FIG. 1A

Title: METHODS AND SYSTEMS FOR PRODUCING SILICON, E.G., POLYSILICON, INCLUDING RECYCLING BYPRODUCTS

Abstract: Systems and processes are provided for efficient, cost-effective production of silicon by chemical vapor deposition. Reaction byproducts are recycled for use within the systems and processes without recovery and external processing of the byproducts. The systems and processes provide savings in both capital and operating costs.
METHODS AND SYSTEMS FOR PRODUCING SILICON, E.G.,
POLYSILICON, INCLUDING RECYCLING BYPRODUCTS

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims benefit under 35 U.S.C. 119(e) of US Provisional Patent Application Serial Nos. 61/286,698, filed December 15, 2009; 61/346,395, filed May 19, 2010; 61/361,739, filed July 6, 2010; 61/389,139, filed October 1, 2010; and 61/389,674, filed October 4, 2010; each entitled "METHODS AND SYSTEMS FOR PRODUCING SILICON, E.G., POLYSILICON, INCLUDING RECYCLING BYPRODUCTS" and incorporated herein by reference in their entirety.

TECHNICAL FIELD

This disclosure generally relates to the field of systems and processes for the production of silicon, e.g., polysilicon. This disclosure relates in particular to production of silicon by chemical vapor deposition and recycling of reaction byproducts to improve the cost effectiveness of silicon production.

BACKGROUND

The demand for silicon, specifically polysilicon, is very large due to its use in a variety of applications, in particular the semiconductor and the solar power (i.e., photovoltaic) industries. The semiconductor industry has typically required silicon of higher purity than that required by other industries, although others, such as those manufacturing solar wafers, have now begun using higher purity silicon as well. Because of the demand for silicon, production plants have been built at various locations throughout the world. Facilities may be very large, designed to produce silicon at levels of thousands of metric tons annually.
Processes for producing polysilicon may be carried out in different types of reaction devices, including chemical vapor deposition reactors and fluidized bed reactors. Various aspects of the chemical vapor deposition (CVD) process, *i.e.*, the Siemens or "hot wire" process, have been described, for example in a variety of U.S. patents or published applications (*see*, *e.g.*, U.S. Patent Nos. 3,011,877; 3,099,534; 3,147,141; 4,150,168; 4,179,530; 4,311,545; and 5,118,485).

Silane and trichlorosilane are both used as feed materials for the production of polysilicon. Silane is more readily available as a high purity feedstock because it is easier to purify than trichlorosilane. Production of trichlorosilane introduces boron and phosphorus impurities, which are difficult to remove because they tend to have boiling points that are close to the boiling point of trichlorosilane itself. Although both silane and trichlorosilane are used as feedstock in Siemens-type chemical vapor deposition reactors, trichlorosilane is more commonly used in such reactors. Silane, on the other hand, is a more commonly used feedstock for production of polysilicon in fluidized bed reactors.

Silane has drawbacks when used as a feedstock for either chemical vapor deposition or fluidized bed reactors. Producing polysilicon from silane in a Siemens-type chemical vapor deposition reactor may require up to twice the electrical energy compared to producing polysilicon from trichlorosilane in such a reactor. Further, the capital costs are high because a Siemens-type chemical vapor deposition reactor yields only about half as much polysilicon from silane as from trichlorosilane. Thus, any advantages resulting from higher purity of silane are offset by higher capital and operating costs in producing polysilicon from silane in a Siemens-type chemical vapor deposition reactor. This has led to the common use of trichlorosilane as feed material for production of polysilicon in such reactors.

Silane as feedstock for production of polysilicon in a fluidized bed reactor may be advantageous in terms of electrical energy usage compared to production in Siemens-type chemical vapor deposition reactors. However,
there are disadvantages that offset the operating cost advantages. In the fluidized bed reactor, the process itself may result in a lower quality polysilicon product even though the purity of the feedstock is high. For example, the process may form polysilicon dust, which may interfere with operation by forming particulate material within the reactor and may also decrease the overall yield. Further, polysilicon produced in a fluidized bed reactor may contain residual hydrogen gas, which must be removed by subsequent processing. In addition, polysilicon produced in a fluidized bed reactor may also include metal impurities due to abrasive conditions within the fluidized bed.

Thus, although high purity silane may be readily available, its use as a feedstock for the production of polysilicon in either type of reactor may be limited by the disadvantages noted.

In summary, use of silane as a feedstock for the production of polysilicon by either Siemens-type chemical vapor deposition reactors or fluidized bed reactors is limited because of considerations of cost and/or quality of the polysilicon produced. Thus, there remains a need in the industry for a capital and operating cost effective process by which to convert silane to polysilicon while retaining the high quality inherent in use of silane as a feedstock.

Reactions taking place in CVD reactors release gaseous materials that include reaction byproducts, i.e., excess reactants that have not undergone conversion in the CVD reactor, and oily polymeric materials such as polysilyl compounds. Byproducts include various chlorosilanes, in particular silicon tetrachloride, as well as hydrogen chloride. Methods have been proposed and are utilized to improve efficiency of the processes, to decrease operating costs, and to deal with environmental issues arising from release and disposal of byproducts of polysilicon production. There remain, however, unfilled needs for further improvements to process efficiencies, including recycling of byproducts and reactants, and savings on plant construction and operating costs. These include in particular increased efficiencies and cost
savings associated with reuse and/or disposal of byproducts and excess reactants.

