

## Electronic Silicon Technology 1950-2007

John C. Schumacher Ph.D.  
Peak Sun Silicon Corporation  
Carlsbad, CA 92008

### Introduction

The proceedings of a conference of the Electrochemical Society, entitled *Semiconductor Silicon 1998*, present a detailed account of the history of the development of semiconductor devices over the then 52 years since the invention of the point-contact transistor. It is presented from the perspective of silicon Device and Defect Physics.

A rich history of technology development also exists for the Chemistry/Chemical Engineering aspects of Electronic Grade ("EG") silicon preparation. Unfortunately, this history does not appear to be documented except in the patent literature, and there generally only in great detail but narrow scope. Thus, it is felt that a "user friendly" account of the development of EG silicon from the perspective of a chemist or chemical engineer trying to actually produce it would be useful.

One application for such an historical perspective could be when approaches for new development in the EG silicon field are under consideration, as is the case in 2007. This revisiting of EG silicon methodology has arisen as suppliers struggle to produce 12" and larger diameter wafers in quantity for semiconductor device fabrication, and to produce low-cost, low-

energy-investment silicon substrate material for crystalline silicon photovoltaic ("PV") solar electric generators.

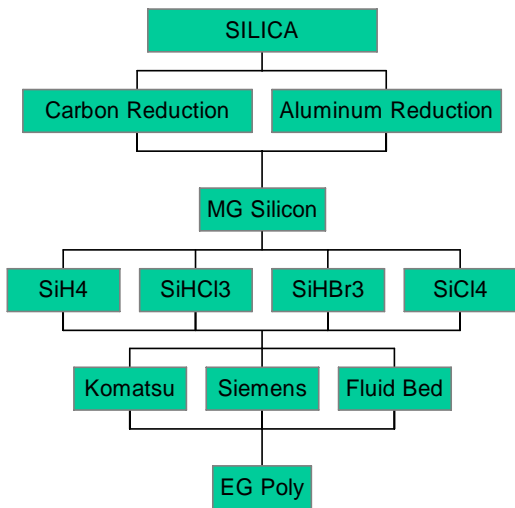
### Semiconductor Silicon

Silicon is the predominant element employed in creating semiconductor devices. However, as pointed out in *Semiconductor Silicon 1998*, even as late as 1965, germanium transistors outsold silicon transistors 334 million to 275 million units per year. Silicon's dominance has developed for several reasons. From a physics standpoint, the reasons include the large band gap and the passivating and gettering characteristics of the surface oxide. From the ChE perspective, reasons include the fact that it is the second most plentiful element in the earth's crust, and that there are several technology paths theoretically possible for conversion of plentiful and cheap low grade material, into the ultra high purity material required in semiconductor device fabrication.

Alternative paths theoretically possible for this conversion are shown in Figure 1.

# Metallurgical Silicon Production

Metallurgical silicon is produced in vast quantities for use as a hardening agent in steel alloys, and sells for about \$1/lb. As can be seen, two possible paths exist for metallurgical grade silicon production: Carbon and Aluminum reduction. Both are



practiced in the marketplace. However due to the fact that the latter alternative leaves a higher percentage of metallic impurities in the metallurgical material, the former process has come to be the "process of choice" for producing starting material for silicon electronic applications. In this process, carbon and silica are mixed in a large electric arc furnace and reacted according to  $\text{SiO}_2 + \text{C} \Rightarrow \text{Si} + \text{CO}_2$ . The product produced by Elkem Corporation of Norway commands more than 50% of the electronic silicon starting material market.

## Electronic Grade Silicon Production

EG silicon production technology has evolved in three waves over the past 50 years. These are:

- Initial efforts, from 1950 to 1960, which focused on achieving repeatable purity and manufacturability.
- The LASSA ("Large Area Silicon Solar Array") Project wave from 1975 to 1985 where cost and energy investment reductions and continuous melting compatibility were sought. Among other approaches, a TBSFB process was funded.
- The FB wave (1980-1995) where a scalable, production worthy FB process to produce EG poly was sought.

Beginning in 2005 a rapidly growing market and high prices attracted several new entrants to polysilicon manufacturing.

## Initial Efforts

Efforts to produce ultra high purity silicon and germanium followed shortly after the invention of the transistor at Bell Labs on 23 December 1947. These efforts were based on the realization at that time of the fact that minority carrier lifetimes were crucial to device performance, and were dependant on chemical purity and microstructural homogeneity throughout the crystal.

