separated from a gas inlet area 12 through a
distribution plate 16. A heater 13 is attached to the
chamber 14 in order to provide heat to it. The
distribution plate 16 is here a part of the wall of the
30 chamber and in this example furthermore the bottom of
the chamber 14. It should however be realised that it
may as an example also be a part of the side wall of

the chamber. The plate has furthermore a first side 20,
which faces the chamber 14 and a second side 18 that
faces the gas inlet area 12. In this first embodiment
there is also one distribution plate. It should be
5 realized that it is possible to use more than one such
plate. The plate is here furthermore shown as being
planar. It should be realized that it is not limited to
being planar but may have any suitable shape. It may
for instance be curved or bent. The shape of the
10 distribution plate may furthermore be adapted to the
intended shape of the reactor chamber 14.

The plate is perforated, which means that a gas G can
come from the gas inlet area 12 and enter the chamber
15 14 via the distribution plate 16, where the
distribution plate 16 here has the function to
distribute the gas evenly in the chamber 14. The plate
16 is furthermore thermally connected to a heat
diverting element, here in the form of a heat sink 17.
20 In one variation of the invention the heat sink and
distribution plate together make up a gas distribution
arrangement of the invention. In other variations only
the distribution plate makes up such a gas distribution
arrangement. The heat sink may here be further cooled
25 by a cooling media, typically a cooling fluid, which
may be circulated in a loop. A cooling fluid may be a
liquid like water or a gas such as air.

Fig. 2 shows a view from above of the distribution
30 plate 16. It is thus a view displaying the first side
of the plate. The plate has a set of holes 22, which
are provided in a pattern. These holes go through plate

from the first to the second side, i.e. they are
throughholes. In the disclosed variations of the
invention they are placed on the plate in a gas
distribution pattern or a distribution scheme designed
5 for providing a good gas distribution in the chamber.
We have here illustrated a square pattern. Other types
of gas distribution patterns are however possible. Here
it should also be known that the distance between the
holes should be higher than the hole diameter and this
10 distance should typically be at least five times higher
and with advantage at least ten times higher than the
hole diameter in order to provide good flow conditions
in the chamber. This would naturally depend on the type
and layout of the reactor. As an alternative the holes
15 may be randomly distributed.

In some embodiments of the invention the distance
between the holes is about seventeen times higher than
the diameter. The hole density may also be higher than
20 500 holes/m^2, with advantage higher than 1000 holes/m^2,
advantageously higher than 3000 holes/m^2 and in some
embodiments about 3500 holes/m^2. In the figure a line
B-B through the centre of the plate is also shown

25 Fig. 3 shows a cross sectional view of the plate
according to a first embodiment of the invention taken
along line B-B in fig. 2.

As can be seen the first side 20 is comprised or is
30 made of a first material 24, which material surrounds
the holes and has a first thermal conductivity. The
first material may surround the holes in a direction

that is perpendicular to the length direction of the
holes. Here also the holes 22 are shown. The first
material 24 is a substantially non-compressible fibrous
material which is machinable, such as packed ceramic
5 fibre insulation. These holes 22 have walls that are
at least partly made up of a third material, which
material has a third thermal conductivity. In the
figure also the second side 18 of the plate 16 is
shown. The second side comprises or is made of a second
10 material 28 surrounding the holes and having a second
thermal conductivity. Also the second material may
surround the holes in a direction that is perpendicular
to the length direction of the holes. In this first
embodiment of the invention the distribution plate 16
15 is formed through a base plate or base section on which
insulation is placed, where the insulation is made of
the first material 24 and the base plate or base
structure of the second material 28. Furthermore in
this first embodiment the second and third materials
20 are the same material and therefore the second and
third thermal conductivities are the same. The walls of
the holes are therefore, in this first embodiment
wholly provided through the base plate. This means
that the walls of the holes are obtained through
25 protrusions that stretch out from the base plate
through the insulation towards the first side 20. The
second and third materials here have a higher thermal
conductivity than the first material and for instance
more than 100 times higher. The material of the walls
30 and base plate are in this example a metal, which in
the first embodiment is aluminium. It should however be
realized that other materials may be used, such as for

instance steel, copper or even graphite. It is an
advantage if the material chosen has properties which
make it resistant to any reaction with the gas coming
into contact with the material. For example, when
5 chlorosilanes are used, corrosion-resisting alloys such
as Inconel© may be preferred to aluminum.

Each hole thus has at least one wall. In case the holes
have a circular or elliptical cross-section each hole
10 will only have one wall. However, if the walls have
square or rectangular cross-section, then they will
have four walls and if they have triangular cross-
section they will have three walls.