A major cost in both plant construction and operation relates to building and operating facilities to handle byproducts, in particular silicon tetrachloride. In the production of polysilicon by the CVD or Siemens process, even if conversion of trichlorosilane to silicon were complete, nearly three moles of silicon tetrachloride byproduct would be produced for each mole of silicon deposited in the CVD reactor. In fact, typically 20% or less of the trichlorosilane is converted to silicon in a single pass through the reactor. Conversion efficiency depends on a variety of factors, including composition of the gas delivered to the reactor, design of the reactor, and operating conditions, such as silicon-to-chlorine ratio, temperature, and pressure. However, regardless of the conversion efficiency, reaction stoichiometry in the CVD reactor still dictates that silicon tetrachloride must be a major byproduct resulting from the conversion in the reactor and a primary component of the gaseous material released from the CVD reactor. Typically the components of the gaseous material are separated and either recycled at some point back into the feed for the CVD reactor or recovered for other uses or discarded. In particular, silicon tetrachloride is separated from the other components of the gaseous material and is either discarded or reprocessed in a separate facility to convert it to trichlorosilane to be reintroduced as feed material to the CVD reactor. If discarded, it is not only of environmental concern but also represents loss of a very large proportion of the silicon in the initial feed to the CVD reactor. Thus, the silicon tetrachloride recovered from the gaseous material released from the CVD reactor is more typically reprocessed in thermal converters in a physically and often geographically remote facility to form additional trichlorosilane. The thermal converters operate at temperatures typically in excess of 1000°C, a temperature which is achieved by passing electricity through a carbon electrode. Disadvantages of converting silicon tetrachloride to trichlorosilane by use of thermal converters thus include very high electrical energy requirements, which represent a large proportion of the
cost of operating a chemical vapor deposition polysilicon production facility. Further, in such a process, the thermal converters typically convert only about 20% of the silicon tetrachloride to trichlorosilane per pass through the converter and thus separation, e.g., by distillation, and multiple passes are required. It is estimated that the cost for building the plant for thermal conversion of silicon tetrachloride represents 10-20% of the capital cost for building an entire polysilicon production facility. It is further estimated that the cost for operating the plant for thermal conversion of the silicon tetrachloride represents 10-20% of the cost for operating the entire polysilicon production facility. Further, because of the use of a carbon electrode, trichlorosilane produced in the thermal conversion process may be contaminated by carbon/graphite originating in the process. The trichlorosilane produced thus requires further purification to yield a material of purity appropriate for production of high purity silicon such as for use in the semiconductor or increasingly in the solar energy industry, thereby adding to both the capital and operating costs. A further disadvantage of the use of thermal converters is that the process yields a significant amount of dichlorosilane byproduct. Although dichlorosilane may be converted to silicon in the CVD reactor, the silicon so produced may not be within required specifications unless the process is very carefully controlled. Excess dichlorosilane may also be produced in the upstream operations in the polysilicon plant. Because of the production of excess dichlorosilane, it may typically accumulate in storage tanks. Accumulated amounts of dichlorosilane must thus ultimately be destroyed in an environmentally acceptable manner, e.g., in a waste treatment facility, a practice which is widely used in the silicon industry. Elimination of processes which produce excess dichlorosilane and thus the need to discard this material would provide significant savings in operating a polysilicon production facility.

Many polysilicon production processes currently in use produce not only chlorosilanes as byproducts, but also hydrogen chloride. Like the chlorosilanes, hydrogen chloride also includes a potentially useful component of the processes for producing polysilicon, namely chlorine. Thus, as with
chlorosilane byproducts, there may also be advantages to recycling hydrogen chloride. For example, since chlorine-containing trichlorosilane is a primary reactant fed to a CVD reactor to produce polysilicon, recycling any byproduct that may return chlorine to the process may be advantageous. Further, although there is a market for purified hydrogen chloride for uses other than polysilicon production, such uses require purification of the hydrogen chloride. Thus, processing the hydrogen chloride byproduct to be suitable for other uses typically requires building and operating additional facilities, or at least additional systems, for purification and storage of the hydrogen chloride.

Cycling hydrogen chloride back into some aspect of the polysilicon production process may thus be advantageous for a variety of reasons. However, suitability of recycling hydrogen chloride depends on the processes used in producing polysilicon.

Certain processes for producing polysilicon readily allow efficient, cost-effective cycling of hydrogen chloride back into the process. However, because reactions of hydrogen chloride with various compounds in the processes, e.g., silicon or silane, may be highly exothermic, recycling may present challenges. For example, recycling hydrogen chloride may result in marked temperature increases within the systems, requiring cooling mechanisms and/or careful control of reaction conditions. Because some commonly used processes for polysilicon production include exothermic reactions, facilities designed for such processes include systems for temperature control, specifically cooling. Such systems may thus readily handle temperature increases that may result from reactions that occur by cycling hydrogen chloride back into the processes. On the other hand, polysilicon production processes that do not include highly exothermic reactions do not generate heat and thus do not require such cooling systems. Facilities designed for such processes thus may be less suitable for recycling the hydrogen chloride byproduct.

