This paper first appeared in the ninth print edition of *Photovoltaics International* journal.

Integrated loops: a prerequisite for sustainable and environmentally-friendly polysilicon production

Sebastian Liebischer, Dieter Weidhaus & Dr. Tobias Weiss, Wacker Chemie AG, Munich, Germany

ABSTRACT

The photovoltaic market, which is dominated by polysilicon-based crystalline solar cells, has been developing rapidly, with growth rates in the double-digit range for several years. In order to meet increasing demand for hyperpure polysilicon, manufacturers need to adhere to environmentally-friendly production processes with low energy consumption. This article highlights the key processes needed to manufacture hyperpure polycrystalline silicon and explores the related challenges and solutions for sustainable polysilicon production. Our findings prove that only an intelligent interaction of all necessary process steps fulfils the requirements for minimized production residue volumes and low energy consumption. Totally integrated production loops for all essential media are prerequisite to reach these targets. Once implemented, these highly efficient production processes serve as an excellent platform technology for the continued healthy growth of the PV industry.

Introduction

Global warming and limited availability of fossil fuels have been driving the need for increased and more reliable sources of renewable energy. Due to its increasing competitiveness, photovoltaics has become the strongest-growing technology in the renewable energy sector with an impressive compound annual growth rate of 43% (2007–2014; see Fig. 1).

Although a variety of PV technologies is being explored, only a limited number is suitable for and has reached mass-production scale. Of those, crystalline-based PV is the clearly dominating technology with a share of more than 80% in 2009's PV market [2].

The basic raw material for crystalline PV cells is polysilicon. Its semiconducting properties are used to convert sunlight into electricity. Silicon is the second most abundant element in the earth's crust. Therefore, its availability is basically unlimited. Large-scale metallurgical processes are employed to convert quartz (SiO_2) into raw silicon (98-99% purity) for numerous technical applications. However, sophisticated production technology is needed to convert raw silicon into the hyperpure polysilicon needed for photovoltaic applications.

"The deflation of the recent polysilicon price bubble has rendered many new projects uncompetitive."

Established polysilicon producers support this strong PV market growth by making huge investments to increase their capacities accordingly (Fig. 2). Unfortunately, long lead times for new capacities and exploding short-term demand may result in severe undersupply situations like that experienced in 2007/2008. The resulting price bubble has attracted many new market entrants. However, only suppliers with state-of-the-art technology and cost structures will be competitive in the long run. Consequently, the deflation of the recent polysilicon price bubble has rendered many new projects uncompetitive in terms of quality and cost. A highly efficient use of energy and raw materials is vital to achieving state-of-the-art cost structures and an environmentally-benign polysilicon production process.

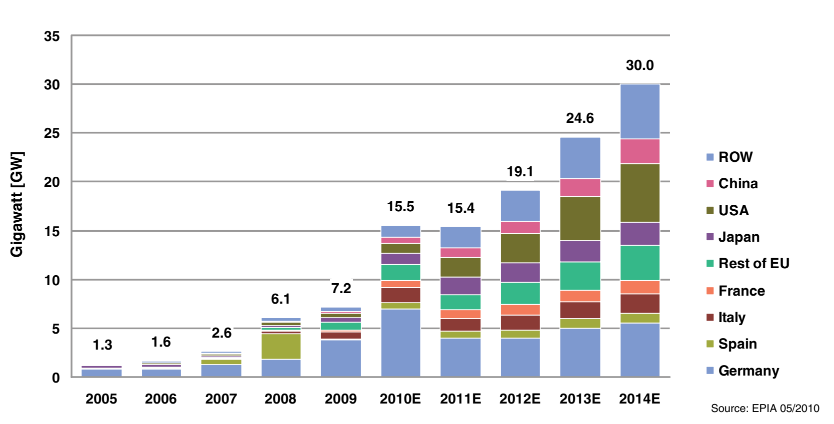

Figure 1. Historical annual PV market development and forecast from 2005 to 2014 [1].