By the late 1950's silicon purification methods had moved from the laboratory to the pilot plant stage. Potential paths described in Figure 1 were investigated with

the leading candidate techniques emerging as:

- The Du Pont process (US Patents 3012862, 4084024)
- The Iodide process (US Patent 3020129)
- The Siemens process (GDR Patents 1065564, 1102117, 1233815 and UK Patent 904239)
- The Komatsu process (in Japan)

The Du Pont process involved reduction of tetrahalosilane ( $\text{SiX}_4$ ) or trihalosilane ( $\text{SiHX}_3$ ) ( $\text{X}=\text{chlorine, bromine or iodine}$ ) with hydrogen, zinc or cadmium in a fluid or moving bed reactor, following preparation of the halosilane from metallurgical grade silicon and a halide or hydrogen halide. The process suffered from formation of both large quantities of amorphous silicon dust and explosive polymers when run with chlorosilanes. Bromosilanes and iodosilanes

were not actually tested in the development program that revealed these problems.

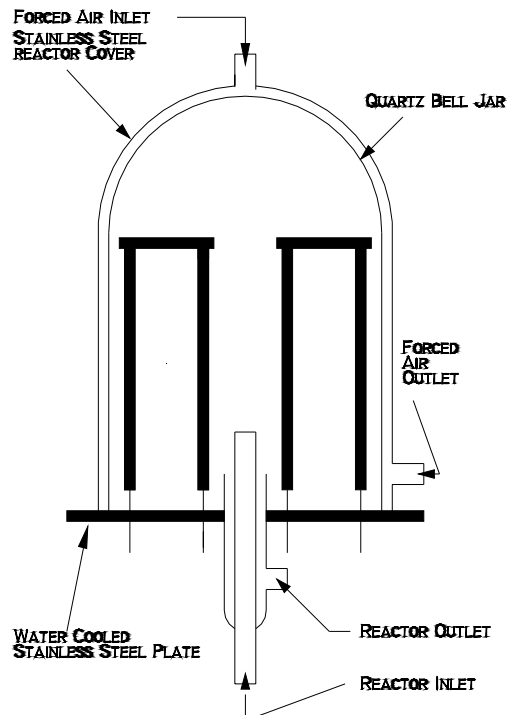
The Iodide process was based on reaction of metallurgical grade silicon with iodine, followed by  $900^\circ\text{C}$  thermal decomposition of the iodide on a "seed particle or heated filament". High purity was achieved.

The Siemens process required formation of a mixture of chlorosilanes from the reaction of metallurgical silicon with  $\text{HCl}$  over a copper catalyst, followed by separation, purification and decomposition of Trichlorosilane on heated wires in a bell jar reactor, to form high purity silicon.

The Komatsu process was identical to the Siemens process on the front end, however Silane ( $\text{SiH}_4$ ) was isolated, purified and decomposed in a Siemens-like bell jar reactor, rather than the  $\text{SiHCl}_3$  of the Siemens process. The thinking by

proponents of this approach in Japan was that higher purity could be achieved via the Silane route rather than the TCS route. This has over time been borne out in practice for bell jar reactors similar to that depicted in Figure 2.

Of the initial options, the Siemens process proved to be the process of choice. This was due in part to the metallic impurities generated by metallic reduction and the formation of amorphous dust in the Du Pont fluid bed reactor. Both could be avoided by hydrogen



dilution/reduction and heterogeneous nucleation on the heated Siemens reactor rods. Additionally, the choice was based in part on the accessibility of chlorosilanes, available from the siloxane polymer manufacturing industry, which were both more plentiful and less costly than iodine based alternatives. The need for hydrogen dilution to avoid homogeneous nucleation, along with explosive polymer formation in downstream exhaust systems remained important negative features of the Siemens process.

Nonetheless, the great majority of the electronic grade polysilicon produced in 2006 was created using the Siemens process. This is an energy intensive, low efficiency open-loop process which consumes resources both in producing silicon and in abatement/disposal of the corrosive/explosive reaction byproducts. However steady incremental improvements in energy and material use efficiency of the Siemens process have been made by its many practitioners over the 50+years since its invention as described in US Patents 4331698, 4454104, 4464222, 5063040 and 5910295 among others, for example.