15 The parts of the holes that stretch through the
insulation 24 are here formed as tubes having an inner
surface with an inner diameter and an outer surface
with an outer diameter. Furthermore a first section of
this tube at a first end of the tube facing the first
20 side 20 has an outer surface with an increasing outer
diameter from a first to a second outer diameter in the
direction from the first side 20 towards the base plate
28. The outer diameter thus increases from a first
outer diameter that is essentially equal to the inner
25 diameter of the tube to a second larger diameter. In
this embodiment the tube wall made up of the inner and
outer surfaces has a linearly increasing wall thickness
in the first section, which makes the holes have a
conical shape facing the chamber, i.e. in the opposite
30 direction.

This means that at the first side 20 the holes are
surrounded by insulation 24 right up till the inner
diameter. It should here be realized that as an
alternative it is possible that the tubes have the same
5 outer diameter all the way to the base plate 28.

The base plate may be cooled, for instance using the
previously mentioned heat sink.

10 A chemical reaction in the reactor for which the
distribution plate can be employed may require a high
temperature difference between the chamber and the gas
inlet area during transport to the chamber. In for
instance silicon production, where silanes like
15 monosilane or trichlorosilane are used as gas, the
temperature in the chamber may need to be above 700°C,
for instance around 710°C or 800°C, while the
temperature in the gas inlet area typically is below
420°C and with advantage slightly lower, such as a
20 temperature in the range of 250°C to 400°C and more
preferably 300°C to 350°C. The reason for this is that
at 420°C silane starts to decompose, while good crystal
structures are obtained at 710°C. This means that the
latter temperature is present at the first side 20 of
25 the distribution plate 16, while the former is present
at the second side 18.

This also means that if nothing is done, the
throughholes will exhibit a gradual increase in
30 temperature from the second 18 to the first side 20.
However, this also means that parts of the holes will
have the temperature at which the gas decomposes. The

result is that material, and in this example silicon, will be deposited on the walls of the holes. This will lead to the holes becoming clogged, which will result in the chemical process becoming less and less

5 effective. This also means that it may be necessary to replace distribution plates frequently.

This problem of clogging is thus serious and needs to be addressed. At the same time it is important that the

10 heat of the chamber is not lost via the distribution plate, which leads to an unnecessarily high energy consumption.

These and other problems are according to the invention

15 addressed through keeping the temperature of the holes as close to the temperature of the gas inlet area as possible. This is combined with keeping the temperature at the first side of the plate, the side facing the chamber, at the chamber temperature.

20

This is according to the invention solved through the first side of the distribution plate comprising a first material surrounding the holes and having a first thermal conductivity for retaining the chamber

25 temperature combined with using the second material of the base plate having a second thermal conductivity cool the holes of the distribution plate.

The thermal conductivity of the second material is with

30 advantage higher than the thermal conductivity of the first material.

The thermal conductivity of the second material is with advantage at least 100 times higher, with advantage 1000 times higher and according to the first embodiment about 3000 times higher than the thermal conductivity

5 of the first material. Here the first material, i.e. the insulation, may have a thermal conductivity of 0.08 W/m-K while aluminium may have a thermal conductivity of 237 W/m-K.

10 The heat that is transferred to the holes will be led away from the walls to the base plate and into the optional heat sink, which will prevent clogging.

Through the use of insulating material, the temperature

15 of the chamber will be held high also adjacent to the first side of the distribution plate, which ensures a good chemical reaction. As small amounts of heat from the chamber is transferred to the holes, it is also clear that the energy losses are small, even in the

20 case that a heat sink is connected to the distribution plate, which furthermore leads to an economical operation of the device with optimal heat and energy savings. In this way the energy consumption of the chemical reaction chamber is reduced. Another advantage

25 of the invention is that the net heat transport through the distribution plate is reduced. Yet another advantage is that a high temperature gradient is sustained over the distribution plate thereby enabling more advantageous process parameters. The construction

30 of the distribution plate is also robust.

Here the conical shape of the holes has the further
advantage of reducing the amount of heat transferred
into the holes from the chamber even further.

5   It is possible to vary the design of the holes in
several ways in order to improve the ability to keep
the whole temperature down and lower the heat
dissipation from the chamber even further.

10 Fig. 4 shows a cross section of a part of plate with a
first variation of the hole according to a second
embodiment of the invention.

The wall of the hole is here in the bottom made up of
15 the second material 28 of the base plate, which as one
example is aluminium. However the part that protrudes
through the insulation 24, which in this embodiment is
a tube only including the first section 29, is made of
another material, which is here anisotropic graphite.
20 Here the whole part of the tube stretching up through
the insulation is made of this other material, the
third material 26. The outer diameter D_o of the outer
surface in this section 29 is here furthermore
increasing in the direction from the chamber to the
25 base plate. It is increased from the first outer
diameter that is equal to the inner diameter D_i to the
second outer diameter. The outer surface having the
outer diameter D_o is here curved and the radius of this
outer surface may more particularly increase
30 essentially exponentially or logarithmically.
Furthermore in this second embodiment the part of the
hole wall that is provided with this third material is

anisotropic and has a higher thermal conductivity along
the length of the hole than radially away from the
hole. This means that the first section 29 is
anisotropic. In this second embodiment this higher
5   thermal conductivity furthermore follows the curvature
of the outer diameter D_o.