Among the various processes involved in producing polysilicon, the methods of making trichlorosilane to be supplied to the CVD reactor differ in
important respects. In a common process, for example, metallurgical grade silicon and hydrogen chloride react to form trichlorosilane. Following purification, the trichlorosilane is fed to the CVD reactor. In such processes, certain byproducts of the CVD reaction, such as silicon tetrachloride, may typically be discarded or thermally converted to trichlorosilane with associated disadvantages, including high capital costs during construction and high electrical energy costs during operation. Others may be cycled back into certain points in the process, such as hydrogen and hydrogen chloride. Because hydrogen chloride is utilized in such polysilicon production facilities, byproduct hydrogen chloride can be readily cycled back into the process. In particular, because reaction of hydrogen chloride with metallurgical grade silicon in such processes is highly exothermic, the facilities designed and built to make polysilicon according to these processes include specialized cooling systems suitable to handle the recycled hydrogen chloride byproduct. Because of the cooling and energy requirements, the cost of building and operating such facilities is high.

Another of the current processes for producing polysilicon combines metallurgical grade silicon, silicon tetrachloride and hydrogen to produce the trichlorosilane for the CVD reactor. In such processes, the reactions are endothermic. Thus, facilities designed to produce polysilicon by such processes do not have the same equipment and operating requirements as those designed for processes using hydrogen chloride. In particular, such facilities do not require specialized cooling systems. Thus, making plants for such processes suitable for recycling hydrogen chloride byproduct would require significant additional capital and operating costs and introduce inherent reactor complexity due to co-reaction of silicon tetrachloride and hydrogen chloride under significantly different fluidization regimes. Thus, different approaches for recycling hydrogen chloride may be advantageous in polysilicon production facilities or processes that have not been designed and built to handle reactions utilizing hydrogen chloride, particularly highly exothermic reactions.
BRIEF SUMMARY

Needs exist in the polysilicon industry for (1) more cost-effective use of silane as a feedstock for the CVD reactor; (2) alternatives to the use of thermal converters in the trichlorosilane-based CVD process; (3) lower capital and operating costs in the CVD process; (4) improved methods for control of dichlorosilane concentration in trichlorosilane feed to CVD reactors; (5) effective methods for recycling byproducts from the CVD reactor, in particular silicon tetrachloride and hydrogen chloride; and (6) overall more cost-effective production of high purity polysilicon.

Improved processes for handling the silicon tetrachloride and hydrogen chloride made during the production of polysilicon in a chemical vapor deposition facility could provide both capital and operating cost savings. For example, eliminating the need for thermal conversion of silicon tetrachloride to trichlorosilane could provide a cost savings of 10-20% compared to a typical facility for producing polysilicon by chemical vapor deposition. Significant cost savings could also be realized by controlling the chlorine balance throughout the processes, for example by limiting production of and optimally recycling hydrogen chloride. Such may yield an additional 10-20% savings in the cost to manufacture polysilicon. Eliminating the requirement for co-reaction of silicon tetrachloride and hydrogen chloride, using methods described herein, would allow better plant utilization with fewer shutdowns for cause. Further, use of higher purity silane in such an improved process employing chemical vapor deposition reactors, e.g., Siemens-type reactors, could provide silicon suitable for applications requiring higher purity silicon.

A method of producing silicon may be summarized as including reacting a disproportionation reactor feed comprising silane and silicon tetrachloride by a disproportionation reactor; performing a chemical vapor deposition on a mixture from the disproportionation reactor by a chemical vapor deposition reactor to deposit silicon on a substrate within the chemical vapor deposition reactor; and recovering silicon from the chemical vapor deposition reactor.
The method may further include separating hydrogen from a byproduct mixture of the chemical vapor deposition comprising hydrogen and silicon tetrachloride to yield a composition comprising silicon tetrachloride; mixing the composition comprising silicon tetrachloride and a composition comprising silane by a pre-disproportionation reactor silane/chlorosilane mixer to yield the disproportionation reactor feed comprising silane and silicon tetrachloride; controlling the temperature of the disproportionation reactor feed comprising silane and silicon tetrachloride by a pre-disproportionation reactor temperature controller; and reacting the components of the disproportionation reactor feed comprising silane and silicon tetrachloride by the disproportionation reactor to form a disproportionation reaction product comprising dichlorosilane, trichlorosilane and silicon tetrachloride. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include mixing a composition comprising dichlorosilane and a composition comprising silane. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include mixing a composition comprising trichlorosilane and a composition comprising silane. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include mixing a composition comprising hydrogen chloride and a composition comprising silane. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include mixing a composition comprising liquid or vapor silane and a composition comprising liquid or vapor silicon tetrachloride. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 10 psig to about 500 psig. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one of both of the pre-
disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 50 psig to about 300 psig. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 150 psig to about 200 psig. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure of about 180 psig. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 500 psig to about 2500 psig. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 1500 psig to about 2500 psig. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 1800 psig to about 2200 psig. Mixing the composition comprising silicon tetrachloride and a composition comprising silane may include providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-
disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure of about 2000 psig.