## The LASSA Wave

The second historical thrust forward of the EG Silicon industry was the resurgence of interest in alternatives to the Siemens process, sparked by the Large Area Silicon Solar Array ("LASSA") Project Silicon Material Task, initiated by DOE in February 1975 and managed by the

California Institute of Technology Jet Propulsion Laboratory ("JPL"). The "need" described in the Task RFP was for a low cost (\$12/Kg), low energy intensity (1-2 year Energy Investment Payback) "PV" Grade poly that would be suitable as feed to processes such as the Tyco Edge Defined Film Fed growth process or the Westinghouse Dendritic Web growth process, for continuous growth of silicon sheet to be used in fabrication of silicon solar cells for terrestrial applications. One should note that purity requirements were relaxed but not defined for PV as opposed to EG silicon. Award recipients included:

- Dow (now Hemlock): Study of Upgraded Raw Materials and Materials of Construction in Electric Arc Furnace Reduction of Silica with Graphite.
- Union Carbide Corporation: Study of Low Cost Ion-Exchange Membrane Separation of Silane to be reacted in a Free Space Reactor with subsequent consolidation via melting (US Patent 4354987). The Free Space/Melting approach proved impractical and was replaced eventually with a Siemens type reactor and fluid bed reactor approach.
- Battelle: Na reduction of Trichlorosilane in a rotating drum reactor.
- Texas Instruments: Multiple melting/Improved oxide flux in Metallurgical Technique Upgrades.
- JC Schumacher Company: Closed-Loop, Low Temperature Fluid Bed Reactor deposition using tribromosilane to form granular EG silicon (funded 2 years later in 1977).

- Stanford Research Institute: Sodium reduction of fluosilicic acid

Of these approaches, only the Schumacher FB and UCC Siemens type reactor processes produced PV or better silicon, and only the latter approach was commercialized. Neither of the two funded Metallurgical upgrade approaches (out of 6 total Grants) could meet Solar Grade ("PV") purity requirements and turned out to be too energy intensive. Metallic reduction processes also could not achieve even PV Grade purity.

The UCC silicon business located in Moses Lake WA, was operated for several years but eventually sold to Komatsu Corporation in partial settlement of an Unfair Competition suit brought by UCC against the Japanese semiconductor industry. Komatsu combined the UCC low cost, Silane ion-exchange separation process (US Patent 4676967) developed by UCC with its reactor technology to create Advanced Silicon Materials Inc. ("ASiMI"). Komatsu eventually sold its assets to REC of Norway which continues to produce EG polysilicon via the Komatsu process in WA and MT today.

The Komatsu process operated by REC, is the second most prevalent electronic grade polycrystalline silicon technology in 2007. This approach melds as mentioned previously, the Siemens-like batch, bell jar SiH<sub>4</sub> deposition reactor developed in Japan by Komatsu, in the early stages of that country's entry into the

semiconductor device fabrication field, with the low cost ion-exchange technique for separation of silane from the mixture of chlorosilanes produced in hydrochlorination of metallurgical silicon, developed by Union Carbide. The highest purity EG poly available is in fact produced in this way.

## The Third Wave: Fluid Bed Processes for Production of EG Polysilicon.

There are 3 approaches to FB Poly: These are described in terms of their working fluid as the following "routes":

- Silane (US Patents 4684513, 4820587, 4424199, 4743344, 4519999, 5798137, 5810934)
- Trichlorosilane (US Patents 3594215, 3963838, 4092446, 4117094, 4154870, 4207369, 5374413 )
- Tribromosilane (US Patent 4318942)

Corporate players in the FB Poly development field at various times during the third wave included:

- JC Schumacher Company
- Texas Instruments
- Great Lakes Chemical Corporation
- Union Carbide Corporation
- Ethyl Corporation
- Korea Research Institute
- Wacker Chime (Huls)

## Genesis of Interest in EG Silicon Fluid Bed Technology

Any chemical engineer looking at the Siemens EG silicon process "which was developed by physicists", will exclaim "I can do that better, faster, cheaper!" Thus FB technology was examined at the outset of EG silicon development by Chemical Engineers at Du Pont as pointed out previously. The trick was in achievement of the requisite purity which was accomplished first by practitioners of the Siemens process. Risk averse manufacturing organizations simply licensed this process and proceeded.