This has the advantage of even further reducing the
heat transfer from the reaction chamber to the hole
10 while maximizing cooling of the whole throughhole surface
thanks to favored heat exchange with the heat sink.
Operating parameters will be set such as to keep gas
temperature close to the inner wall lower than the
decomposition temperature at the outlet of the through-hole.
15

A second variation of the hole according to a third
embodiment of the invention is shown in fig. 5. Here
the part of a hole wall extending above the base plate
is also anisotropic and has a higher thermal
20 conductivity along the length of the hole than at right
angles to the hole, i.e. radially. However in this
embodiment the direction of higher thermal conductivity
is parallel with the hole, i.e. with the hole axis. The
first section 29 with increasing outer diameter is here
25 also shaped as in the first embodiment. The tube of
third material in this third embodiment thus has a
first section 29 with an increasing outer diameter
providing a linearly increasing wall thickness in the
direction from the first side towards the base plate
30 28. There is also a further section 30 of the tube
having a constant outer diameter. This further section
30 here rests on the base plate 28. Both the first and

the second sections 29 and 30 are here anisotropic with
the same direction of thermal conductivity in parallel
with the hole length.

5 A third hole variation according to a fourth embodiment
   is shown in fig. 6. Here the same direction of thermal
   conductivity and first tube section shape is provided
   as in the third embodiment. However, in this case the
   third material stretches down into the base plate in
10 the same way as it stretches into the insulation. There
   is thus here a second section 31 of the tube of third
   material with an outer diameter providing a linearly
   diminishing wall thickness, which second section 31
   stretches from the insulation 24 all the way down to
15 the gas inlet area. The second section thus has an
   outer surface with a diameter that decreases linearly
   from the second outer diameter to a third outer
   diameter in the direction towards the second side,
   which third outer diameter in this case is equal to the
20 first outer diameter. In this fourth embodiment the
   base plate is furthermore different in that it is also
   anisotropic and may for instance be made of graphite.
   The second material 28 may thus be graphite. However,
   here the base plate has a higher thermal conductivity
25 in the radial direction from the hole than in the
   length direction along the length of the hole. This
   improves the ability to keep the hole temperature low
   even further.

30 The thermal conductivity along the hole may be at least
   four times higher than the thermal conductivity
   radially away from the hole, preferably at least 20 and

with advantage at least 100 times higher. As an example
it may be approximately 120 times higher.

It should here be realised that the fourth embodiment
5 may be varied in that the first and second sections of
   the third material may have the same shape and thermal
   conductivity direction as the first section of the
   third material in the second embodiment.

10 An example of one way of operating the device will now
   be described with reference being made to fig. 7, which
   shows a flow chart of a method of transporting gas to
   the chamber 14. The method is a part of a chemical
   process, which is here the process of producing silicon
15 wafers based on the gas silane.

In the method, the gas is provided at a first
temperature T1 in a gas inlet area, step 32, which
temperature may be 200°C. The reaction chamber is also
20 heated to a second temperature T2, step 34, which
   second temperature is here a temperature of 600°C.
   However, it shall be appreciated by those skilled in
   the art that operation parameters will depend on the
   process considered and the gas used. For example, when
25 using Chlorosilanes, temperatures will be generally
   higher.

In order to keep the heat from dissipating, the heat of
the reaction chamber is furthermore stopped from
30 reaching the gas inlet area using the first side of the
   distribution plate, step 36, i.e. using the first
   material having the first thermal conductivity. This

19

first side may here have a third temperature T3. The
gas is also transported from the gas inlet area through
the holes in the distribution plate to the reaction
chamber, step 38, and this transporting is made while
5 cooling the holes using the base structure of the
distribution plate. This cooling of the walls will lead
to the gas being transported through the holes also
being cooled.

10 Through this way of operating, the heat in the chamber
is to a high degree retained in the chamber, here at
the temperature where silane decomposes and the heat of
the chamber is stopped from escaping through the
distribution plate by the use of the insulation, which
15 is beneficial for the energy consumption of the device.
At the same time cooling of the hole walls ensures that
clogging is avoided.

In a further embodiment of the above method there is an
20 additional method step whereby the gas is heated in the
inlet area 12 and/or is heated prior to entering the
inlet area 22.

