

# The Benefits of Chlorine Chemistry in Semiconductors and Other Silicon-Based Products

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## The Benefits of Chlorine Chemistry in Semiconductors and Other Silicon-Based Products

Chlorine chemistry is central to the production of the highly purified silicon that is required for the manufacture of silicon-based integrated circuits, solar cells, silicone-based products, glass optical fibers and high purity fumed silica. In the United States and Canada, these industries are quite large, amounting to \$50 billion in sales at the wholesale level and much more at the consumer level. No chlorine-free processes have been developed that can produce silicon of the purity required for these products, so the absence of chlorine chemistry would force consumers to seek products made from alternate materials. This report estimates the benefits of chlorine chemistry in the production of silicon-based products by examining the differences in costs and the utility to consumers between chlorine-free substitutes and the chlorine-based products that they currently use.

Other materials could be substituted for silicon in the manufacture of **integrated circuits** and **solar cells**. For example, gallium arsenide is currently used in certain applications like cellular telephones where its electrical properties are superior to those of silicon and its much higher cost can be justified. For many other applications, it is not uniquely well suited and consumers could experience performance losses. Production volumes of gallium arsenide would have to increase by two orders of magnitude, however, if it were to substitute for all current uses of semiconductor grade silicon, and this would require massive capital investments in production plants for its extraction and purification, wafer production, and in the integrated circuit fabrication plants. For United States and Canadian consumers, the net economic benefit in the manufacture of integrated circuits and solar cells is estimated to be about \$15.5 billion per year.

A variety of currently available elastomers and resins could be substituted for **silicone** products. While many of them are lower in cost than the silicone-based products they would replace, they do not have all of the attributes that consumers currently require and would be imperfect substitutes. Consumers would suffer loss of utility if forced to rely on them. For United States and Canadian consumers, the net economic benefit in the manufacture of silicones is estimated to be about \$1 billion per year.

In the absence of **glass optical fibers**, high-speed and high-bandwidth communication over long distances would take place via metallic electrical conductors, which are more costly to install and maintain than fiber optic cables. For United States and Canadian consumers, the net economic benefit in the manufacture of glass optical fiber is estimated to be about \$2.5 billion per year.

In the aggregate, the total benefit to consumers for these end uses is approximately \$19 billion per year. These benefits are extremely large relative to the amount of chlorine that is consumed to produce them – less than 0.5% of the total chlorine consumption in North America.

## Introduction

Silicon, the second most abundant element on earth, comprises more than a quarter of the earth's crust but is never found pure in its elemental state. It occurs naturally in a variety of silicate minerals, in rocks such as granite, as the main constituent of silica sands, and as the gemstones opal and amethyst. Purified silicon is far more valuable to consumers than these gems, however, when it is contained in products that are made from it using chlorine chemistry.

The chemical and physical properties of silicon, particularly its high melting and boiling points and its propensity to react with oxygen, make it difficult to isolate and purify under mild conditions. Nevertheless, its value as an alloying agent and as a reductant for more chemically active metals has led to its large-scale production for metallurgical uses. About 175,000 metric tons per year of silicon in ferrosilicon are consumed in the United States as an alloying agent in steel and cast iron, and another 165,000 metric tons per year of silicon metal are consumed as an alloying agent in aluminum and in the production of silicon-containing products that are based on chlorine chemistry.<sup>1</sup> Silicon is produced commercially by reducing quartzite or silica sand with carbon in electric furnaces at temperatures of 1,900 to 2,000 degrees centigrade. The silicon that is produced, typically in the range of 96-99% purity, is suitable for metallurgical uses but is not acceptable for higher-valued semiconductor applications.

Silicon of much higher purity is required for the manufacture of silicon-based semiconductors that are the foundation for the integrated circuit chips that underlie consumer electronic goods, and for the solar panels that generate greenhouse gas-free electricity directly from sunlight. Higher purity silicon is also required for the intermediate materials that are converted into the numerous silicone-based consumer and industrial products, for the production of the glass used in high-speed, high-bandwidth fiber optic cables, and for products that contain high purity, high surface area fumed silica. All these materials use chlorine chemistry in their manufacture even though chlorine is not contained in the final products.

The market size of these silicon-based industries in the United States and Canada is large, amounting to nearly \$50 billion at the wholesale level in 2004. The semiconductor industry is by far the largest market segment followed by silicones, as shown in Table 1. The market value of final products made from these silicon-based building blocks is substantially larger. In the case of semiconductors, for example, the quoted market size is approximately \$165 billion.<sup>2</sup>

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<sup>1</sup> U.S. Geological Survey Minerals Yearbook, *Silicon-2004*.

<sup>2</sup> 2006 US Industry & Market Outlook, Barnes Reports, [www.barnesreports.com](http://www.barnesreports.com).