The disproportionation reactor may include a catalyst. The catalyst may include a polymeric ion exchange resin. The catalyst may include a metal. The catalyst may include copper. The catalyst may include copper-infused essentially pure silicon.

Controlling the temperature of the disproportionation reactor feed comprising silane and silicon tetrachloride may include controlling the temperature of the disproportionation reactor feed in a range of from about 55°C to about 500°C. Controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may include controlling the temperature of the disproportionation reactor feed in a range from about 300°C to about 500°C. Controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may include controlling the temperature of the disproportionation reactor feed in a range from about 200°C to about 400°C. Controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may include controlling the temperature of the disproportionation reactor feed in a range from about 90°C to about 200°C. Controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may include controlling the temperature of the disproportionation reactor feed in a range from about 30°C to about 90°C. Controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may include controlling the temperature of the disproportionation reactor feed in a range of from about 55°C to about 75°C. Controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may include controlling the temperature of the
disproportionation reactor feed in a range of from about 60°C to about 70°C. Controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may include controlling the temperature of the disproportionation reactor feed to about 60°C.

Mixing a composition comprising silane and a composition comprising silicon tetrachloride may include mixing a composition comprising silane in a vapor phase, a liquid phase, or a vapor-liquid mixed phase and a composition comprising silicon tetrachloride in a vapor phase, a liquid phase, or a vapor-liquid mixed phase.

The method may further include controlling the composition of the composition comprising silicon tetrachloride or the rate at which the composition comprising silicon tetrachloride is supplied to the pre-disproportionation reactor silane/chlorosilane mixer such that the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride ranges between about 2:1 and about 3.9:1. The ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may range between about 2.5:1 and about 3.5:1. The ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may range between about 2.8:1 and about 3.3:1. The ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may be about 2.8:1. The ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may be about 3:1. The ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may be about 3.2:1. The ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride may be about 3.3:1.

The method may further include separating silicon tetrachloride from a product of the disproportionation reaction in a post-disproportionation reactor silicon tetrachloride separator to yield a post-disproportionation reactor
silicon tetrachloride-rich stream and a post-disproportionation reactor trichlorosilane-rich stream.

The method may further include adjusting silicon tetrachloride content of the disproportionation reactor feed using the silicon tetrachloride separated from the product of the disproportionation reactor in the post-disproportionation reactor silicon tetrachloride separator.

The method may further include separating dichlorosilane from the post-disproportionation reactor trichlorosilane-rich stream by a post-disproportionation reactor dichlorosilane separator to yield a post-disproportionation reactor dichlorosilane-rich stream.

The method may further include determining dichlorosilane concentration in a feed to the chemical vapor deposition reactor; and adjusting the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor. Adjusting the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor may include adding the post-disproportionation reactor dichlorosilane-rich stream to the feed to the chemical vapor deposition reactor. Adjusting the concentration of dichlorosilane in the chemical vapor deposition reactor may include adding dichlorosilane separated from a chemical vapor deposition reactor effluent mixture from which hydrogen and hydrogen chloride have been removed.

The method may further include separating dichlorosilane from trichlorosilane in the post-disproportionation reactor trichlorosilane-rich stream by a post-disproportionation reactor dichlorosilane/trichlorosilane separator to yield a post-disproportionation reactor dichlorosilane-rich/trichlorosilane-depleted material and a post-disproportionation reactor trichlorosilane-rich/dichlorosilane-depleted material. The post-disproportionation reactor dichlorosilane-rich/trichlorosilane-depleted material may be essentially pure dichlorosilane.

The method may further include determining dichlorosilane concentration in the post-disproportionation reactor dichlorosilane-rich/trichlorosilane-depleted material.
The method may further include determining trichlorosilane concentration in the post-disproportionation reactor trichlorosilane-rich/dichlorosilane-depleted material.

The method may further include storing the dichlorosilane-rich/trichlorosilane-depleted material in a dichlorosilane storage system.

The method may further include storing the trichlorosilane-rich/dichlorosilane-depleted material in a trichlorosilane storage system.

The method may further include mixing the dichlorosilane-rich/trichlorosilane-depleted material to yield a chemical vapor deposition reactor feed; and supplying the feed to the chemical vapor deposition reactor. Mixing the dichlorosilane-rich/trichlorosilane-depleted material with the trichlorosilane-rich/dichlorosilane-depleted material may include mixing dichlorosilane-rich/trichlorosilane-depleted material from the dichlorosilane storage system.

Mixing the dichlorosilane-rich/trichlorosilane-depleted material with the trichlorosilane-rich/dichlorosilane-depleted material may include mixing trichlorosilane-rich/dichlorosilane-depleted material from the trichlorosilane storage system. Mixing the dichlorosilane-rich/trichlorosilane-depleted material with the trichlorosilane-rich/dichlorosilane-depleted material to yield a chemical vapor deposition reactor feed may include adjusting a ratio of chlorine to silicon in the chemical vapor deposition reactor feed.