The gas in the holes would normally receive heat from
25 the upper part of the distribution plate, i.e. from the
part of the plate that is closest to the reaction
chamber. This heat is removed by the cooling provided
through the invention. The gas will also receive heat
directly from the reaction chamber. This heat transfer
30 can be influenced by the speed which the gas is passed
through the distribution plate. The heating can thus
also be regulated through the velocity of the gas.

20

The example of a chemical process that was given above
was the production of silicon. The invention is
naturally not limited to this field but may be used for
5 other types of processes, such as for instance oil and
gas production processes.

A hole wall or base structure being described as
anisotropic may be obtained in different ways. It is
10 for instance possible that the material used as a wall
or base structure is as such thermally anisotropic.
However it is also possible to obtain anisotropy
through assembly of different isotropic layers of
material, where the interfaces between the layers cause
15 the anisotropy.

There are thus several ways in which the anisotropic
walls can be obtained. It is for instance possible to
provide the walls based on using highly anisotropic
20 flexible materials, shaping them according to the
desired function and binding them together with a high
temperature binder. This is for instance described at
http://www.techapps.com/thermal-straps.html. As an
example it is possible to bake highly conductive
25 graphite strings in a sintered material such as silicon
nitride, silicon carbide or other suitable material. .
As an alternative it is possible to produce a synthetic
custom carbon design directly (premature technology),
which is described at
30 http://www.asbury.com/images/pdf/SyntheticGraphitePartI
.pdf. This may be done by a number of methods. The
whole or parts of a hole wall may be produced from a

synthetic graphite material produced from high
temperature treatment of carbon particles of different
properties.

5   There is yet a further way in which the invention may
    be provided, which is shown in fig. 8, which
    essentially shows the same insulation 24, base plate 28
    and tube 26 as fig. 5. However, in this embodiment of
    the invention the distribution plate comprises a
10 further material 40. This further material 40 is
    furthermore provided at the second side of the
    distribution plate. The second side here thus comprises
    the further material. Here the second material 28 has a
    higher thermal conductivity than the further material
15 40 and in one specific variation of the invention the
    further material is the same as the first material.
    This further material may therefore also be insulation.
    It can in this way be seen that a distribution plate
    can also be provided in the form of a cooling base
20 structure sandwiched between two layers of insulation,
    which base structure may then cool the holes, with
    advantage through being connected to a heat sink.

    A number of tests have been performed on the
25 distribution plate described in the first embodiment.

    In one experiment a cooling media was passed through
    the heat sink. In this example, the inlet temperature
    of the cooling media was 10°C while the outlet
30 temperature was 44°C. This setup resulted in a
    temperature of 278°C at the first side of the plate in
    the chamber while the temperature at the second side of

the plate was about 35°C. A considerable temperature
difference was thus observed. A further test of the
plate was done with water at boiling temperature. The
water inlet was reduced to a bare minimum such that the
5   whole heat sink reservoir reached boiling. At the
    outlet of the heat sink there was provided a 1.5 m high
    vertical section which overflowed when the water level
    got too high. This setup yielded a close to constant
    temperature around the heat sink and the extracted heat
10 was removed as evaporation energy. By using this setup
    the second side of the distribution plate would hold a
    constant temperature T1 of about 78°C while the
    temperature T3 at the first side reached 423 C. Further
    into the chamber an even higher temperature T2 of 650°C
15 was obtained.

    The results of the last test are shown in a graph in
    fig. 9.

20 With reference to figs. 10 and 11, there is shown a
    further embodiment of the invention which comprises an
    additional layer 50. This further embodiment is shown
    in fig. 11 in relation to the second variation of the
    walls shown in fig. 5 and the same reference numbers
25 have been used to designate corresponding elements.
    However, it should be appreciated that the additional
    layer 50 of the further embodiment may also be applied
    to any one of the device embodiments described herein.

30 The layer 50 is a substantially planar structure and is
    located adjacent the first side 20. However, it should
    be appreciated that the layer 50 may be another shape

which substantially matches the shape or contour of the
first side 20. The layer 50 has a typical thickness of
2mm or lower. Preferably the layer 50 is located using
mechanical clamping means around the outer
5 circumference of the layer 50 and/or the layer 50 is
attached to the first side 20 using a suitable
adhesive. In an alternative variation the layer 50 is
a silicate, such as a silicon dioxide, silicon carbide,
silicon nitride or similar type of material, which is
10 formed onto the first surface by a suitable process.
The layer 50 is formed with a series of holes 52 which
align with the throughholes 22 of the distribution
plate. The layer 50 is preferably made from a material
which will substantially withstand the abrasive action
15 of the fluidizing bed. A preferred material for the
layer 50 is silicon, but other suitable materials may
be used. The purpose of the layer 50 is to provide a
protective layer over the first side 20 in order to
protect the first material 24 and help prevent any
20 material contaminants coming from the first material 24
into the reaction chamber 14.