Integration levels of polysilicon production

By far the most common approach to producing polysilicon globally is the so-called 'Siemens process', which involves the deposition of polysilicon from trichlorosilane (TCS). TCS and hydrogen are fed to heated silicon rods within special reactors. A pyrolysis reaction takes place at the hot silicon surface and elemental silicon is deposited on the rod's surface. In this process, two main reactions of TCS have to be considered:

$$4\,SiHCl_3 \rightarrow Si + 3\,SiCl_4 + 2\,H_2 \qquad (1)$$

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

TCS as feedstock is obtained by chlorination of metallurgical silicon. The corresponding process is carried out in fluidized bed reactors, in which finely-ground metallurgical silicon reacts with hydrogen chloride (HCl):

$$Si_{mg} + 3\,HCl \rightarrow SiHCl_3 + H_2 \qquad (3)$$

This crude TCS is purified by multiple distillation steps to reach the required

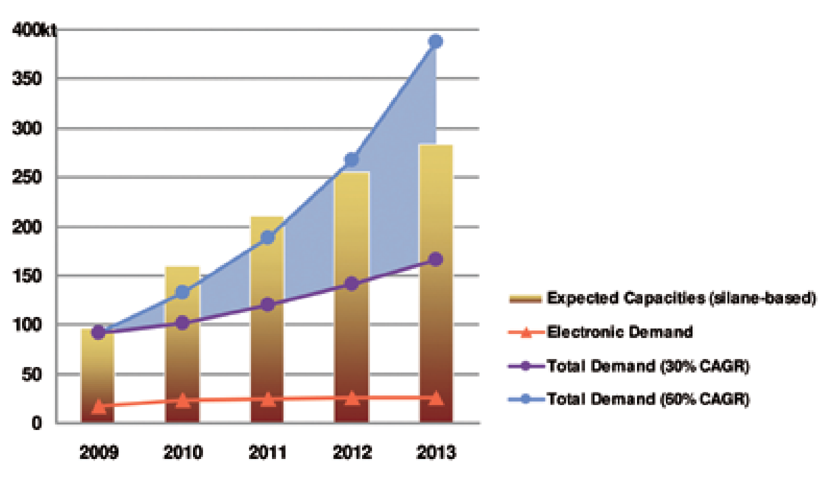

Figure 2. Global polysilicon supply and demand [3].

purity for deposition feedstock.

Following Equations 1 and 2, up to three-quarters of the TCS is converted to tetrachlorosilane (STC) and does not contribute to polysilicon deposition. Consequently, a maximum of about 18kg of STC is generated per kg of deposited polysilicon. It goes without saying that an economic recovery method is necessary for this by-product – a fact that unfortunately has not been taken properly into consideration by all newcomers in the past [4].

Established polysilicon producers are utilizing several methods of STC recovery. One option is to use STC as feedstock for the value-adding production of pyrogenic silica:

$$SiCl_4 + 2\,H_2 + O_2 \rightarrow SiO_2 + 4\,HCl \quad (4)$$

If this is the only possible route for STC, the production of polysilicon and pyrogenic silica are coupled, which can quickly lead to restrictions. Therefore, the conversion of STC back to TCS by hydrogenation is mainly used to recover the STC for the production of polysilicon:

$$SiCl_4 + H_2 \rightarrow SiHCl_3 + HCl \quad (5)$$

In either case, production of pyrogenic silica or STC conversion, HCl is generated as a by-product which can be fed back into the TCS synthesis.

Besides STC, there are further chlorosilane by-products generated during TCS synthesis and polysilicon deposition. The expense of processing these by-products can be minimized by linking the polysilicon production with that of organofunctional silanes, silicates and silicones. Predetermined loss of material can be converted into value-adding products if this is done properly. Fig. 3 shows a corresponding closed-loop production system in operation at WACKER POLYSILICON's Burghausen site.