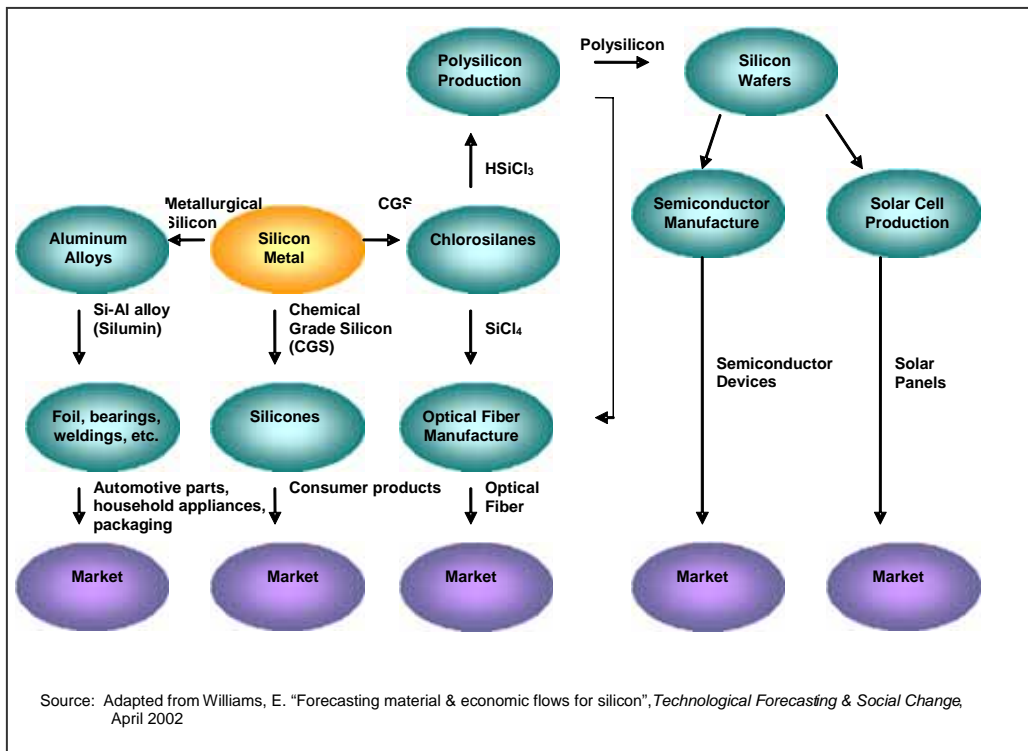
**Table 1**  
**Estimated Market Size of Silicon-based Industries**  
**in the United States and Canada, 2004**  
**(Billions of US Dollars)**

	United States	Canada	Total
Semiconductors	\$40.0	\$3.5	\$43.5
Solar Cells	0.8	0.1	0.9
Optical Fibers	0.4	0.1	0.5
Silicones	3.0	0.5	3.5
Fumed Silicas	0.4	<0.1	0.5
Total	\$44.6	\$4.2	\$48.9

Source: Semiconductor Industry Association, Gartner Group, KMI Research, Corning, Inc., International Energy Association, MineSet Partners, Natural Resources Canada, Communications Today, and Global Insight estimates.

In the following sections, we describe the properties of the silicon-based materials in semiconductors, solar panels, silicones, fiber optic cable, and fumed silica that make them so beneficial to consumers and the issues surrounding the use of substitutes that are not based on chlorine chemistry. The benefits of chlorine chemistry in the production of silicon-based products can be determined from the differences in the costs and the utility to consumers of the chlorine-free substitutes and the chlorine-based ones that they currently use.

**Figure 1**  
**Polysilicon Manufacturing Supply Chain**



## Chlorine Chemistry in the Production of Silicon-Based Products

Chlorine is used as a facilitator in the production of the high-purity silicon-based materials that are subsequently converted into a variety of consumer products. Chlorine is used to produce mixtures of volatile chlorosilanes which can be purified at much lower temperatures than would be possible with elemental silicon. The highly purified silanes are then converted further into chlorine-free intermediate or final products, and the chlorine is recycled to produce more chlorosilanes. Only small amounts of chlorine, less than one half percent of total chlorine production, are consumed in the processes, mainly in the formation of inorganic chlorides of the impurities in the raw silicon and other chlorinated byproducts.

**Semiconductors:** In the production of extremely pure silicon for use in the manufacture of semiconductors and solar panels, process conditions are set to favor the formation of trichlorosilane. Other silanes, such as mono-, di- and tetrachlorosilane, are separated from the trichlorosilane and the latter is put through purification steps that can reduce impurities to below the part-per-billion level. The purification steps operate at temperatures at which the silanes are stable, but when the purified trichlorosilane is heated to temperatures above 1,100 degrees centigrade, it decomposes to form elemental silicon, producing chlorine and other silanes that are recycled within the process. The silicon is deposited as polycrystalline material on rods that are “grown” in specially designed decomposition reactors until they reach the desired size. The rods are then removed from the reactor and broken up for packaging and sale.

**Silicones:** In the production of silicones, chlorine is first reacted with methanol to produce methyl chloride that is, in turn, reacted with impure silicon to produce a mixture of methyl chlorosilanes. These compounds are volatile and are separated to produce the desired intermediate, purified dimethyldichlorosilane. This compound is then reacted with water vapor to form low molecular weight polymers, or oligomers, of dimethylsiloxane and the facilitating chlorine is recycled to produce more methyl chloride. The oligomers can then be converted into silicone products with a wide range of desirable properties by proper selection of conditions in the final polymerization steps or by incorporating other organic constituents into the polymers.

**Optical Fiber:** Tetrachlorosilane is the starting material for the production of the special glass that is required for optical fibers. A number of techniques may be used to form the fibers, but they all start with highly purified tetrachlorosilane, which is a vapor at slightly above ambient temperature. The vapors are heated to temperatures over 1,500 degrees centigrade and are reacted with oxygen or water vapor, which converts the silane into silica, releasing the chlorine. The silica condenses and the fine particles agglomerate on a substrate to form the glassy phase and the chlorine is separated for recycle. The substrate is processed further to draw the silica into the small-diameter fibers that are used to make fiber optic devices.

**Fumed Silica:** Tetrachlorosilane is also the starting material for the production of high purity fumed silica. The fumed silica, which is composed of very small particles that have extremely large surface areas, is formed by flame hydrolysis of the silane under conditions that are similar to those used for the production of optical fibers. Fumed

silicas made this way are used as fillers in a variety of specialized consumer and industrial applications such as spark plugs, printing inks, and pharmaceuticals.