In this further embodiment of the device, the inlet
area 12 is provided with means (not shown in fig. 10)
25 for changing the temperature of the gas in the gas
inlet area 12. The means for changing the temperature
of the gas is preferably a heating means, which could
be any suitable thermal heat source such as an
electrical heater or a fluid heat exchanger. The
30 thermal heat source either changes the temperature of
the gas in the inlet area 12, or alternatively the heat
source changes the temperature of the gas prior to

entering the inlet area 12. Preferably the heat source
increases the temperature of the gas in the inlet area
12. In this embodiment the temperature of the gas in
the inlet area 12 is ideally substantially close to,
5 but less than, the optimum gas reaction temperature,
for example the decomposition temperature of the gas.
The benefit of having the gas in the inlet area 12
close to the reaction temperature is that the loss of
temperature of the gas due to passing through the
10 throughholes 22 will not significantly affect the
efficiency of gas chemical reaction of the gas after
exiting the throughholes 22 into the reaction chamber
12. If the temperature of the gas remains close to the
reaction temperature while travelling from the inlet
15 area 12 to reaction chamber 14 then the gas will react,
for example decompose, in a shorter time and/or
distance after exiting from the throughholes 22 than
the time or distance achievable if the temperature of
the gas is significantly less than the reaction
20 temperature on exiting the throughholes 22. It should
be appreciated that on the one hand the temperature of
the gas should be controlled as described previously in
order to help prevent clogging, but on the other hand
the efficiency of the chemical reaction in the chamber
25 14 is improved if the gas exiting the throughholes 22
is as near as possible to the ideal required reaction
temperature of the gas. The skilled person will
understand that in some arrangements the level of
temperature control may be less and will depend on the
30 type of characteristics gas or fluid, such as
susceptibility to decomposition, being transported and
the particular process parameters.

While the invention has been described in connection
with what is presently considered to be most practical
and preferred embodiments, it is to be understood that
5 the invention is not to be limited to the disclosed
embodiments, but on the contrary, is intended to cover
various modifications and equivalent arrangements.

CLAIMS

1. A gas distribution arrangement, for a fluidized bed
   reactor for silicon production, comprising a
5 distribution plate (16) for separating a chemical
   reaction chamber (14) from a gas inlet area (12) and
   having a first side (20) arranged to face the
   chemical reaction chamber and a second side (18)
   arranged to face the gas inlet area, the
10 distribution plate comprising a set of throughholes
   (22) stretching between the first and the second
   side, wherein:
   the first side of the plate comprises a first
   material (24) surrounding the holes and having a
15 first thermal conductivity, and
   the plate also comprises a second material (28)
   forming a base structure also surrounding the holes
   and having a second thermal conductivity.

20 2. The gas distribution arrangement according to claim
   1, wherein the second material has higher thermal
   conductivity than the first material.

3. The gas distribution arrangement according to claim
25 1 or 2, wherein the second side of the distribution
   plate comprises the second material.

4. The gas distribution arrangement according to claim
   1 or 2, wherein the second side of the distribution
30 plate comprises a further material (40).

5. The gas distribution arrangement according to claim 4, wherein the second material has higher thermal conductivity than the further material.

6. The gas distribution arrangement according to claim 4 or 5, wherein the further material is the same as the first material.

7. The gas distribution arrangement according to any previous claim, wherein each throughhole has at least one wall at least partly made of a third material (26) having a third thermal conductivity and where the second material is in thermal contact with the third material.

8. The gas distribution arrangement according to claim 7, wherein the thermal conductivity of the third material is higher than thermal conductivity of the first material.

9. The gas distribution arrangement according to claim 7 or 8, wherein the holes are at least partly defined by tubes made of the third material with an inner surface having an inner diameter (D_i) and an outer surface having an outer diameter (D_o), where the tubes comprise a first section (29) at a first end facing the first side and in which the outer diameter increases from a first outer diameter to a second outer diameter away from the first end.

10. The gas distribution arrangement according to claim 9, where the first outer diameter is equal to the inner diameter (D_i).

11. The gas distribution arrangement according to claim 9 or 10, wherein the first section (29) is anisotropic with higher thermal conductivity in a direction along the length of the corresponding hole than radially away from the hole.

12. The gas distribution arrangement according to claim 11, wherein the outer surface of the first section (29) is curved and the direction of higher thermal conductivity of the anisotropic first section follows the curvature of the outer surface.

13. The gas distribution arrangement according to claim 11, wherein the outer surface of the first section (29) has a linearly increasing outer diameter and the direction of higher thermal conductivity of the first section stretches in parallel with the throughhole.

14. The gas distribution arrangement according to any of claims 9 - 11, wherein each tube comprises a second section (31) at a second end facing the second side and in which the diameter of the outer surface diminishes from the second outer diameter to a third outer diameter towards the second end.