In a standalone polysilicon production process as shown in Fig. 4, approximately 100% of the STC can be recycled to TCS for polysilicon production. The major challenge of such a plant is the optimization of each single process step and the steps' interaction to minimize all kinds of chlorosilane by-products which are not usable for polysilicon deposition.

In any case, a highly integrated closed-loop production process is a prerequisite for a sustainable and economical production of polysilicon. Energy-efficient processes and the minimization of residue are further technological factors that can contribute to a highly efficient polysilicon production process. The following section discusses some aspects of this task in detail.

Challenges in production of trichlorosilane

As noted above, metallurgical-grade silicon is used as a feedstock to synthesize solar-grade TCS. Impurities in the silicon metal significantly impact TCS quality and the productivity of the production process. Many earlier investigations were generally limited to the influence of metallurgical-grade silicon on TCS selectivity. However, in addition to this very important aspect, there are still many other issues that influence cost, quality, safety and environmental impact. Fig. 5 shows in detail the process for manufacturing TCS.

Chlorosilanes are obtained by reacting metallurgical-grade silicon with HCl. This reaction can be carried out in a fluidized-bed reactor at temperatures of 300-400°C. The reaction conditions in the fluidized bed are influenced by reactor design, particle size distribution of the silicon feed, and HCl flow.

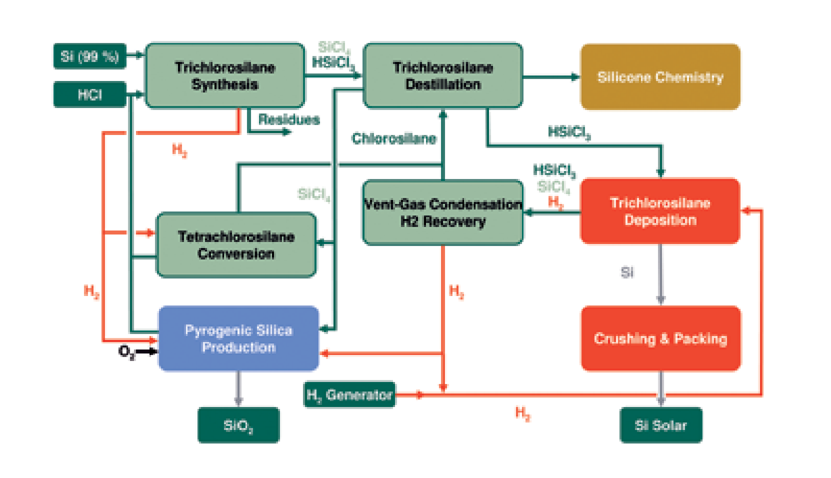

Figure 3. Integrated product flow at WACKER POLYSILICON's Burghausen site.

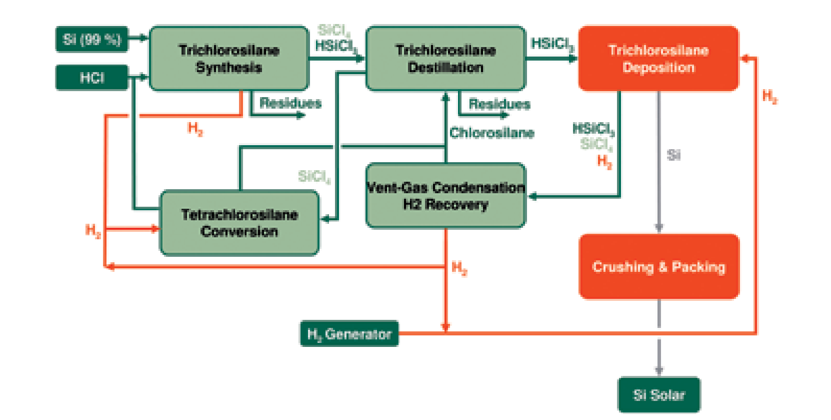

Figure 4. Standalone polysilicon production.