The method may further include vaporizing the disproportionation reaction product in a pre-CVD reactor vaporizer to yield a vaporized disproportionation reaction product; mixing hydrogen with the vaporized disproportionation reaction product to yield a mixture of hydrogen and disproportionation reaction product; and performing chemical vapor deposition on the mixture of hydrogen and disproportionation reaction product by the chemical vapor deposition reactor to deposit silicon on the substrate within the chemical vapor deposition reactor. Mixing hydrogen with the vaporized disproportionation reaction product may include mixing hydrogen with the vaporized disproportionation reaction product by a pre-CVD reactor mixer.
Mixing hydrogen with the vaporized disproportionation reaction product may include mixing hydrogen with the vaporized disproportionation reaction product in the chemical vapor deposition reactor.

The method may further include releasing from the chemical vapor deposition reactor an effluent mixture comprising hydrogen, silicon tetrachloride, and one or more of hydrogen chloride, dichlorosilane and trichlorosilane.

The method may further include cooling by a post-CVD reactor first cooler the effluent mixture from the chemical vapor deposition reactor to yield a vapor-liquid two-phase mixture.

The method may further include removing oily contaminants, including polysilyl materials, from the effluent mixture cooled by the first cooler.

The method may further include separating by a post-CVD reactor decanter the vapor-liquid two-phase mixture from the first cooler to yield a vapor phase and a liquid phase.

The method may further include converting the vapor phase from the decanter to a vapor-liquid two-phase mixture by a post-CVD reactor compressor.

The method may further include cooling by a post-CVD reactor second cooler the vapor-liquid two-phase mixture or the vapor phase from the compressor.

The method may further include supplying the effluent mixture from the chemical vapor deposition reactor to a post-CVD reactor in situ hydrogen chloride reactor; and converting hydrogen chloride in the effluent mixture from the chemical vapor deposition reactor to chlorosilanes by the post-CVD reactor in situ hydrogen chloride reactor. A residence time of the effluent mixture from the chemical vapor deposition reactor within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 10 minutes. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 5 minutes. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen
chloride reactor may be less than about 1 minute. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 0.5 minute. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 0.1 minute.

The method may further include heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor. Heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger may include heating the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 200°C to about 700°C. Heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger may include heating the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 300°C to about 600°C. Heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger may include heating the effluent mixture from the chemical vapor deposition reactor to a temperature of about 500°C. The in situ hydrogen chloride reactor heat exchanger may exchange heat from an effluent from the post-CVD reactor in situ hydrogen chloride reactor to the effluent mixture from the chemical vapor deposition reactor before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor.

The method may further include heating the effluent mixture from the chemical vapor deposition reactor by a post-CVD reactor startup heater before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor via the in situ hydrogen chloride reactor heat exchanger.

The method may further include cooling by a post-CVD reactor first cooler an effluent mixture from the post-CVD reactor in situ hydrogen
chloride reactor to yield a vapor-liquid two-phase mixture; separating by a post-CVD reactor decanter the vapor-liquid two-phase mixture from the first cooler to yield a vapor phase and a liquid phase; converting the vapor phase from the decanter to a vapor-liquid two-phase mixture or a vapor phase by a post-CVD reactor compressor; and cooling the vapor-liquid two-phase mixture from the compressor system by a post-CVD reactor second cooler.

The method may further include separating the hydrogen from the chemical vapor deposition reactor effluent mixture by a post-CVD reactor hydrogen separator to yield a post-CVD reactor hydrogen-rich stream and a post-CVD reactor hydrogen-depleted stream. The concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream may be less than 15 weight%. The concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream may be less than 10 weight%. The concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream may be less than 5 weight%. The concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream may be less than 1 weight%. The concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream may be less than 0.1 weight%.

The method may further include mixing by a pre-CVD reactor mixer the post-CVD reactor hydrogen-rich stream with a post-disproportionation reactor trichlorosilane-rich stream from a post-disproportionation reactor silicon tetrachloride separator.

The method may further include mixing the post-CVD reactor hydrogen-depleted stream and a post-disproportionation reactor silicon tetrachloride-rich stream from the post-disproportionation reactor silicon tetrachloride separator by a pre-disproportionation reactor chlorosilane mixer.

The method may further include determining amounts of elemental silicon and elemental chlorine in the post-CVD reactor hydrogen-depleted stream and in the post-disproportionation reactor silicon tetrachloride-rich stream prior to mixing the post-CVD reactor hydrogen-depleted stream and the post-disproportionation reactor silicon tetrachloride-rich stream.
The method may further include mixing by the pre-disproportionation reactor chlorosilane mixer amounts of the post-CVD reactor hydrogen-depleted stream; the post-disproportionation reactor silicon tetrachloride-rich stream; and, as required, a feed of purified silicon tetrachloride, trichlorosilane, dichlorosilane, or a mixture of one or more of purified silicon tetrachloride, trichlorosilane, or dichlorosilane; and controlling the amounts of elemental chlorine and elemental silicon supplied from each source to maintain a selected ratio of chlorine to silicon in the disproportionation reactor feed.