The starting material for the production of these silanes is silicon that has been reduced carbothermically in high temperature electric furnaces. The reduction process itself reduces the impurities content of the raw material but a number of elements remain whose concentrations have to be reduced further by orders of magnitude. The compositions of typical grades of silicon metal are shown in Table 2.

**Table 2**  
**Typical Silicon Metal Compositions**

Element	Metallurgical Grade <sup>1</sup>	Chemical Grade <sup>2</sup>
Silicon, %	96-99	>98.9
Iron, %	0.4-1.0	0.1-0.5
Aluminum, %	<0.5	0.2-0.4
Calcium, %	0.2-0.3	0.02-0.2
Manganese, ppm		<800
Titanium, ppm		<800
Boron, ppm		<20
Lead, ppm		<10
As, C, Cu, Mg, Mo, Na, P, Sb, and W	Also present	Also present

<sup>1</sup> Used in alloying applications

<sup>2</sup> Used for production of chlorosilanes

Source: Global Insight, Inc.

The purity level required for these elements depends on the application. Not all of these elements are equally deleterious, affording manufacturers some flexibility in the purification processes. Boron and phosphorous content must be reduced to very low levels for most applications, however. The earliest attempts to obtain higher purity material from metallurgical and chemical grade silicon were based on the low temperature, selective acidic dissolution of granular silicon, but such techniques are not adequate for the efficient production of material with impurities reduced to the parts per billion level.

Molten silicon can be purified further using a technique called zone melting, or zone refining. Low levels of most impurities can be attained using this technique, but yield losses are very high unless the initial impurities content is quite low, and it is not commercially feasible to purify metallurgical or chemical grade silicon to semiconductor grade by zone refining.

Currently, chlorosilane chemistry is the dominant commercial technology to purify metallurgical grade silicon because the chlorine chemistry results in the formation of volatile compounds of silicon that can then be separated and purified under milder conditions of temperature and pressure and at lower cost than is currently possible with other technologies. Conceptually, other chemistries could become the basis for chlorine-free routes to high purity silicon-based products. A number of processes based on

fluoride chemistry were proposed in the 1970s and 1980s, since fluorosilanes are even more volatile than their chlorosilane analogs.<sup>3</sup> None of these processes have been commercialized, or even demonstrated in semi works-scale pilot plants, because they do not appear to offer significant benefits vis-à-vis chlorine-based technology. The limitations of the proposed processes include increased complexity, more extreme operating conditions of temperature and pressure, complexities with the handling of corrosive byproducts, and questions regarding the ability to produce silicon with extremely low impurities content.

More recently, some preliminary work has been undertaken on the development of novel chlorine-free technology for the development of solar-grade silicon.<sup>4</sup> The proposed process<sup>5</sup> is based on ethanol and the catalyzed formation of volatile ethoxysilanes instead of chlorosilanes or the fluorosilanes. This process is still in the earliest stages of development with plans being developed for a 400 kilogram per year capacity pilot plant, about one ten-thousandth the size of a commercial plant. The process as conceived will operate at temperatures between 200 degrees and minus 80 degrees centigrade, and at pressures as low as one eighth of an atmosphere. Reaction times as long as 20 hours will be required in some steps, and various catalysts and intermediates will have to be recovered, purified and recycled. It is not clear from the available data whether the silicon produced by this process will be suitable for semiconductor applications. It may have to be refined further using zone melting or other techniques. In addition, users of this process will have to find outlets for more than six times as much silica sol as the amount of purified silicon produced. It is not apparent that the potential economic advantages of such a process are sufficient to warrant the considerable risks and additional development expenses that will have to be born prior to its commercialization.

In summary, none of the chlorine-free processes that have been proposed can be considered as realistic candidates to displace the current chlorine-based process for the production of highly purified, semiconductor grade silicon and the products based on them. Therefore, in the absence of access to chlorine chemistry, consumers would have to find substitutes for the products currently made from chlorine-based high purity silicon. The current technology is capital and know-how intensive. Investments on the order of \$6,500 per metric ton of annual capacity are required to produce integrated circuit (IC) grade polycrystalline silicon.<sup>6</sup> While prices for polycrystalline silicon are strongly influenced by the supply-demand balance for the material, in normal markets the value of the silicon metal is increased from less than \$2 per kilogram to more than \$30 per kilogram.<sup>7</sup> Such prices are justified only when a material is uniquely suited to its intended use.

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<sup>3</sup> See, e.g., US 4,138,409, US 4,172,883, and US 4,529,576, U.S. Patent and Trademark Office.

<sup>4</sup> D.S.Strebkov et al, *Chlorine Free Technology for Solar-Grade Silicon Manufacturing*, NREL/CP-520-36750, August, 2004.

<sup>5</sup> See also US 6,103,942, U.S. Patent and Trademark Office.

<sup>6</sup> *Solar Powered: An Emerging Growth Industry Facing Severe Supply Constraints*, Piper Jaffray, October, 2005.

<sup>7</sup> *Silicon-2004*, op cit, Piper Jaffray, op cit.