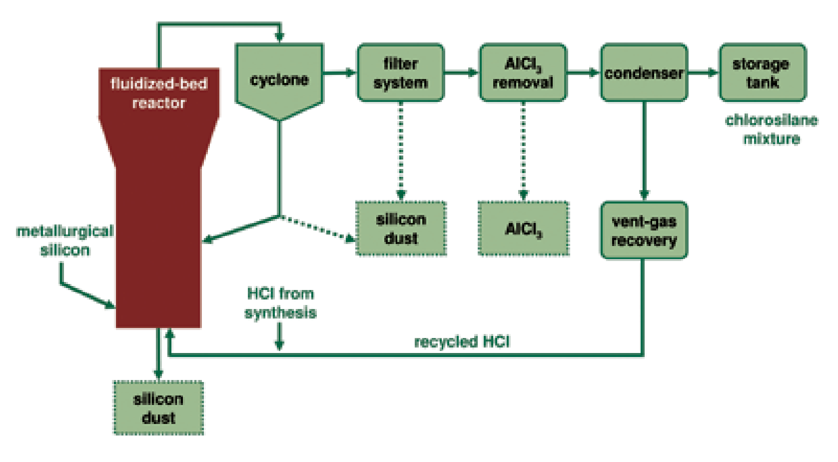

Figure 5. TCS synthesis.

At an integrated closed loop production site, the TCS production should be continuously optimized towards minimizing the amount of by-products. The HCl first-pass yield should reach almost 100% and the TCS selectivity might be up to 90%. The result is a small loop of HCl and only a small formation of STC which saves energy in vent-gas recovery and in STC conversion. Furthermore the use of metallurgical-grade silicon with a well-selected composition of non-silicon metals (Fe, Al) reduces the production of undesired high and low-boiling chlorosilanes and metal chlorides.

Silicon metal wastes

Together with the metallurgical-grade silicon, impurities such as slags, calcium, aluminium and iron compounds are introduced into the reactor. Some of these are elutriated from the reactor as fines with the product gas stream; others remain with the bulk material in the reactor where they accumulate. These are two methods of producing silicon-containing wastes.

"If a particular impurity level is exceeded, the reactivity of the bulk material decreases."

On the one hand, dust particles are continuously elutriated from the reactor. A first dust fraction is separated by a cyclone in order to be fed back to the reactor. A second dust fraction, which is collected by filters, is even finer than the first fraction and contains a high concentration of impurities. On the other hand, impurities accumulate in the reactor during the continuous TCS synthesis. If a particular impurity level is exceeded, the reactivity of the bulk material decreases, which can even lead to a shutdown of the reactor. At this point, the bulk material has to be removed from the reactor.

An important feature of a properly designed reactor system is the selective control of bulk material impurity levels and silicon loss minimization, both controlled by fines discharge [5]. Benefits are high reactor productivity and low amounts of silicon-containing residues. There are two methods of disposal of such residues, the first of which is treatment with lime, which transforms the residues into innocuous substances that can easily be land-filled. However, this procedure entails a certain amount of effort and cost. The second option is to sell the previous by-products to metallurgic and cement industries – an economically and ecologically sound and reasonable option as the substances can then be used for other processing purposes.

$AlCl_3$ removal

Under TCS synthesis conditions, most of the aluminium contained in metallurgical-grade silicon reacts with hydrogen chloride. The resulting $AlCl_3$ sublimates at temperatures over 150°C and passes through the filter system along with the gaseous silanes. However, if the gas temperature drops below 150°C, $AlCl_3$ desublimates and is deposited on the inner walls of the equipment or the piping.

Therefore, it is extremely important to have an effective method for separating $AlCl_3$ completely from the product gas and then removing it from the process; otherwise the $AlCl_3$ would be deposited on downstream equipment like pipes, tanks and even distillation columns. Cleaning of contaminated equipment can lead to a severe safety problem due to the high reactivity and exothermic potential of $AlCl_3$. Methods for removing $AlCl_3$ from the process have been described in different publications [6,7].