The method may further include separating by a post-CVD reactor hydrogen chloride separator hydrogen chloride from the post-CVD reactor hydrogen-depleted stream to yield a post-CVD reactor hydrogen-depleted, hydrogen chloride-rich stream and a post-CVD reactor hydrogen-depleted, hydrogen chloride-depleted stream.

The method may further include transporting the post-CVD reactor hydrogen-depleted, hydrogen chloride-rich stream from the post-CVD reactor hydrogen chloride separator to a hydrogen chloride storage system.

The method may further include transporting the post-CVD reactor hydrogen-depleted, hydrogen chloride-depleted stream from the post-CVD reactor hydrogen chloride separator to a pre-disproportionation reactor chlorosilane mixer.

The method may further include separating by a post-CVD reactor chlorosilane separator silicon tetrachloride from dichlorosilane and trichlorosilane in the hydrogen-depleted, hydrogen chloride-depleted stream to yield a post-CVD reactor silicon tetrachloride-rich stream and a post-CVD reactor dichlorosilane-rich, trichlorosilane-rich stream.

The method may further include separating the dichlorosilane from the trichlorosilane in the post-CVD reactor dichlorosilane-rich, trichlorosilane-rich stream by a dichlorosilane/trichlorosilane separator to yield a post-CVD reactor dichlorosilane-rich stream and a post-CVD reactor trichlorosilane-rich stream.
The method may further include mixing the post-CVD reactor trichlorosilane-rich stream with a post-disproportionation reactor trichlorosilane-rich stream.

The method may further include mixing the post-CVD reactor silicon tetrachloride-rich stream and the post-CVD reactor dichlorosilane-rich stream by a post-CVD reactor chlorosilane mixer. Mixing the silicon tetrachloride-rich stream and the dichlorosilane-rich stream by a post-CVD reactor chlorosilane mixer may include selecting an amount of dichlorosilane and adding the amount of dichlorosilane to the post-CVD reactor chlorosilane mixer thereby controlling the concentration of dichlorosilane in the feed to the disproportionation reactor and the chemical vapor deposition reactor. Controlling the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor may include controlling the ratio of chlorine to silicon in the feed to the disproportionation reactor. Controlling the ratio of chlorine to silicon in the feed to the disproportionation reactor may include controlling one or more of make-up silicon tetrachloride, trichlorosilane, and dichlorosilane added to the feed to the disproportionation reactor.

The method may further include supplying dichlorosilane from the dichlorosilane/trichlorosilane separator to the chemical vapor deposition reactor. Supplying dichlorosilane from the dichlorosilane/trichlorosilane separator to the chemical vapor deposition reactor may include adjusting the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor.

The method may further include storing all or a portion of the dichlorosilane in a dichlorosilane storage system or disposing of the dichlorosilane by a dichlorosilane disposal system.

The method may further include separating hydrogen and hydrogen chloride from the chemical vapor deposition reactor effluent mixture by a post-CVD reactor hydrogen/hydrogen chloride separator to yield a hydrogen/hydrogen chloride-rich stream and a hydrogen/hydrogen chloride-depleted stream; separating the hydrogen from the hydrogen chloride in the
hydrogen/hydrogen chloride-rich stream by a pre-CVD reactor hydrogen/hydrogen chloride separator; and transporting the hydrogen chloride from the pre-CVD reactor hydrogen/hydrogen chloride separator to a hydrogen chloride storage system.

The method may further include mixing by a pre-CVD reactor mixer the hydrogen from the pre-CVD reactor hydrogen/hydrogen chloride separator with a disproportionation reactor trichlorosilane-rich stream from the post-disproportionation reactor silicon tetrachloride separator.

The method may further include feeding the hydrogen-depleted, hydrogen chloride-rich stream from the post-CVD reactor hydrogen chloride separator and silane to a pre-disproportionation reactor silane/hydrogen chloride reactor; and reacting the silane with the hydrogen chloride by the pre-disproportionation reactor silane/hydrogen chloride reactor to yield chlorosilanes including trichlorosilane and silicon tetrachloride. A temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor may range between about 50°C and 700°C. The temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor may range between about 100°C and 600°C. The temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor may range between about 300°C and 500°C. The temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor may be about 500°C. A molar ratio of silane to hydrogen chloride in the feed to the pre-disproportionation reactor silane/hydrogen chloride reactor may range from about 0:1 to about 2:1. The molar ratio of silane to hydrogen chloride may range from about 0:1 to about 1.5:1. The molar ratio of silane to hydrogen chloride may range from about 0:1 to about 1:1. The molar ratio of silane to hydrogen chloride may be about 0.33:1. Reacting the silane with the hydrogen chloride by a pre-disproportionation reactor silane/hydrogen chloride reactor may include reacting the silane with the hydrogen chloride in the presence of a metal-containing catalyst. The metal-containing catalyst may include copper. The metal-containing catalyst may include copper-infused essentially pure silicon.
The method may further include mixing by the pre-disproportionation reactor chlorosilane mixer amounts of the post-CVD reactor hydrogen-depleted, hydrogen chloride-depleted stream; the chlorosilanes from the pre-disproportionation reactor silane/hydrogen chloride reactor; a silicon tetrachloride-rich stream from a post-disproportionation reactor silicon tetrachloride separator; and, as required, a feed of purified silicon tetrachloride, purified trichlorosilane, purified dichlorosilane, or a mixture of one or more of purified silicon tetrachloride, purified trichlorosilane, or purified dichlorosilane; and controlling the amounts of elemental chlorine and elemental silicon supplied from each source to maintain a selected ratio of chlorine to silicon in feed to the disproportionation reactor.