A chemical engineer looking at the Czochralski ("CZ") process for single crystal silicon ingot growth will ask, "why do we have to do it this way, when if it were a continuous process, the product would be more uniform, and the process better, faster and cheaper?" This observation would be based on the fact that solute concentrations in a liquid and solid in equilibrium are different. Thus since CZ ingot growth is a batch process, the multi-component melt composition, and therefore ingot composition, changes continuously from top to bottom of the ingot as the melt is solidified. However this "axial composition gradient" can be eliminated by adding to the melt, exactly what you freeze out of it, in every differential time element. This continuous process is termed Continuous Melt Replenishment ("CMR").

A Fluid Bed product that is granular, uniform in size, melts "well" and has the

requisite purity would appear to offer a path to the answer to the CMR process. In addition, even if this grand objective of continuous CZ were not attainable, one would be left with better, faster and cheaper EG silicon, a tremendous advantage in the intensely competitive EG silicon marketplace where profitability is only rarely seen. Thus there is downside protection and tremendous upside potential in pursuit of FB EG silicon technology.

## Fluid Bed EG Silicon Development past the Initial Attempts by Du Pont

### **JC Schumacher Company**

proposed the TBSFB process in response to the LASSA project RFP in March 1975. JPL managers of the LASSA project dismissed the proposal calling the Company a "non-viable proposer" since it had only 3 employees and \$23,500 in revenues at that time. The Company was invited to attend the Project Progress conferences as a result of its innovative proposal.

By 1978, JC Schumacher Company which had continued self funded development of the TBSFB process, had become "viable". As a result JPL invited an unsolicited proposal which was funded. Successful project results were presented at the LASSA conferences for two years. Thereafter JPL and NREL funding for its TBSFB activities was declined by the Company due to the excessive, time consuming reporting requirements. Funding of TBSFB efforts out of cash flow was

resumed. Patents coverage for the process began to issue starting with US Patent 4318942 in 1982.

During the period 1982-87, JCSchumacher Company was approached as an acquisition target by many large chemical companies seeking an entry into the lucrative specialty electronic chemicals marketplace. Included were both Great Lakes Chemical Corporation and Ethyl Corporation, who dominate the world bromine market, and were suppliers to the TBSFB project among other Company activities including  $\text{BBr}_3$  and  $\text{PBr}_3$  production. A joint venture on the TBSFB project was explored with both Great Lakes and Ethyl, with serious negotiations entered into with Great Lakes during 1983-84. These were not concluded successfully for administrative not technology reasons. Cash flow funding of the project continued, with construction of a 40 MTPY EG polysilicon and Continuous Melt Replenishment ("CMR") process demonstration unit in 1985. Subsequently joint development negotiations were held with a group of potential strategic partners which included Kawasaki Steel, Toyo Soda (now Tosoh) and Elkem during 1986-87. These negotiations again were ultimately unsuccessful for administrative reasons. As a result, the PDU was never run and was dismantled in 1991. The technology remains intact in a "mothballed" state, until commercialization funds are available.

In this regard, a proposal was submitted by JC Schumacher successor **La**

**Costa Materials Technology**, to the National Renewable Energy Laboratory ("NREL") Photovoltaic Materials and Processes ("PVMaT") Phase 5 Solicitation in September 1997, for completing demonstration of the process. The PVMaT Project charter is to seek and encourage technologies which "enable" manufacturability of PV cells and arrays. As such the Phase 5 Solicitation did not seek polysilicon proposals, but did allow them. Although the La Costa proposal was found to be in the "competitive" range, it was not funded due to a combination of its position within the range, and the total funding available for Phase 5. One small effort poly process proposal based on upgrading Metallurgical Grade Silicon was funded in Phase 5. The Project has not been successful in meeting product purity objectives as of 8/2001.

**Texas Instruments**, long a proponent of internal development of processes for production of its sophisticated materials requirements, had also begun development of a Trichlorosilane ("TCS") fluid bed process during the 1960's which resulted in issuance of US Patent 3594215 in 1971. Many others followed. This effort was continued through the 1970's and early 1980's, but was not funded by or developments reported to, the LASSA Project. Patents covering the process include among others US Patents 3594215, 3963838, 4117094 and 4213937. TI commercialized the process in a plant at Sherman TX, using the product for its internal needs for several years. The

process was eventually abandoned due to excessive levels of carbon contamination. Interestingly, product inventories remaining from this activity were able to be sold in Korea, at a handsome profit during the silicon shortage of 1995.