Despite the problems associated with $AlCl_3$, a certain level of aluminium in the bulk material is necessary to achieve a high reactivity and TCS selectivity. However, an excessive amount of aluminium quickly increases the costs of $AlCl_3$ workup and disposal. The challenge therefore is to optimize the aluminium content and the operation mode of the reactor in such a way that the reactivity does not decrease, but less $AlCl_3$ is produced. The removed $AlCl_3$ can be treated in the same way as silicon metal residues. Due to the potential high purity of re-sublimated anhydrous $AlCl_3$, this by-product can also be recovered and sold, e.g. as a catalyst.

Condensation and vent-gas recovery

Downstream of TCS synthesis, dust separation and $AlCl_3$ removal, the gas stream is condensed and separated into a liquid fraction (crude silane) and a gaseous fraction that contains mainly hydrogen and a small amount of HCl and non-condensed chlorosilanes. The liquid chlorosilane fraction is stored in tanks and is subsequently distilled. The gaseous

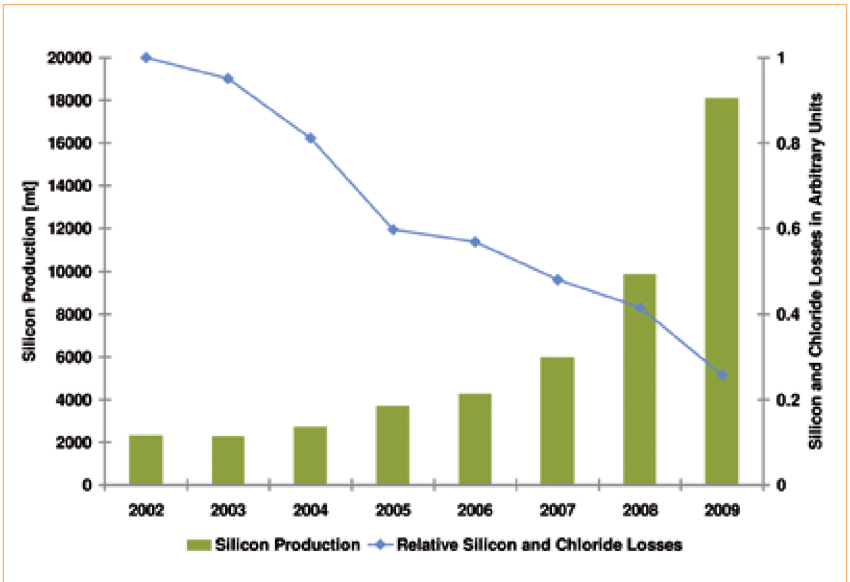

Figure 6. Development of residues at WACKER POLYSILICON in comparison to the correlating polysilicon output.

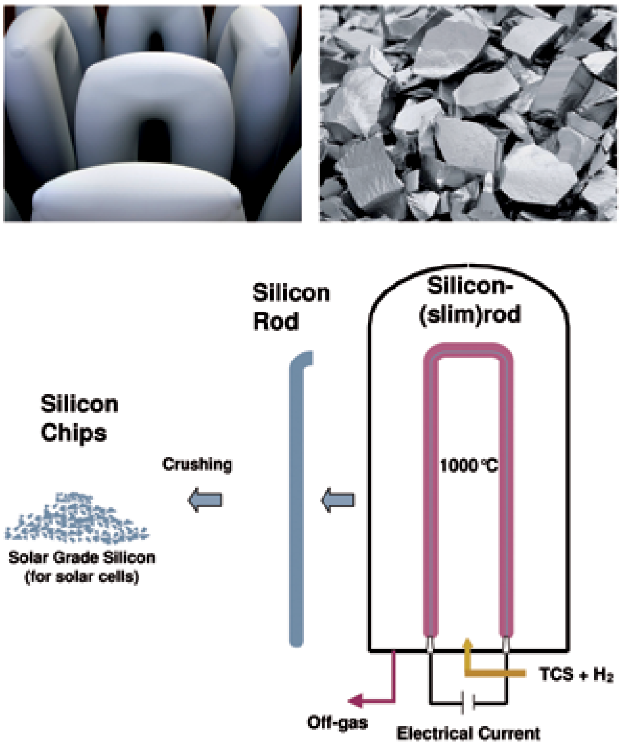

Figure 7. Schematic representation of the rod deposition process.

fraction is purified in a gas recovery unit. Hydrogen chloride is then fed back to the TCS synthesis, while chlorosilanes are condensed and recovered for distillation. Hydrogen can be recovered with high purity, suitable for use in STC hydrogenation. By using an appropriate vent-gas recovery, the disposal of residues can be avoided.