15. The gas distribution arrangement according to any of claims 11 - 14, wherein the base structure is

29

anisotropic having higher thermal conductivity
radially away from the hole than along the length of
the hole.

5 16. The gas distribution arrangement according to any
    of claims 7 - 15, wherein the third material is the
    same as the second material.

    17. The gas distribution arrangement according to any
10 previous claim, further comprising at least one heat
    diverting element (17) connected to the base
    structure.

    18. The gas distribution arrangement according to any
15 previous claim, wherein the chemical reaction
    chamber comprises a fluidized bed reactor for
    producing silicon.

    19. The gas distribution arrangement according to any
20 previous claim wherein the holes are positioned in
    the plate according to a gas distribution pattern.

    20. The gas distribution arrangement according to any
    previous claim wherein the distribution plate (16)
25 comprises a layer located adjacent the first side
    (20).

    21. The gas distribution arrangement according to
    claim 20 wherein the layer located adjacent the
30 first side (20) is a silicate material.

30

    22. The gas distribution arrangement according to any
    previous claim, wherein the gas distribution
    arrangement comprises means for changing the
    temperature of a gas within the gas inlet area (12).
5
    23. A gas distribution arrangement according to any
    previous claim, wherein the gas distribution
    arrangement is for a chemical reaction chamber.

10 24. A device (10), for handling a chemical reaction in
    a fluidized bed reactor for silicon production,
    comprising:
    a chemical reaction chamber (14),
    a gas inlet area (12), and
15 a distribution plate (16) for separating the
    chemical reaction chamber from the gas inlet area,
    where the distribution plate is a distribution plate
    as defined in any previous claim.

20 25. A device (10) as defined in claim 25, wherein the
    device (10) comprises a reaction chamber for a
    fluidized bed reactor for silicon production.

    26. A device according to any one of claims 24 and 25,
25 wherein the device is for handling a chemical
    reaction in a chemical reaction chamber.

    27. A method of providing a chemical reaction in a
    fluidized bed reactor chamber for silicon production
30 with a gas comprising the steps of:
    providing (32) the gas G at a first temperature T1
    in a gas inlet area (12),

heating (34) the reaction chamber (14) to a second
temperature T2,

preventing (36) heat of the reaction chamber from
reaction the gas inlet area using a first side (20)

5   of a distribution plate (16), which first side is
made of a first material (24) having a first thermal
conductivity, and

transporting (38) the gas from the gas inlet area
through holes (22) in the distribution plate to the

10   reaction chamber, while cooling the holes using a
base structure of the distribution plate, which base
structure is of a second material (28) having a
second thermal conductivity and also surrounds the
holes.

15

28. A method of providing a chemical reaction chamber
with a gas as defined in claim 28, wherein the
method comprises an additional step whereby the gas
temperature is altered in the inlet area (12) and/or

20   the gas temperature is altered prior to entering the
inlet area (22).

29. A method of providing a chemical reaction chamber
with a gas as defined in claim 29, wherein the gas

25   temperature is increased in the inlet area (12)
and/or is increased prior to entering the inlet area
(22).

30. A method according to any one of claims 27 to 29,

30   wherein the method is for providing a chemical
reaction in a chemical reaction chamber.

31. An arrangement as described herein with reference
to the figures.

32. A device as described herein with reference to the
5   figures.

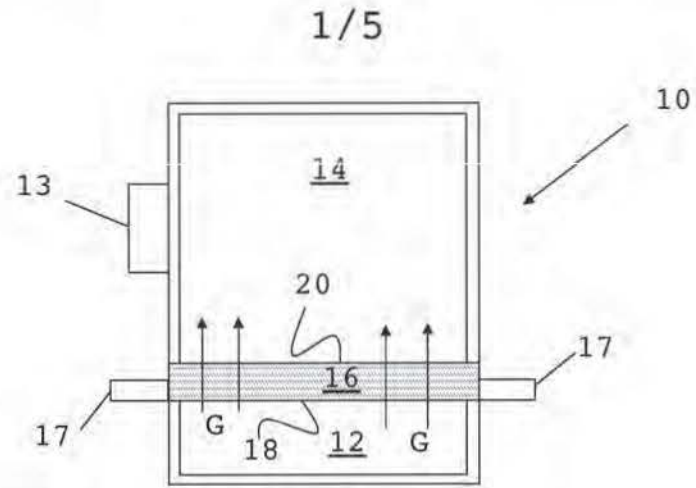33. A method as described herein with reference to the
figures.