**Union Carbide** FB poly activities were initiated as part of the LASSA project, which funded construction and operation of a pilot plant in Washougal, WA, just across the river from Portland, OR. A series of patents were issued to this activity including US Patents 4292344, 4684513, 4818495, 5139762, 5798137, and 5810934. The Washougal plant was eventually decommissioned and the activities later continued in Moses Lake, WA until just recently under the aegis of ASiMI. The process has not as yet been commercialized. UCC briefly explored acquiring the Schumacher FB technology in 1996.

**Ethyl Corporation** following breakdown of talks with JC Schumacher Company, proceeded to develop a Silane based FB EG silicon process described in US Patent 4784840 during the mid 1980's, and commercialized it in the later part of the decade. The product was not widely accepted for many reasons including the fact that Ethyl was the only source of granular poly. Others saw this market opportunity and attempted to capitalize on it with non FB techniques to produce granular poly such as described in US Patent 5021221. Prior to construction and commissioning of its 1200 MTPY

commercial plant in Pasadena TX, Ethyl negotiated an annual purchase agreement with Monsanto Electronic Materials Corporation ("MEMC"). Eventually, unsatisfied with its return on its EG silicon investment, Ethyl Corporation sold the business to MEMC which continues to operate it today.

**Great Lakes Chemical Corporation** following the breakdown in negotiations with JC Schumacher Company with respect to a TBSFB JV, purchased the now idle Battelle Memorial Institute sodium reduction of Trichlorosilane plant, moved it to Tennessee, and proceeded to attempt to develop a TCSFB process for several years. Many of the original team of developers of the TI TCSFB process were hired for this activity. Initial attempts focused on use of a quartz FB reactor, but eventually the change was made to silicon carbide lined stainless steel as had been the case at TI. The predictable result was the same in both cases, product not suitable for electronic ("EG") applications due to excessive carbon contamination and project termination.

**Huls and Korea Research Institute**, formed a cooperative venture, following the licensing of Huls' Siemens process technology by POSCO Steel of Korea in the late 1980s, to investigate TCSFB technology. Patents issued on the technology developed include US Patents 4786477, 5063040, and 5374413. The approach utilized in these efforts focused on microwave heating of a quartz FB reactor. The activity was transferred from Korea to Germany in the wake of the recent Korean

financial crisis. Development activities continue, although the process has not as yet been commercialized.

## Fluid Bed Process Technology

### *Product Characteristics*

To start with, optimum EG FB silicon product characteristics are such that continuous or semi-continuous single crystal growth is made easier, not more difficult by its use. This set of characteristics is described in many places including US Patent 5810934, Column 13, line 50 and following lines. In particular, it is desirable to have large, dense, spherical, metallic beads with a monodisperse particle size distribution. Many problems result from not having this type of product morphology which are also described in USP 5810934 in great detail. They can be summarized however as impurity gas inclusions, surface oxide impurities, particle fragility etc. all of which result in melting difficulty and crystal growth reactor contamination.

### *Nucleation versus Growth.*

#### (1) Formation of Amorphous, Sub-Micron Diameter Silicon "Dust".

The ability of a given chemical species to cross the phase boundary from vapor to solid is dependant upon the spontaneous formation via thermal fluctuation of what is known as a "critical nucleus" of the solid phase. This is an array of  $n$  molecules of sufficiently high value of  $n$ , that the energy created by all  $n$  molecules

crossing the phase boundary, will be greater than the work required to create a surface (area) of an array of that number of atoms in the new phase. In fact it is more precisely the interfacial area between the initial and final phases for  $n$  atoms (molecules). It becomes easier to overcome this phase change energy barrier as  $n$  increases as a result of the fact that surface area/volume decreases as diameter increases.

Both Silane and Trichlorosilane are relatively small molecules and arrays of molecules with a small surface area/molecule can easily be created as a result. Thus both can achieve a critical nucleus at a low value of  $n$ . Since the frequency of formation of an array of number  $n$  is inversely proportional to the value of  $n$ , the smaller  $n$  the more frequently such an array is formed by thermal fluctuations.  $\text{SiH}_4$  and  $\text{SiHCl}_3$  thus have a natural propensity towards easily crossing the phase boundary from vapor to solid phase. (This process of "self nucleation" through thermal fluctuations is termed "homogeneous" nucleation.) As a result vast quantities of submicron diameter amorphous silicon dust is naturally formed in the process of producing silicon from Silane or Trichlorosilane. Descriptions of this phenomenon abound in the Silane and Trichlorosilane patent literature regardless of the type of reactor employed.