Chlorosilane distillation residues

The distillation of hyperpure TCS separates chlorosilane fractions that are enriched with certain impurities, for example, boron and carbon-containing compounds, which can be found in low and high-boiling fractions. As a matter of principle, these fractions enriched with impurities have to be discharged from the distillation system to achieve the high quality standards required for hyperpure TCS. If precautionary measures are not taken, the disposal of these contaminated fractions is associated with high silicon and chloride losses.

> "Small fractions with impurities have to be discharged for achieving the high purity of TCS."

Within an integrated chemical production site, all these fractions can be recycled and thus do not require disposal measures. Depending on the main component of the respective fraction – dichlorosilane, TCS or STC – and the concentration of the impurities, customized solutions can be developed to utilize these fractions. This significantly reduces the loss of silicon and chloride equivalent, which in turn means lower disposal costs, low environmental impact and low production costs of the main product, hyperpure TCS.

In a standalone polysilicon plant, the by-products formed in the TCS reaction have to be avoided. This can be done as noted by using appropriate metallurgical-grade silicon and an optimized operation mode of the TCS reactor. Secondly, the amount of discharged chlorosilane fractions from the distillation has to be reduced to a minimum by concentrating the impurities in the

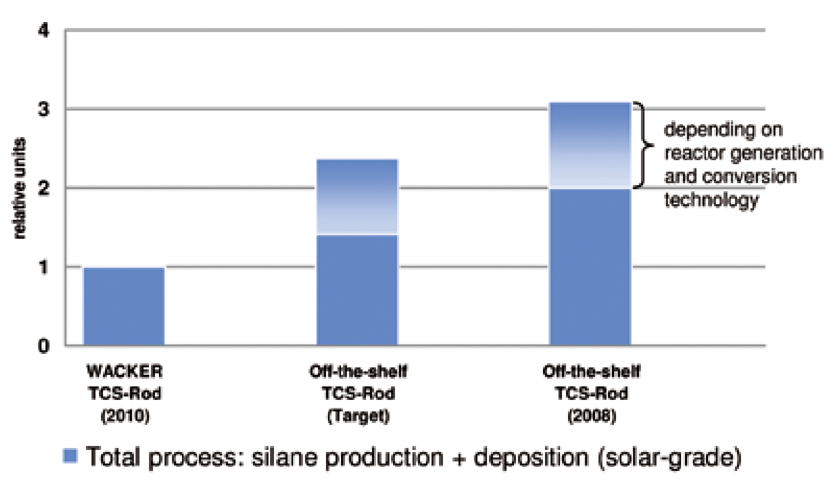

Figure 8. Specific energy consumption of various technologies for the production of polysilicon [3].

discarded streams to a maximum level. The high-boiling fraction of chlorosilanes can be recovered in several ways, for example by feeding it back to the fluidized bed reactor [8]. Low-boiling chlorosilanes can be chlorinated to TCS, which can be recycled and used for polysilicon deposition [9].

However, small fractions with impurities have to be discarded for achieving the high purity of TCS. The streams containing these highly concentrated impurities can be treated in a caustic scrubber system where the chlorosilanes react to NaCl (cooking salt) and silica (SiO_2), both of which are non-toxic and can be disposed of properly. Despite the exponential growth of production capacities, the relative amount of silica and salt discharged has decreased significantly in the last few years due to the use of advanced technologies (see Fig. 6).