10
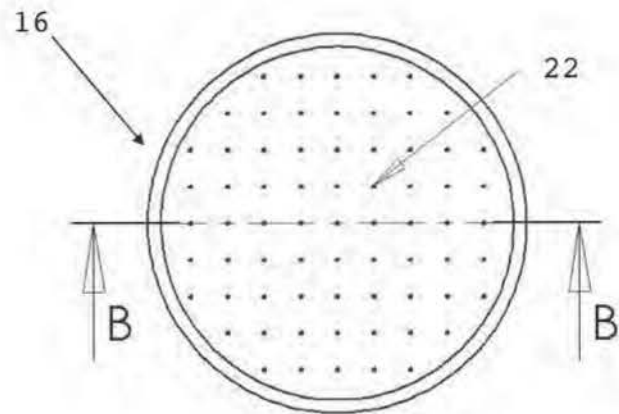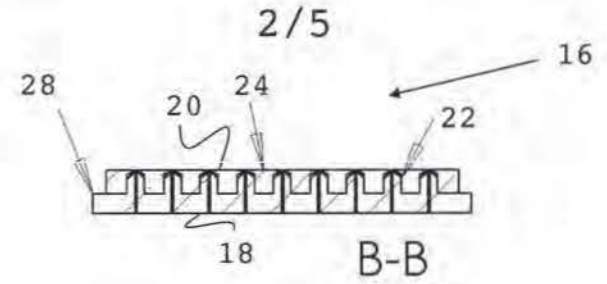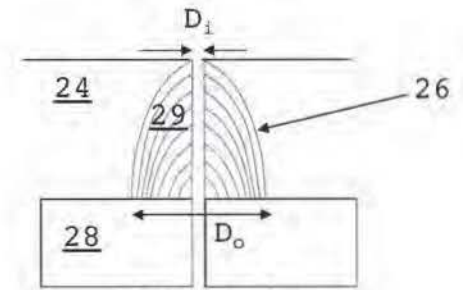
1/5

FIG. 1

FIG. 2

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FIG. 3

FIG. 4
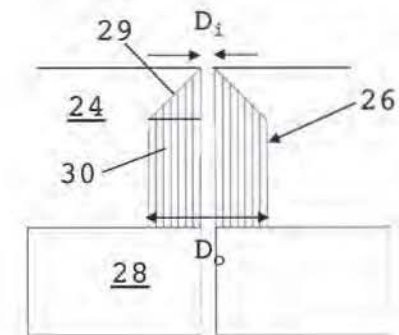

FIG. 5

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FIG. 6

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FIG. 8

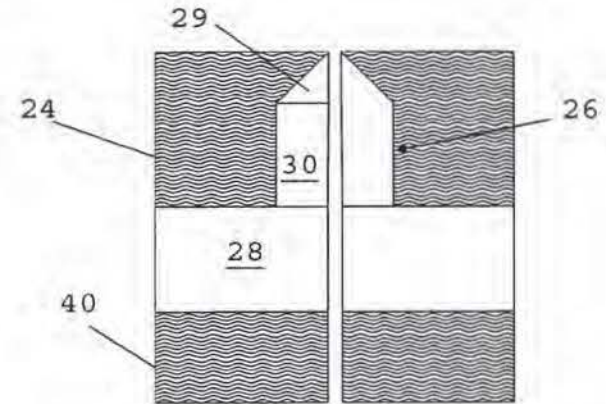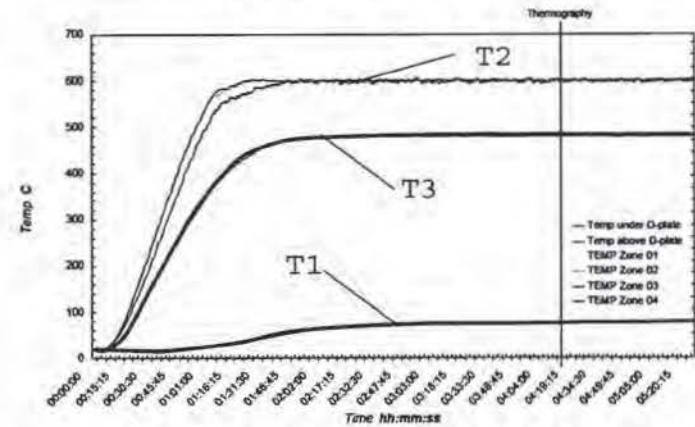| 32 | PROVIDE GAS IN GAS INLET AREA AT |
34	HEAT CHAMBER TO T2
36	PREVENT HEAT IN CHAMBER FROM REACHING GAS INLET AREA
38	TRANSPORT GAS FROM CHAMBER VIA DISTRIBUTION PLATE WHILE PERFORMING COOLING
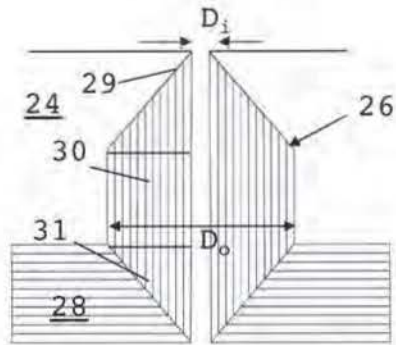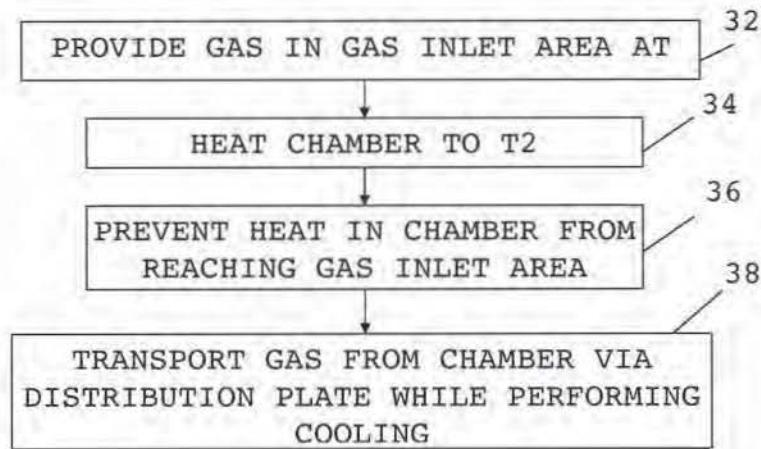
FIG. 7

