Siemens and Siemens-like Processes for Producing Photovoltaics: Energy Payback Time and Lifetime Carbon Emissions

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Polysilicon photovoltaics will play a significant role in meeting the world's shortfall in electrical energy this century. The photovoltaic industry relies on high-purity silicon produced in the Siemens process. New Siemens-like processes (which convert metallurgical silicon to trichlorosilane and deposit purified silicon through the decomposition of silane) and metallurgical processes for producing solar silicon are under development. Their energy payback time and lifetime carbon emissions are reviewed. The history of development of Siemens and Siemens-like processes is summarized.

INTRODUCTION

Substantial growth in the renewable energy sector will occur this century. By 2050 the world's oil production will be half of what it is today.[1] Capping CO_2 in the atmosphere at 450 ppmv will require its sequestration. Estimates are that with the cap the world's shortfall in electrical energy will be 1.4 terawatt-year (TWy) in 2030.[2]

Polysilicon photovoltaics (PVs) are expected to dominate the market for the next 15 years.[3] Feltrin and Freundlich analyzed the availability of resources for the different PVs.[2] They concluded that only silicon and dye sensitized TiO_2 have sufficient ore reserves to produce electrical energy at the TWy level. Attention is focused on the role Siemens and Siemens-like processes will play in meeting demand for purified silicon for PVs, their energy payback time (EPBT) and carbon footprint.

How would you…

…describe the overall significance of this paper?

Advancement in production of silicon using Siemens and Siemens-like processes for solar cells is reviewed. The legacy of recently built Siemens plants will be with us for 15 years or more, but recent developments with Siemens-like processes involving the decomposition of silane are expected to supersede the older process that relies on decomposition of trichlorosilane. Data involving the life cycle assessment of solar cells formed from silicon produced with these processes are reviewed and compared to numbers generated for electricity produced using fossil fuels.

…describe this work to a materials science and engineering professional with no experience in your technical specialty?

Recent published numbers on the life cycle assessment for photovoltaic modules are presented. These numbers are far more comprehensive than previously published numbers. For example, they include the energy cost of multiple inverters and decommissioning of the solar module.

…describe this work to a layperson?

Not too long ago discussing the virtues of using solar cells for producing electricity would importune comments suggesting that solar cells required more energy than they produce, and thus their energy payback time exceeded the expected lifetime of a solar module. It is time to erase those comments from the human memory. Today's photovoltaics return far more energy than that embodied in the life of a solar system, energy-payback-times are under 2 years, and lifetime carbon emissions per kilo-Watt-hour are a small fraction of emissions produced in generating electricity from fossil fuel plants.

DISCUSSION

Siemens Process

The history of the Siemens process, too extensive to present here, is contained in the patent literature. For those wanting to explore the literature, a list of patents is provided in Tables I and II.

The traditional multistep Siemens process in Figure 1 produces high purity polysilicon involving:

1. Hydrochlorination of metallurgical silicon (m-Si) forming trichlorosilane ($HSiCl_3$ or TCS)
2. Purification of TCS by distillation
3. TCS decomposition to produce purified silicon
4. Recycle H_2(g) and unreacted TCS

The Siemens process meets standards for both the electronics and photovoltaic industries.[4] Trichlorosilane is formed in a fluidized bed reactor (FBR) at temperatures of 583 K to 623 K and at 50 bar. Distillation columns are used to remove $SiCl_4$ and other high boilers from TCS that is subsequently decomposed on silicon rods heated to 1,373 K (Figure 2).[4]

The containment envelope is cooled to minimize deposition of silicon on its walls. Bell jars have been replaced by steel envelopes that have made it possible to increase the size of the reactor so that more rods can be accommodated. Heat transferred from the hot rods to the cooled walls of the envelope constitute 90% of the total energy expenditure.[4]

Improvements in the Siemens process involve the deposition reactor and recycle of byproducts. The patent literature outlined in the tables reveals that there has been an effort to replace the rods with an FBR, based on the following issues:[4]

- High energy consumption
- Need for two power supplies as rods require preheating to 673

K before electric current can be passed through them

- Graphite connecters between rods and electrical supply are a source of contamination
- Power failure leads to process termination
- Hot spot formation leads to failure of the rod
- Gas flow and electrical power need to be adjusted throughout the process

An FBR eliminates many of these issues as they are operated continuously, and the silicon particles charged to the reactor provide a higher surface area for deposition of silicon.