STC conversion

Another key component of a closed-loop system is STC conversion. Besides the hydrogenation gas phase process as described in Equation 5, the fluidized bed hydrochlorination process is an alternative conversion path:

$$3\,SiCl_4 + Si + 2H_2 \rightarrow 4\,SiHCl_3 \qquad (6)$$

Comparing these two processes, it can be said that there are no silicon or chloride losses in the conversion of STC by hydrogenation. A further advantage is that compared to the hydrochlorination process, there is no need for a copper catalyst to be used – as a result, no copper-containing residues are created when utilizing conversion by hydrogenation [10].

Polysilicon deposition

The deposition of polysilicon takes place in special deposition reactors. During the batch process, pure silicon grows on electrically heated silicon rods. After reaching a predetermined diameter, the batch process is stopped; the rods are removed from the reactor and crushed for further use in the solar industry (see Fig. 7).

In principle, the deposition step produces no chemical waste that needs careful handling, because the vent gas of the deposition reactors is collected and recycled for re-use. Therefore, highly-integrated vent gas recovery systems are beneficial, not solely for environmental protection regulations, but also for economic reasons as the price for key raw materials such as metallurgical-grade silicon and hydrogen is increasing continuously.

The main focus in polysilicon deposition is on the reduction of energy consumption by optimizing the deposition reactors continuously. In public, the production of solar-grade feedstock via gas phase deposition has frequently been criticized for being too costly with regard to the high energy consumption of the deposition process [11]. This criticism is based on the belief that high temperatures in chemical processes basically lead to high energy consumption, a belief that is misleading in the case of polysilicon deposition. In principle, the deposition of polysilicon does not consume energy at all: the level of energy demand during deposition is mainly influenced by energy losses and not by the reaction itself.

Much effort has been put into the design of the reactor with the aim of reducing energy losses of polysilicon deposition. The major principle – the topic of many articles and patents to do with deposition reactors – is 'economy of scale' [10,12]. As a rule of thumb, there are three ways of increasing the output of deposition reactors, the most common of which is by increasing the number of rods in the reactor. As a consequence, polysilicon can grow on more rods, increasing the output per batch process significantly. An increase in rod length has a similar effect, while the third approach of increasing the predetermined rod diameter can also lead to decreases in specific energy losses.

Besides improving the reactor's design, optimizing the deposition process also enhances efficient raw material usage and reduces energy consumption. One of the key parameters in this process is the deposition temperature. A higher deposition temperature increases the deposition rate and reduces deposition time without loss of reactor output. This reduction of deposition time is by far more effective for decreasing energy losses than running the deposition process at lower temperatures. This means that, within a certain range, high temperatures in polysilicon deposition can even support energy savings and are thus a prerequisite for a sustainable polysilicon production. As a result, the task of an optimized deposition process is to reduce the deposition time in order to minimize energy losses and to achieve the highest possible reactor output and highest polysilicon quality simultaneously.

Most of the energy for polysilicon production is used during the deposition process. Nevertheless, for a complete overview, it is useful to look at the whole specific energy consumption per kg of polysilicon. Fig. 8 illustrates this consumption, highlighting the potential differences between polysilicon producers as an immense diversity of applied technologies with significant differences in energy consumption is currently available.

> "Optimizing the deposition process also enhances efficient raw material usage and reduces energy consumption."

As a result of all these time-consuming developments, customer-orientated products and a sustainable polysilicon deposition process with high output, yield and quality can be achieved and by-products and residues can be minimized.

After harvesting, the silicon rods have to be crushed as shown in Fig. 7. This crushing system requires a great deal of effort in order to minimize the loss of polysilicon – especially in regard to the unavoidable dust formation. New high-quality crushing systems that allow the use of all polysilicon fractions have appeared on the market. These systems do not contaminate the polysilicon and are optimized in such a way that even the smallest fractions and polysilicon dust are of highest purity. Essentially, it is possible to prevent polysilicon loss during crushing.