The method may further include reacting by a post-CVD reactor silane/hydrogen chloride reactor the hydrogen-depleted, hydrogen chloride-rich stream from the post-CVD reactor hydrogen chloride separator with silane and the chemical vapor deposition reactor effluent mixture.

The method may further include adjusting the temperature of the chemical vapor deposition reactor effluent mixture in the post-CVD reactor silane/hydrogen chloride reactor to between about 200°C and about 600°C prior to mixing the hydrogen-depleted, hydrogen chloride-rich stream with the silane and the chemical vapor deposition reactor effluent mixture in the post-CVD reactor silane/hydrogen chloride reactor. Adjusting the temperature of the chemical vapor deposition reactor effluent in the post-CVD reactor silane/hydrogen chloride reactor may include adjusting the temperature by a post-CVD reactor heat exchanger. Adjusting the temperature of the chemical vapor deposition reactor effluent mixture in the post-CVD reactor silane/hydrogen chloride reactor prior to mixing the hydrogen chloride with the silane and the chemical vapor deposition reactor effluent mixture may include adjusting the temperature to between about 400°C and about 500°C. A molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor silane/hydrogen chloride reactor may range from about 0:1 to about 2:1. A molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor
silane/hydrogen chloride reactor may range from about 0:1 to about 1.5:1. A molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor silane/hydrogen chloride reactor may range from about 0:1 to about 1:1. A molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor silane/hydrogen chloride reactor may be about 0.33:1.

The method may further include adjusting the flow in the post-CVD reactor silane/hydrogen chloride reactor such that a residence time of the hydrogen chloride-silane-CVD effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor is sufficient to allow complete reaction of the hydrogen chloride and the silane. The post-CVD reactor silane/hydrogen chloride reactor may include one or more reaction chambers of sufficient total volume to provide a residence time appropriate to allow complete reaction of the hydrogen chloride and the silane. The residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor may be less than about 10 minutes. The residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor may be less than about 5 minutes. The residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor may be less than about 1 minute. The residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor may be less than about 0.5 minute. The residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor may be less than about 0.1 minute.

The method may further include mixing one or more of monochlorosilane, dichlorosilane, and trichlorosilane with the disproportionation reactor feed by a pre-disproportionation reactor chlorosilane mixer prior to reacting the disproportionation reactor feed by the disproportionation reactor. A molar ratio of the one or more of monochlorosilane, dichlorosilane, and trichlorosilane to silicon tetrachloride may range from about 0 to about 3:1. The molar ratio of the one or more of monochlorosilane, dichlorosilane, and trichlorosilane to silicon tetrachloride may range from about 0 to about 2.5:1. The molar ratio of the one or more of monochlorosilane, dichlorosilane, and
trichlorosilane to silicon tetrachloride may range from about 0.1:1 to about 1:1. A molar ratio of the one or more of monochlorosilane, dichlorosilane, and trichlorosilane to silicon tetrachloride may be about 0.5:1.

The method may further include converting low boiling phosphorus contaminants to intermediate and high boiling phosphorus contaminants by the disproportionation reactor. Low boiling phosphorus contaminants may include PH$_3$ and PH$_2$Cl. Intermediate boiling phosphorus contaminants include PHCl$_2$. High boiling phosphorus contaminants include PCl$_3$.

The method may further include separating silicon tetrachloride and intermediate and high boiling phosphorus contaminants from low boiling phosphorus contaminants in a disproportionation reaction effluent by a post-disproportionation reactor silicon tetrachloride separator.

The method may further include separating the high boiling phosphorus contaminants from the silicon tetrachloride and the intermediate boiling phosphorus contaminants in a high-boiling phosphorus separator.

The method may further include discarding the high boiling phosphorus contaminants.

The method may further include cycling the intermediate boiling phosphorus contaminants to the disproportionation reactor; and converting intermediate boiling phosphorus contaminants to high boiling phosphorus contaminants by the disproportionation reactor.