Improvements in the process involves the recycle of byproducts and a decrease in production of $SiCl_4$.[15] Three moles of $SiCl_4$ are formed per mole of polysilicon produced, and must be disposed of.[4]

Siemens-like Processes

Renewable Energy Corporation (REC) is bringing its FBR process on line, a process pioneered by Union Carbide.[4] A key aspect of the process involves using $SiCl_4$ as a feed material for reaction with m-Si and H_2 in producing TCS.

Trichlorosilane is cleaned by passing it through a distillation column, and two redistribution reactors where TCS is converted to silane. The silane is passed through a final distillation column and then fed to the decomposition reactor.

Renewable Energy Corporation has used the standard decomposition reactor in Figure 2, but with silane as the feed material in lieu of TCS. They have developed an FBR for decomposition of silane that is projected to save between 80 to 90 percent of the energy consumed in the traditional Siemens process.

Life Cycle Assessments for Embodied Energy, EPBT, and CO_2 Emissions

Life cycle assessment (LCA) is a tool to evaluate the energy required over the lifetime of a system. Zhai and Williams employed the hybrid-LCA, a top down and bottom-up process.[31] For polysilicon PVs the calculations begin with mining of silica and conclude

Table I. Chemistry of Siemens Process and Siemens-like Processes

U.S. Patent	Date	Company	Description of Technology
3,012,862[5]	1961	du Pont	Production of high purity Si by decomposition of $SiCl_4$, $SiBr_4$, SiI_4, and TCS using H_2, Zn, and Cd.
3,020,129[6]	1962	General Electric	Process for purification of m-Si by forming SiI_4 and decomposing the iodide.
4,084,024[7]	1978	J.C. Schumacher Co.	Process for producing e-Si by vapor phase reduction of halosilane with H_2.
4,092,446[8]	1978	Texas Instruments	A mass balanced closed Si refinery developed for producing e-Si from m-Si.
4,213,937[9]	1980	Texas Instruments	A balance, closed cycle Si refinery system for producing e-Si from m-Si.
4,318,942[10]	1982	J.C. Schumacher Co.	A low temperature, close-loop decomposition process for producing high purity silicon from $SiHBr_3$.
4,464,222[11]	1984	Monsanto Co.	Method for increasing Si deposition rates from halide-hydrogen gases by introducing small amount of silane.
5,021,221[12]	1991	Aero Chem. Research	Vaporized Si-halide reacted with alkali metal vapor producing liquid Si-droplets.
5,063,040[13]	1991	Huels Atiengesell-schaft	Method for increasing trichlorosilane yield in hydrochlorination of Si in FBR.
5,910,295[14]	1999	MEMC Electronic Mat.	Closed process for producing e-Si from silane and fume silica from $SiCl_4$.
7,708,970[15]	2010	Wacker Chemie	Method for recycling high boilers to TCS decomposition reactor without loss of efficiency.