## Alternative Technologies and the Value of Chlorine Chemistry

### *Polycrystalline silicon in semiconductor manufacturing*

The production of silicon-based integrated circuits, the “chips” familiar to consumers, is the basis of much modern technology. These products surround us, being incorporated into computers, communication devices, automobiles, military equipment, satellites, and toys. Their production is a highly complicated, capital and know-how intensive proposition whose technology evolves continuously and with remarkable rapidity. Globally, the demand for high purity silicon in semiconductor manufacture is estimated to be approximately 20,000 metric tons per year.<sup>8</sup>

Typically, the highly purified polycrystalline silicon material is re-melted and small amounts of impurities, called dopants, are added to the melt in precisely controlled amounts to impart certain desired electrical and physical properties to the silicon. The melt is then processed further by a technique called the Czochralski process to produce a single crystal of silicon that may be up to 300 mm in diameter and 2 meters long. The single crystals are then sliced into wafers with thicknesses of about 0.75 mm and the wafers are polished to achieve extremely uniform surfaces. Although these processes are commercially mature, they can produce some pieces that contain chemical or physical defects that make them unsuitable for semiconductor use. Material that cannot be recycled for reprocessing may be sold to the manufacturers of silicon-based solar panels whose quality requirements are somewhat less stringent.

The wafers are then subject to a series of processing steps that produce the integrated circuits and give the chips their functionality. The specific operations, number of steps and their sequence depend on the circuit design and they can number in the hundreds. Many dozens of individual devices can be made on a single wafer. These activities are performed in highly automated fabrication plants under ultra clean conditions and with a high degree of reliability – target yields exceed 90%. Demands for higher performance have led to the development of ever more complex circuits with higher speed capabilities, and the complexity of the fab shops where the chips are manufactured has increased apace. The investment in a new chip plant may exceed \$2 to \$3 billion, a daunting sum for the production of components that may have a product life of two years or so before becoming “last generation.”

Investments of this magnitude simply cannot be made if there is any uncertainty with regard to the ability to process the wafers upon which the circuits are laid down. It has been estimated that about forty billion square centimeters of wafers were produced globally for IC use in 2004<sup>9</sup> with a value of approximately \$7.5 billion.<sup>10</sup> At the wafer level, then, the value of the silicon has increased from less than \$40 per kilogram to about \$1,000 per kilogram of silicon. Global semiconductor sales for 2004 topped some \$200 billion, of which the United States and Canadian markets accounted for over \$40

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<sup>8</sup> *Silicon-2004*, op cit.

<sup>9</sup> *Ibid.*

<sup>10</sup> *Chemical & Engineering News*, Vol 84, No 31, pg 30, July 31, 2006.

billion.<sup>11</sup> These materials are the foundation for the \$165 billion industry per year semiconductor industry in the United States, and billions of dollars more enter North America as components of consumer and industrial goods.<sup>12</sup> This value amounts to about \$10,000 per kilogram of silicon that was consumed in the production of these products.

Silicon is not the only material that can be used to make semiconductor devices. Silicon germanide, germanium itself, and numerous other compounds from elements within Groups II through VI in the periodic table, can have semi-conducting properties. Germanium, gallium nitride, and gallium arsenide, in particular, have established histories of use in the manufacture of electronic components and are employed where their specific properties provide advantages compared to the use of silicon. The value of these materials in the form of substrates for integrated circuits has been estimated to be about one twelfth of the value of silicon wafers,<sup>13</sup> but the amount of material involved is much lower than that because material and processing costs are significantly higher than they are for silicon. While there is less commercial history behind the use of other materials to replace silicon in semiconductor devices, it is unlikely that, given current technology, any of them could overcome silicon's cost and performance advantages except in limited, specific applications.

Germanium was displaced by silicon in most uses because silicon is more economical and has better thermal stability. Germanium's electro-optic properties favor its use in devices that involve infrared detectors. While it also is used as an alloy with highly purified silicon in the fabrication of high-speed integrated circuits, it cannot be considered a substitute for silicon in this analysis because it, too, is purified using chlorine chemistry.

Gallium arsenide is used in high-speed circuits and has some properties, such as higher breakdown voltage and electron mobility, that are superior to silicon and favor its use in specific applications such as mobile telephones and satellite communications. However, its lower drift velocity of electrons, or hole mobility, means that gallium arsenide circuits can have higher power consumption than those based on silicon, and it is not possible to form a stable, adhering insulating layer on gallium arsenide that is analogous to the layer of SiO<sub>2</sub> that is incorporated easily onto silicon-based circuits. Finally, silicon's better mechanical and processing properties permit the production of wafers with diameters of 300 mm or more, whereas the maximum diameter attainable with gallium arsenide is currently limited to about 150 mm. This means that up to four times as many circuits can be put on a silicon wafer compared to one made of gallium arsenide, a significant processing advantage. Thus, there are some applications for which gallium arsenide is uniquely suited, and many applications for which it is not. Gallium arsenide is costly to manufacture and, at the end of a product's useful life, disposal of gallium arsenide components is a significant issue.

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<sup>11</sup> Semiconductor Equipment and Material Industry (SEMI), Air Products, Inc., and Semiconductor Industry Association (SIA) reports.

<sup>12</sup> *2006 US Industry & Market Outlook*, Barnes Reports, [www.barnesreports.com](http://www.barnesreports.com).

<sup>13</sup> *Chemical & Engineering News*, op cit.

Some of the cost disadvantages of gallium arsenide are due to the diseconomies of scale inherent in its current, low volume of production. Production at much larger scale would decrease these disadvantages significantly. Worldwide primary production of gallium in 2004 was about 70 metric tons, of which about 25 metric tons was consumed in the United States.<sup>14</sup> Far more arsenic is produced annually than is required for current gallium arsenide production, but order-of magnitude capacity expansion would be required to purify it to the grade required for semiconductor use. However, the cost of the starting materials will always be markedly higher than for silicon, which is made from sand.