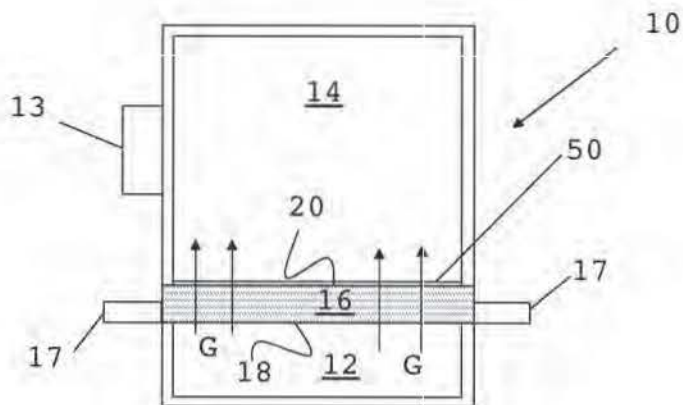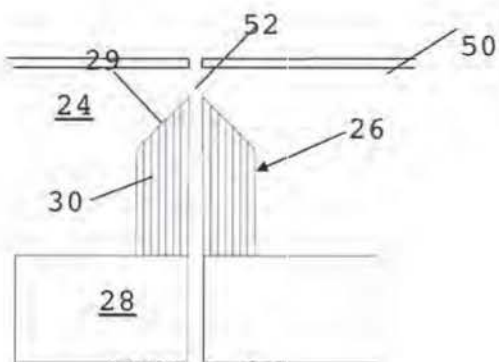FIG. 9

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FIG. 10

FIG. 11

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INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/058775

A. CLASSIFICATION OF SUBJECT MATTER
INV. B01J8/44   C01B33/027
ADD. B01J8/18   C01B33/107

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No
X	WO 03/035548 A2 (SILICON TECHNOLOGIES AS [NO]; HUGO FRANZ [DE]; BJOERSETH ALF [NO]; CEC) 1 May 2003 (2003-05-01) abstract page 6, paragraph 2 - page 7, paragraph 3; figure 5 claim 1	1-33
X	US 3 295 221 A (JOY DAVID S) 3 January 1967 (1967-01-03) column 3, line 17 - line 32; figure 3 claim 1	1
A	US 2010/264362 A1 (CHEE YONGCHAE [US] ET AL) 21 October 2010 (2010-10-21) abstract; claim 1; figure 5	1-33

-/--

[X] Further documents are listed in the continuation of Box C.   [X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
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Date of the actual completion of the international search

18 June 2012

Date of mailing of the international search report

26/06/2012

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Form PCT/ISA/210 (second sheet) (April 2005)

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 3 889 631 A (LACKEY JR WALTER J ET AL) 17 June 1975 (1975-06-17) cited in the application abstract claim 1; figure 1 -----	1-33

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 03035548	A2	01-05-2003	AU DE WO	2002350543 A1 10151159 A1 03035548 A2	06-05-2003 30-04-2003 01-05-2003
US 3295221	A	03-01-1967	NONE		
US 2010264362	A1	21-10-2010	KR KR US US US WO	20100133347 A 20110133419 A 2010264362 A1 2011297884 A1 2012114546 A1 2011153295 A1	21-12-2010 12-12-2011 21-10-2010 08-12-2011 10-05-2012 08-12-2011
US 3889631	A	17-06-1975	NONE		