Tribromosilane instead, as a result of the large size and mass of the bromine atom requires a large  $n$  value critical nucleus array and naturally prefers if

possible to overcome the energy barrier to phase change by undergoing nucleation on an already existing substrate surface, which is termed "heterogeneous" nucleation. This occurs when the interfacial energy between the atom adsorbed on the substrate ("adatom"), and the substrate reduces the work required per atom to change phases. Additional atoms which arrive go to growing the new phase ("growth") rather than added nucleation. In such a process as is found with TBS, growth is favored over nucleation so that no submicron amorphous silicon dust is produced.

As a result of the tendency to homogeneous nucleation, the Siemens, Ethyl (MEMC) and ASiMI processes must among other limitations, utilize large excesses of hydrogen to dilute the reaction mixture to the point where dust formation is suppressed to the extent possible within the limits of economics (cost of hydrogen).

## (2) "Natural" Product Morphology

In the case of **TBS** as mentioned previously large, dense, spherical monodisperse granules are routinely formed, practically no matter how the reactor is run. From the first to the last JC Schumacher run, this was the result. The process is "robust" in the extreme.

For **Silane** on the other hand, sintered arrays of smaller particles, with a wide disparity in particle size, as exemplified by the early Ethyl process product, appear

to be the "natural", easily achievable result. This type product is filled with absorbed gases and flies apart with a "popcorn" effect on heating. To be sure, as explained in great detail in US Patent 5810934, a Silane FB reactor can be forced to produce the desired product by concurrent execution of a large number of strategies during deposition reactor operation.

MEMC has after developing many incremental improvements over the years successfully operated this complicated, non-robust process with a small operating window, achieving stable, high volume operation for long periods of time.

The issue of homogeneous nucleation is obviated in the **TCS** Siemens process by a combination of dilution and heated substrate rods presented for heterogeneous nucleation and growth. This situation can be approximately duplicated by getting the "beads" present in a FB reactor hot enough, and in early enough contact with incoming TCS (or Silane) to act as a substrate. One way to accomplish this is to use a lined stainless steel reactor so that the high temperatures required can be reached. As TI and Great Lakes have shown however, this stratagem is ultimately unsuccessful for TCS.

An alternative approach to this end is use of microwave heating in conjunction with a quartz reactor as described by the Korea Research Institute. This approach is based on the fact that silicon absorbs microwave energy while quartz does not.

## Reaction Temperature & Materials of Construction

As TI and Great Lakes have shown, the ideal material to use in constructing a FB reactor for EG silicon production is quartz, from a high purity standpoint. Quartz however is not a robust reactor material. Furthermore, silicon and quartz have widely divergent coefficients of thermal expansion. Care must be taken therefore to prevent wall deposits of silicon during FB reactor operation, or the reactor will shatter on cooling as described in US Patent 3963838. This can be accomplished by use of microwave heating in the case of Silane and TCS, or by operating so that etching takes place on the reactor wall rather than deposition as is shown to be possible with TBS in US Patent 4318942.

## Explosive Polymer Formation

It is a well established fact that  $\text{SiCl}_2$  fragments are generated in deposition of silicon from chlorosilanes in poly or Epi reactors, which polymerize into explosive mixtures and deposit in the exhaust ductwork downstream of such reactors. The problem is simply overcome as first shown in US Patent 3594215, by injection of HCl or  $\text{Cl}_2$  into the exhaust stream to "quench" the polymerization. This phenomenon does not occur with TBS as pointed out in US Patent 4318942, so that the TBSFB process avoids this operating complexity and cost.

## Summary

EG silicon was a highly profitable business in 2006, which has not always been the case. However conversion to 400 mm wafers is fast approaching, despite the fact that 300 mm yields are currently below those found with 6" and 8" wafers. A potential solution to this dilemma is use of some version of semi-continuous pulling of 300 mm ingots. For this to have any chance of succeeding, granular EG poly will probably be required.

One commercial granular poly process exists, the MEMC Silane FB process. Two processes have been extensively and at great expense studied over the past 20 to 25 years, but not yet commercialized, the REC Silane FB and the Wacker TCSFB. One process is being reactivated, the Schumacher TBSFB process.

Of these, the TBSFB process is extremely robust in terms of its ability to produce large, dense, spherical granules with a monodisperse particle size distribution.

This process has the potential to enable the substrate needs of the PC industry as well as the requirements of 400 mm wafer manufacturing.