Single crystal wafers of gallium arsenide are difficult to produce using the Czochralski process that is suitable for silicon because of the physical and chemical properties of the compound's melt. Instead, semiconductor grade single crystal gallium arsenide is produced by such processes as the liquid encapsulated Cz (LEC) process, vertical boat (VB) or vertical gradient freeze (VGF) Bridgeman techniques, which are less efficient, more costly, and more difficult to scale-up processes. Currently, the cost of a 100 mm diameter gallium arsenide wafer can be significantly higher than the cost of a 200 mm silicon wafer. This puts the cost of the contained gallium more than an order of magnitude higher than the comparable cost of silicon.<sup>15</sup>

Gallium arsenide wafer production volumes would have to be increased by more than 250 times to produce sufficient material to supply the current demand for semiconductor silicon substrates. Purification of the crude gallium recovered from the usual sources is a costly, multi-step process and many new plants would be required to increase capacity by two orders of magnitude. All of this would require enormous capital investments. The less favorable chemical, electrical, and physical, properties of this material would need to be addressed by design compromises in the manufacture, and probably in the performance, of integrated circuits and the devices made from them. The productivity of fab plants based on 300 mm diameter silicon wafers would be affected adversely if they were forced to process 150 mm diameter gallium arsenide wafers that require different architecture to produce the desired chip performance. Significant capital would be required to accommodate the new production processes that would be required and to cope with environmental issues and productivity losses. Gallium arsenide is more brittle than silicon and must be processed at lower temperatures so that plant productivity would be decreased and yield losses would be increased as well.

We estimate that new investments of the order of \$50 billion would be required for the facilities necessary to extract the required amount of gallium from all available sources, reduce it to elemental form, purify it to semiconductor grade, convert it into gallium arsenide wafers, and process the wafers in existing and new fab plants in North America. This would involve a very large scale-up of existing capacity but no fundamentally new technology. The economies of scale would reduce conversion costs by a factor of three and unit capital requirements by about two times from current levels, but the wafers would still be about five times as costly as the larger silicon wafers because the

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<sup>14</sup> U.S. Geological Survey, Mineral Commodity Summaries, *Gallium*, January, 2005.

<sup>15</sup> Global Insight estimates.

conversion processes are less efficient, and conversion costs in the less productive fab plants would be higher as well.

For United States and Canadian consumers, the net economic benefit of chlorine in the manufacture of semiconductors is estimated to be about \$15 billion per year. These benefits represent the avoided conversion costs associated with the production of gallium arsenide-based devices and the returns to the new capital that would have to be invested to produce them. This is a conservative estimate since we have not included any costs associated with performance losses by using chlorine-free technology in semiconductor devices.

### *Silicon in solar panels*

Solar panels are devices that are used to convert the photon energy in sunlight into electrical energy. The assembled panels, or modules, are made up of an array of smaller, individual solar cells that are mounted on a supporting structure, with conductors interconnecting the cells to collect the electricity that is generated. The solar cells are made from semiconductor materials that absorb the photons and produce electrons by the photovoltaic effect. A variety of semiconductor materials have been used in solar cells. Consumers are perhaps most familiar with these devices in their applications on satellites or where they are used to provide power in locations that are not connected to an electricity grid, such as along remote stretches of highways. Individual cells are used to power handheld calculators, and panels may be installed on commercial or residential building roofs both to satisfy local power requirements and to feed the excess electricity into a grid during periods of peak power generation. In 2004, the United States and Canadian photovoltaic market reached \$920 million, with the commercial sector being the largest market segment. Over 287 peak megawatts of cumulative photovoltaic power capacity have been installed in North America.<sup>16</sup>

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<sup>16</sup> International Energy Agency, Natural Resources Canada

**Table 3**  
**U.S. Shipments of Photovoltaic Cells and Modules by Market Sector, 2004**

Sector and End Use	Crystalline Silicon <sup>a</sup>	Thin-Film Silicon	Concentrator Silicon	2004 Total (kWp)
Market				
Industrial	13%	1%	0%	30,493
Residential	41%	7%	20%	53,928
Commercial	35%	53%	20%	74,509
Transportation	1%	0%	0%	1,380
Utility	0%	0%	60%	3,233
Government <sup>b</sup>	5%	38%	0%	3,257
Other <sup>c</sup>	5%	1%	0%	14,316
Total	100%	100%	100%	181,116
<sup>a</sup> Includes single-crystal and cast and ribbon types.				
<sup>b</sup> Includes Federal, State, local governments, excluding military.				
<sup>c</sup> Other includes shipments that are manufactured for private contractors for research.				

Source: Energy Information Administration

Currently, over 95% of all solar cells are produced from mono or polycrystalline silicon wafers. Present consumption of purified silicon for solar cells is about 75% of that for semiconductor silicon, but is projected to exceed semiconductor silicon consumption before the end of the decade.<sup>17</sup> The silicon is purified by the same process used to produce materials for the semiconductor industry, but solar cells do not require the same very low levels of some impurities. Polycrystalline cells are made by melting the purified polycrystalline silicon, casting the melt into molds, and then sawing the ingots into wafers that have thicknesses of about 0.2-0.3 mm. Monocrystalline wafers are made from the same starting materials and they are grown and cut using the same techniques as in the semiconductor industry. Substrate material can also be made by pulling a ribbon of silicon from a melt, which permits the production of thinner wafers and thereby reducing materials costs. Somewhat lower efficiency cells can be made from amorphous silicon.

A variety of semiconductor materials have been used to manufacture the solar cells in addition to highly purified silicon. They include such compounds as cadmium telluride, copper indium diselenide and copper indium gallium selenide, gallium arsenide, some organic semiconductor materials, and silicon of lower purity. Other materials, including nanotechnology-based compounds and so-called transparent conductors, are being evaluated for use in solar cells but these materials may be years away from commercialization. Different semiconductor materials convert photons to electricity with different efficiencies, as shown in Table 4.