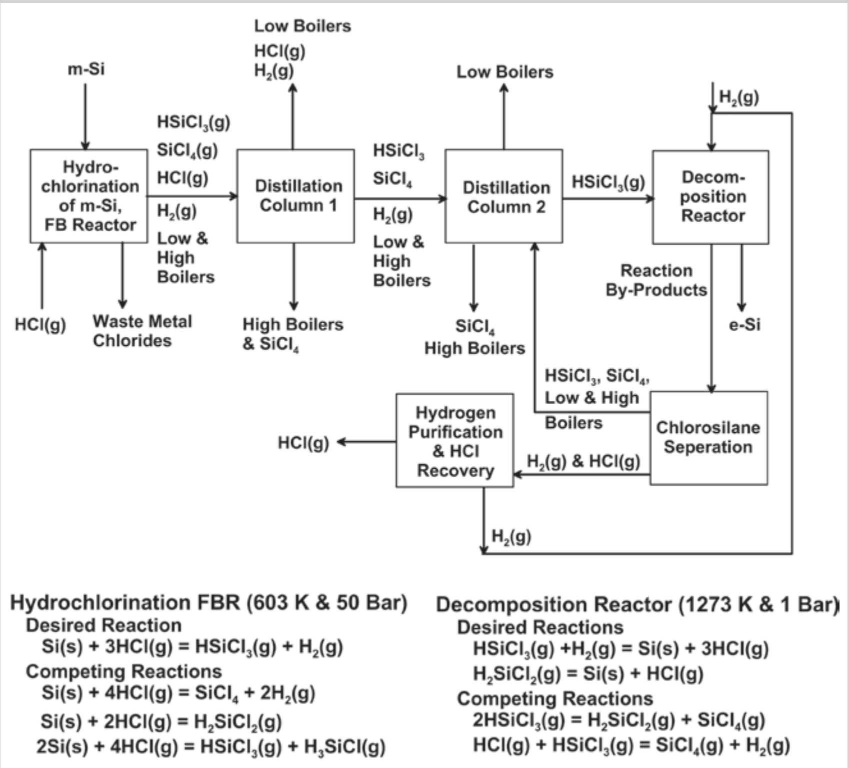

Figure 1. Siemens process after Ref. 4 (e-Si is electronic-grade silicon).

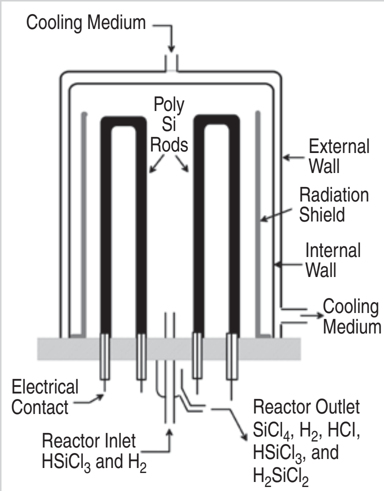

Figure 2. Traditional deposition reactor.

with the end-of-life decommissioning. The embodied energy is based on the gross energy requirement, whereas the EPBT is computed on the basis of the energy actually used, excluding primary energy lost in producing electrical energy.

The EPBT is small, and the overall net energy gain significant. Values for the embodied energy, EPBT, and the lifetime carbon emissions are presented in Figure 4. The embodied energy in a polysilicon solar module produced with the Siemens process in 2007 was 1,210 kWh/m^2 [31] while the annual energy generated is 168 kWh/m^2, and thus over the 30 year life of the system the net gain is 3,830 kWh/m^2. The EPBT computed for 2007 is 2.2 years, and the lifetime carbon emissions amount to 32 g/kWh, and is expected to drop to 24 g/kWh by the end of 2011. Those numbers are compared to carbon emissions from fossil fuel plants in Table III.

Carbon emissions will be reduced further with PVs manufactured using REC's FBR silicon. Use of that silicon in 2011 is expected to reduce the embodied energy from 999 kWh/m^2 to 788 kWh/m^2, a reduction of approximately 20%. That reduction in embodied energy is expected to translate to a similar reduction in the lifetime carbon emission from 21 g/kWh to 17 g/kWh. Elkem Solar has developed a metallurgical process for producing solar silicon. The company estimates that carbon emissions for PVs produced with its new silicon will release 6.5 g/kWh over its life time, and that the EPBT is 1.1 years.[32]

CONCLUSIONS

Polysilicon photovoltaics will play a significant role in meeting the world's shortfall in electrical energy this century. REC's new FBR reactor with decomposition of silane versus TCS is likely to capture a significant portion of the market given its energy savings over the traditional Siemens process. However, the lifetime carbon emissions associated with photovoltaics formed from silicon produced with either the Siemens Process or Siemens-like process are three times greater than for solar cells produced with silicon from Elkem Solar's metallurgical process.

Table II. Fluidized Bed Reactor Technology

U.S. Patent	Date	Company	Description of Technology
3594215[16]	1971	Texas Instruments	Method and apparatus for coating particulate with metal utilizing FBR.
3963838[17]	1976	Texas Instruments	Method for pre-treating wall of FBR so as to have deposits of Si separate from the wall as deposit grows.
4154870[18]	1979	Texas Instruments	Improved methods for inputting Si-seed crystals and extraction of product Si particles from FBR.
4292344[19]	1981	Union Carbide	Capacitive electrical heating of a FBR minimizes undesired coating of Si on wall of the reactor.
4676967[20]	1987	Union Carbide	$SiCl_4$, H_2, and m-Si reacted to form TCS, and DCS that are disproportionated in the presence of an exchange resin forming high purity silane.
4684513[21]	1987	Union Carbide	Improved heating of FBR for production of e-Si.
4784840[22]	1988	Ethyl Corp.	A process to produce polysilicon from a fluidized bed.
4786477[23]	1988	Korea Research Institute	FBR heated with microwaves for preparing polysilicon.
4818495[24]	1989	Union Carbide	Design of FBR for decomposition of silane at a rate 30 times greater than the standard Siemens process.
4820587[25]	1989	Ethyl Corp.	Method for uniting Si dust to form larger particles in FBR.
5139762[26]	1992	Advanced Silicon Mat.	Improved FBR and method for production of high purity Si by pyrolysis of silane.
5374413[27]	1994	Korea Inst. Chem. Tech.	Improved FBR design for deposition of high purity Si on Si-particles using microwaves.
5798137[28] and 5810934[29]	1998	Adv. Silicon Mats.	Process for producing Si beads by CVD on seed particles in combined FBR and CVD reactor.
Appl.2009 /0324479[30]	2009	MEMC Electronic Mat.	Method for directing thermally decomposable compounds to center of FBR to avoid side walls.