Summary

It has been shown that the trichlorosilane-based production of silicon feedstock for the solar industry is sustainable and highly efficient if designed and implemented properly. The process does not generate any permanent, environmentally toxic residues. Implementing a closed-loop product flow enables the safe handling of all main reactants. Moreover, at an integrated production site, almost all by-products can either be recycled or used for other purposes. Ongoing process development continuously minimizes residues and energy consumption and improves product yield significantly. Thus, avoiding waste and recycling by-products is not only an ecological, but also an economical asset as resources such as silicon metal or electrical energy can be used more efficiently. A sustainable, cost-effective production of silicon feedstock will also be possible in future large-scale plants.

Acknowledgement

The authors would like to thank their colleagues in R&D and the corporate departments of WACKER POLYSILICON for their suggestions and assistance in the preparation of this article.

References

[1] European Photovoltaic Industry Association (EPIA) 2010, "Global Market Outlook for Photovoltaics until 2014", p. 8.
[2] *Photon International*, March 2010 edition, p. 195.
[3] Schindlbeck, E. 2010, "Leadership in Polysilicon", *Capital Market Day Wacker Chemie AG*.
[4] Cha, A.E. March 9, 2008, "Solar Energy Firms Leave Waste Behind in China", *Washington Post Foreign Service* [available online at http://www.washingtonpost.com/wp-dyn/content/article/2008/03/08/AR2008030802595.html].
[5] Hesse, K. & Pätzold, U. 2006, "Survey over the TCS process", *Proc. Silicon for the Chemical Industry VIII*, pp. 157-166.
[6] Kroupa, M.G. 2002, "High Boiling Residue Recovery Process for the Synthesis of Trichlorosilane", *Proc. Silicon for the Chemical Industry VI*, pp. 201-207.
[7] Lord, S.M., "Process for removing aluminum and other metal chlorides from chlorosilanes", US Patent 7 736 614, June 15, 2010.
[8] Fabry, L., Stepp, M. & Pätzold, U., "Wiederverwertung von hochsiedenden Verbindungen innerhalb eines Chlorsilanverbunds", Europe Patent 1 991 501/DE102006009954, September 9, 2007.
[9] Burgie, E.A., Heng, O.A. & Lange, T.E., "Treatment of vent gas to remove hydrogen chloride", US Patent 5 401 872, March 28, 1995.
[10] Hazeltine, B. Fero, C. & Qin, W. 2010, "Advancements in the commercial production of polysilicon", *Photovoltaic World*, pp. 16-22.
[11] Hesse, K. 2009, "Advanced Solar-Grade Si Material", in *Springer Series in Optical Sciences 140: High-Efficient Low-Cost Photovoltaics*, Petrova-Koch, V., Hezel, R. & Goetzberger, A. (Eds.), Berlin, Heidelberg: Springer Verlag, pp. 47-55.
[12] Wang, C., Zhu, Q. & Jun, Y., "Energy conservation type polysilicon reduction furnace", PRC Patent/CN201162066, December 10, 2008.

Materials

About the Authors

Dieter Weidhaus received his diploma degree (Dipl. Ing.) in chemical engineering from the University of Stuttgart in 1997. He joined the process development unit of WACKER POLYSILICON in 1997 as a project engineer and is currently managing several projects in this field.

Dr. Tobias Weiss received his diploma degree in chemical engineering from the Friedrich-Alexander University of Erlangen-Nuremberg in 2004. He did his Ph.D. thesis in the field of catalysis and reaction engineering at the Institute of Chemical Reaction Engineering at the University of Erlangen-Nuremberg. In 2007 he joined WACKER and has been a member of the process development unit at WACKER POLYSILICON since 2009.

Sebastian Liebischer received his diploma degree (Dipl. Ing.) in chemical engineering from the Technical University of Munich in 2008. He joined the process development unit of WACKER POLYSILICON in 2008, since which time he has been working in the field of TCS production.

Enquiries

Wacker Chemie AG
Johannes-Hess-Str. 24
84489 Burghausen
Germany