<sup>17</sup> Piper Jaffray, op cit.

**Table 4  
Typical Efficiencies of Some Solar Cell Materials**

	Si <sup>1</sup>	Si <sup>2</sup>	Si <sup>3</sup>	Si <sup>4</sup>	Si <sup>5</sup>	CdTe	GaAs	CuInSe	CuInGaSe
Cell Efficiency	>20%	16%	15%	13%	8%	9%	>30%	11%	20%

<sup>1</sup> High efficiency monocrystalline silicon

<sup>2</sup> Monocrystalline silicon

<sup>3</sup> Polycrystalline silicon

<sup>4</sup> Polycrystalline ribbon silicon

<sup>5</sup> Amorphous silicon

Source: Piper Jaffray and Global Insight estimates

A number of manufacturers produce solar cells and panel modules of various designs and configurations. Production in 2004 was estimated at more than 1,200 megawatts with modules typically priced at about \$3.25 per watt. Production volumes are projected to grow to as high as 5,000 megawatts by the end of the decade.<sup>18</sup> At this time, the purified silicon in photovoltaic cells accounts for about 40% of the cost of polycrystalline wafers, and about 25% of the cost of the modules made from them. Economies of scale at increased production volumes are projected to result in reductions of about 10% in the cost of polysilicon modules by 2010.<sup>19</sup>

Panels made with non-silicon materials will require more cells if their efficiencies are lower, as with CdTe and CuInSe, or fewer if their efficiencies are higher, as with GaAs and CuInGaSe, to produce the same amount of power. The cost of the panel, and the module, depends both on the cost of the cells themselves and the number of them required to collect the sunlight. While gallium arsenide-based panels could require less than half the number of polycrystalline silicon cells to generate the same amount of power, cell material costs could be approximately five times higher than the current cost for high purity silicon. This is estimated to increase the cost of the installed modules to the consumer by more than a third.

None of the other alternative materials – CdTe, CuInSe, and CuInGaSe – are produced in sufficient volume today to permit estimates of their cost at higher production volumes with any confidence. Efforts are underway to fabricate panels based on cells made from lower cost, lower purity silicon, but they will have lower efficiencies than current designs and require much more area to generate equivalent amounts of electricity. At present there is no reason to believe that, after correcting for differences in efficiency, any of these alternatives could serve as the basis for the production of panels at a lower cost than is possible now with purified silicon in the absence of the development of truly breakthrough technology for cell and panel manufacturing.

For United States and Canadian consumers of solar panels, the benefit of chlorine chemistry results from consumers' ability to purchase them at substantially lower cost than would be possible if they had to be made from other materials. We estimate this cost difference in 2004 would have amounted to almost \$0.5 billion per year had the

<sup>18</sup> *Ibid.*

<sup>19</sup> *Ibid.*

alternate, chlorine-free material been gallium arsenide, and that \$10 billion in additional investments would have been required to supply the necessary wafers.

### *Silicone-based products*

Silicones are a class of polymeric compounds whose structure is based on repeating bonds between silicon and oxygen, with methyl and other organic groups bound to the silicon atoms as side chains. By varying the length of the silicon-oxygen backbone, the nature of the side chains and the extent of their cross-linking, manufacturers of silicones can produce materials with a wide range of physical and chemical properties. They can be produced in the form of fluids, gels, emulsions, elastomers or resins and tailored for the intended applications. About three quarters of the silicon metal produced meets chemical grade requirements, and about 90% of that is consumed in the manufacture of silicones.<sup>20</sup> All silicone production is based on chlorine chemistry.

The fundamental chemistry behind the production of silicone has been known for many years and is well understood. No commercially viable, chlorine-free processes have been developed for the production of silicones, although it is conceivable that the necessary chemistry might be developed. However, commercialization of an alternate process is unlikely under normal market conditions, and substitution for chlorine-based silicones would have to occur at the product level.

The first silicone-based products were developed during World War II as industrial products, such as greases and sealants that had properties that were far superior to those derived from petroleum or natural materials. As the producers gained more experience with the chemistry of their manufacture, silicone-based products with greater ranges of properties and applications were produced for consumer as well as industrial markets. Familiar consumer applications include products that serve as caulking compounds, waterproofing agents, and essential ingredients in personal care products. They are also important, if somewhat less visible, as performance products in such applications as specialty rubbers, glazing compounds and insulators, protective coatings for electronic components and adhesives. The properties of the products can be controlled by selection of the chemical structure of the silicone itself, through addition of fillers to elastomers and resins, and by reacting the silicones with other materials such as polyethers and amides to produce silicone copolymers. Some of the many products based on silicones are listed in Table 5. Domestic shipments of silicones in the United States and Canada amounted to approximately \$3.5 billion in 2004, with industrial markets accounting for nearly 60 percent of all shipments.<sup>21</sup>

Consumers have access not only to these products but also to other products that are similar or could be used in the same applications but are not based on chlorine chemistry. The list of other fluids, elastomers and resins that compete with silicon-based products in most applications is extensive. When consumers select silicone-based products, it is because their performance attributes provide them better value in use.

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<sup>20</sup> Silicon-2004, op cit.

<sup>21</sup> Freedonia and Global Insight estimates.