Table III. Estimated Emissions for Production of Electrical Energy [31–34]

CE Energy Source	(gC/kWh)
Coal	300–323
Oil	258–300
Natural Gas	136–178
Siemens	60 (2001)
Polysilicon	33 (2007)
PVs	21 (2011)
REC's FBR Polysilicon PVs	17*
Elkem Solar's ESS 2010 Polysilicon	6.5

* Estimated

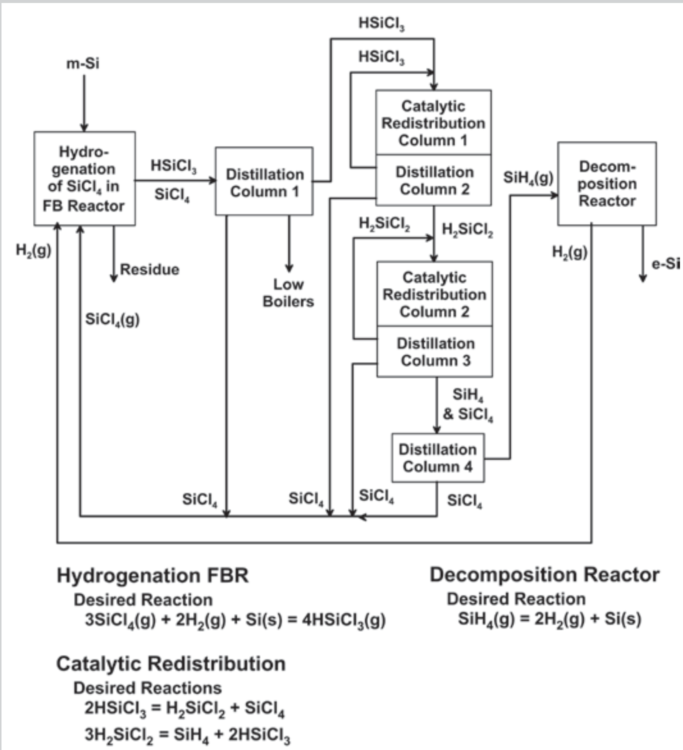

Figure 3. Union Carbide process (after Ref. 4).

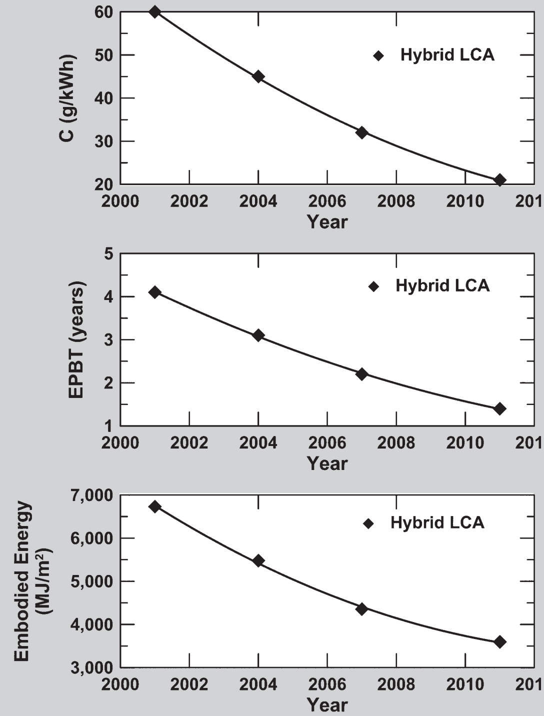

Figure 4. Life cycle assessments for energy, energy payback time, and carbon emissions for polysilicon photovoltaics produced using the Siemens process.[31]

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