**Table 5**  
**Selected Uses of Silicone-Based Products**

Automotive	Engine mount, filler cap o-ring seal, heater hose, power steering oil seal, motor insulation, paints/coatings, shock absorption applications, tires.
Aerospace	Sealant for doors, windows, wings, fuel tanks, hydraulic switches, overhead bins, wing edges, leading gear electrical devices, vent ducts, engine gaskets, electrical wires and black boxes.
Construction	Sealants, caulking products, silicone exterior coatings (e.g. protect against acid rain, salt spray, and gasoline spill).
Electronic	Key pads, keyboards, copier rollers, hardcoating housings for computers, facsimile machines, telephones and home entertainment equipment.
Health	Non-adherent dressings, burn treatment gauzes, cavity wound dressing, skin barrier, scar management, burn masks, pressure sore cushion, contact lens, prosthetic applications, respirators, silicone tubing in medical devices (e.g., drug delivery systems, pacemakers).
Beauty and Personal Care	Shampoos, conditioners, hairstyling products, skin moisturizers, sun protection, aftershaves, cleansing lotions, cold creams, “long-lasting” color makeup, antiperspirant and deodorant products.
Paper and Film Adhesives	Price stickers, decals, reflective films for road signs, security stickers (e.g. motorway passes), “sticky” notes.
Other	Industrial molds, food molds (e.g. for gelatin and cakes), “no-slip” mixing bowls, heat resistant (400-800°F) spatulas, fabric softeners, “wrinkle-resistant” and “easy care” fabrics, sport performance fabrics, snowboards, skis, shock absorbers in running shoes, dry cleaning agent, household polishers, anti-foaming agent in laundry detergents, pacifiers, toys, baby bottle nipples, breast pumps, spill-proof valves.

Source: Center Européen des Silicones, Global Silicones Council, Silicones Environmental, Health and Safety Council of North America, Dow Corning

Depending on the specific application, a number of mineral oils, petroleum based or synthetic oils and greases might be substituted for silicone fluids, but they might not provide equivalent performance in service. Products based on olefinic thermoplastic elastomers, copolyesters, styrene butadiene rubber, or other polymer systems might be substituted for silicone elastomers, but these substitutes might not have all of the desirable attributes of the products they would replace. Other resin systems, including fluoropolymers, polyesters, or polyimides might serve as substitutes for silicone resins, but with some expected loss in utility.

Quantifying the economic benefits to consumers that derive from the use of silicone-based products requires information and data on the performance of the substitutes and the loss in utility that consumers would suffer from imperfect substitution. Imperfect substitutes may have shorter service lives, for example, or increase the maintenance costs in a system to the extent that lifecycle costs exceed those for the initially more costly silicone-based products. For United States and Canadian consumers, the net economic benefit in the manufacture of silicone-based products is estimated to be approximately \$1 billion per year.

## *Optical fiber manufacturing*

Optical fibers, which may be made of plastic or glass, are used as the core of high performance telecommunication systems and in various sensors and illumination systems. Glass optical fibers may have core diameters as small as ten to fifty microns (0.01-0.05 mm) while those made of plastic typically have core diameters of more than 1 mm. A major advantage of glass fibers is that they cause significantly lower attenuation of signal strength than do plastic fibers, so use of the latter is confined to relatively short-range systems. The attenuation is also much lower than that for metallic systems, so far fewer repeaters are required to maintain signal strength in long distance transmission lines. Glass optical fibers are used for high bandwidth, high-speed data communication links that can transmit signals hundreds of kilometers with minimal loss in signal quality. Transmission speeds exceeding 10 gigabits per second are possible versus about 1.5 megabits per second for metallic systems. They are far lighter than equivalent metallic links and do not suffer from crosstalk, which leads to signal degradation in multi-strand conductors, and cannot be easily tapped and so are more secure.

Almost all glass optical fibers are made from silica, although other materials may be used for transmission at wavelengths in the infrared region of the spectrum. The glass must be of very high purity and defect free to be drawn to small diameters and have low attenuation loss, and the starting material for glass optical fibers is highly purified tetrachlorosilane.

Consumers have benefited from fiber optic communications for only the last thirty years or so, but its use has grown more than enough to support both the requirements of increased demand for high bandwidth data transmission and other, less demanding uses. It is not clear that alternates to the use of tetrachlorosilane can be developed to deposit silica of the quality required on preforms. Fluorine compounds have corrosive and toxic properties, and use of volatile organosilanes may present difficulties in achieving the required purity. If a chlorine-free manufacturing process could not be developed, consumers would have to use alternatives such as optical fibers based on other technologies or specialty glasses. The latter could be far more costly than glasses based on silica, or lack properties that would permit them to be used economically in long distance communication systems. The next best-performing general substitutes probably would be metallic, electrical-based transmission systems.

In 2005, worldwide optical fiber demand totaled 55 million kilometers, and the United States and Canada accounted for 30% of worldwide fiber demand that year, or 16.5 million kilometers. The market size for fiber optics is estimated to be about \$500 million.<sup>22</sup> Fiber demand has been increasing rapidly, fueled by competition in the communications industry to deliver integrated voice, data, and Internet services (the so-called "triple play" of services).<sup>23</sup> The benefits of chlorine chemistry to consumers of optical fiber can be measured in the reduced cost and increased efficiency of the tetrachlorosilane-based glass fibers vis-à-vis the available alternatives. For United States

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<sup>22</sup> KMI Research, Corning Inc., Communications Today, and Global Insight estimates.

<sup>23</sup> Corning, Inc.

and Canadian consumers, the net economic benefit in the manufacture of glass optical fiber is estimated to be approximately \$2.5 billion per year.

### *Fumed Silica Manufacture*

Fumed silica, made by the flame hydrolysis of tetrachlorosilane, is composed of high purity silica particles that have very large specific surface areas. It finds use as a viscosity extender and filler in a wide variety of materials including adhesives, sealants, elastomers, resins and coatings, and in such consumer products as cosmetics and pharmaceuticals. Its high purity, small particle size, and high specific surface area improve the properties of the materials into which it is added.

Silica fume, a related material, is produced as a byproduct of the manufacture of ferrosilicon and silicon metal. Silica fume is not pure, since it contains more than trace amounts of materials that are also driven off during the silicon metal manufacturing processes. The presence of these impurities, its uncontrolled vitreous structure and morphology, and lack of control of its properties could make it a poor substitute for chlorine-based silica fume in many applications.

The fumed silica market in the United States and Canada is relatively small, amounting to approximately \$450 million in sales. A significant portion of fumed silica production is used captively. The most likely chlorine-free substitutes are fumed silica made by flame hydrolysis of a fluorosilane, or a calcined silica sol made by chemical precipitation of fluosilicic acid. In both cases the fumed silica product would be more costly than material based on chlorine chemistry, and the difference in cost is the benefit that consumers enjoy with access to the materials available today. Due to its relatively small market size, we have not quantified the net economic benefits. They likely would be far lower than any of the products evaluated above.

### **Summary**

Chlorine chemistry is central to the production of the highly purified silicon that is required for the manufacture of silicon-based integrated circuits and solar cells, silicone-based products, glass optical fibers, and high purity fumed silica. No chlorine-free processes have yet been developed that can produce silicon of the required purity, so the absence of chlorine chemistry would force consumers to seek products made from alternate materials.

Other materials could be substituted for silicon in the manufacture of **integrated circuits** and **solar cells**. For example, gallium arsenide is currently used in certain applications where its electrical properties are superior to those of silicon and its much higher cost can be justified. For many other applications, it is not uniquely well suited and consumers could experience performance losses. Production volumes of gallium arsenide would have to increase significantly, however, if it were to substitute for all current uses of semiconductor grade silicon, and this would require massive capital investments in production plants for its purification, wafer production, and in the integrated circuit fabrication plants. For United States and Canadian consumers, the net economic benefit

in the manufacture of integrated circuits and solar cells is estimated to be roughly \$15.5 billion per year.

A variety of currently available elastomers and resins could be substituted for **silicone** products. While many of them are lower in cost than the silicone-based products they would replace, they do not have all of the attributes that consumers currently require and would be imperfect substitutes. Consumers would suffer loss of utility if forced to rely on them. For United States and Canadian consumers, the net economic benefit in the manufacture of silicones is estimated to be roughly \$1 billion per year.

In the absence of **glass optical fibers**, high-speed and high-bandwidth communication over long distances would take place via metallic electrical conductors, which are more costly to install and maintain than fiber optic cables. For United States and Canadian consumers, the net economic benefit in the manufacture of glass optical fiber is estimated to be about \$2.5 billion per year.

In the aggregate, the economic benefit to United States and Canadian consumers in these end uses amounted to approximately \$19 billion per year in 2004. This result is based on the differences between the current costs for these products and the costs for their substitutes, including losses in utility. These benefits are extremely large relative to the amount of chlorine that is consumed to produce them, less than 0.5% of total chlorine consumption in North America.

### **Silicones: Past, Present, and Future**

***Preserving our past:*** To protect historic buildings and landmarks, preservationists are increasingly turning to silicon-based products, due to their superior resistance to sunlight, ozone, rain, snow, or temperature extremes. Compared to some commonly used organic urethane sealants, silicone sealants can provide protection for more than twice as long. For nearly its first 50 years, Mount Rushmore required annual maintenance that consists of filling cracks with a patching compound of granite dust, white lead, and linseed oil. But as soon as the linseed oil dries out, the cracks reappeared. In the 1990s, the National Park Service chose high performance silicone sealants. Similarly, to restore the Statue of Liberty, which was showing its age and leaking, historical architects selected silicone sealants for its superior adhesion capabilities to copper. Silicone can bond without damage and is compatible with residual original coal tars used 100 years ago. Because silicone rubber can adhere without damaging the original material or surface patina, it was also used to create molds that enabled the restoration of Michelangelo's famous sculpture, Pietà, which was damaged by vandalism in the 1970s.

***Enabling the present:*** After extensive use in the aerospace industry in the 1940s, silicones expanded into healthcare and medical applications during the following decade. Because our bodies do not react strongly to the presence of silicones, the use of silicones facilitates healing and reduces discomfort. From respiratory tubing and impression moulds for bridge and crown reconstruction, to burn treatment gauzes and prosthetics, silicones are the preferred material. In the case of prosthetics, silicones can most closely approximate the consistency of skin and offer exceptional cushioning and comfort. Silicone hydrogel contact lenses allow at least four times more oxygen to flow through the lens into the eyes than traditional soft lenses. Increased oxygen is the key to comfort and to avoiding dryness and infection. Only 6 million Americans have had laser eye surgery, but about 40 million wear contact lenses.

***Protecting our future:*** Nipples for baby bottles are usually made of latex rubber or silicone. Of the two, silicone is the material of choice since latex rubber nipples can release nitrosamines, potent carcinogens, when babies suckle the nipple. Also latex rubber nipples tend to break down faster than silicone nipples. Cracks tend to harbor bacterial growth. Durability, tear-resistance and flexibility are among silicones' most important properties when added to infant care applications. Today, silicones are used in baby bottle nipples, breast pumps, sippy cup valves and pacifiers.

Source: European Chemistry Industry Council (CEFIC), Dow Corning, Centre Européen des Silicones, Environmental Health Association of Nova Scotia, American Academy of Optometry, Market Scope