A method of producing silicon may be summarized as including performing a chemical vapor deposition on a mixture comprising trichlorosilane by a chemical vapor deposition reactor; recovering silicon from the chemical vapor deposition reactor; releasing from the chemical vapor deposition reactor an effluent mixture comprising hydrogen, silicon tetrachloride, and one or more of hydrogen chloride, dichlorosilane, and trichlorosilane; and converting hydrogen chloride in the effluent mixture from the chemical vapor deposition reactor to chlorosilanes by a post-CVD reactor in situ hydrogen chloride reactor.
The method may further include controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a post-CVD reactor heat exchanger before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor. Controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a post-CVD reactor heat exchanger may include controlling the temperature of the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 200°C to about 700°C. Controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a post-CVD reactor heat exchanger may include controlling the temperature of the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 300°C to about 600°C. Controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a post-CVD reactor heat exchanger may include controlling the temperature of the effluent mixture from the chemical vapor deposition reactor to a temperature of about 500°C. The post-CVD reactor heat exchanger may exchange heat from an effluent from the post-CVD reactor in situ hydrogen chloride reactor to the effluent mixture from the chemical vapor deposition reactor before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor. A residence time of the effluent mixture from the chemical vapor deposition reactor within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 10 minutes. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 5 minutes. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 1 minute. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 0.5 minute. The residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor may be less than about 0.1 minute.
The method may further include cooling by a first cooling system an effluent mixture from the post-CVD reactor in situ hydrogen chloride reactor.

The method may further include converting the effluent mixture from the post-CVD reactor in situ hydrogen chloride reactor to a vapor-liquid two-phase mixture by a compressor system.

The method may further include cooling the vapor-liquid two-phase mixture from the compressor system by a second cooling system. The second cooling system may include a second post-CVD reactor heat exchanger.

The method may further include separating hydrogen from the effluent mixture from the post-CVD reactor in situ hydrogen chloride reactor by a post-CVD reactor silicon tetrachloride absorber/hydrogen separator.

The method may further include saturating with trichlorosilane the hydrogen separated by the post-CVD reactor silicon tetrachloride absorber/hydrogen separator.

The method may further include mixing the hydrogen from the post-CVD reactor silicon tetrachloride absorber/hydrogen separator with a feed to the chemical vapor deposition reactor.

The method may further include separating by a post-CVD reactor silicon tetrachloride/trichlorosilane separator trichlorosilane from silicon tetrachloride in the effluent mixture from the post-CVD reactor silicon tetrachloride absorber/hydrogen separator.

The method may further include feeding trichlorosilane from the silicon tetrachloride/trichlorosilane separator to the silicon tetrachloride absorber/hydrogen separator; and reacting the trichlorosilane with silicon tetrachloride in the silicon tetrachloride absorber/hydrogen separator.

The method may further include adjusting the temperature of the trichlorosilane prior to feeding the trichlorosilane to the silicon tetrachloride absorber/hydrogen separator. Adjusting the temperature may include adjusting the temperature to about 35°C.
The method may further include mixing the trichlorosilane from the silicon tetrachloride/trichlorosilane separator with a feed to the chemical vapor deposition reactor.

The method may further include cooling the trichlorosilane; and venting vapor phase lower boiling materials from the trichlorosilane.

The method may further include separating by a high-boiling phosphorus separator high boiling phosphorus contaminants including PCI3 from the silicon tetrachloride.

The method may further include mixing the trichlorosilane with a feed to the chemical vapor deposition reactor.

A method of producing silicon may be summarized as including performing a chemical vapor deposition on a mixture comprising trichlorosilane by a chemical vapor deposition reactor; recovering silicon from the chemical vapor deposition reactor; releasing from the chemical vapor deposition reactor an effluent mixture comprising hydrogen, silicon tetrachloride, and one or more of hydrogen chloride, dichlorosilane, and trichlorosilane; and cooling the effluent mixture from the chemical vapor deposition reactor by a first cooling system.

The method may further include separating by a post-CVD reactor hydrogen separator hydrogen from the cooled effluent mixture from the chemical vapor deposition reactor; and separating by a post-CVD reactor hydrogen chloride separator hydrogen chloride from the effluent mixture from the chemical vapor deposition reactor from which hydrogen has been removed by the post-CVD reactor hydrogen separator.

The method may further include feeding the hydrogen chloride from the post-CVD reactor hydrogen chloride separator and silane to a hydrogen chloride-silane reactor; and reacting the silane with the hydrogen chloride by the hydrogen chloride-silane reactor to produce chlorosilanes including trichlorosilane.

The method may further include reacting by a post-CVD reactor silane/hydrogen chloride reactor the hydrogen chloride from the post-CVD
reactor hydrogen chloride separator with silane and the chemical vapor deposition reactor effluent mixture.

A method of producing silicon may be summarized as including reacting a disproportionation reactor feed comprising trichlorosilane and silane by a disproportionation reactor to form a disproportionation reactor product comprising dichlorosilane, trichlorosilane and silicon tetrachloride; performing a chemical vapor deposition on a mixture from the disproportionation reactor by a chemical vapor deposition reactor to deposit silicon on a substrate within the chemical vapor deposition reactor; and recovering silicon from the chemical vapor deposition reactor. Reacting a disproportionation reactor feed to form a disproportionation reaction product comprising dichlorosilane, trichlorosilane and silicon tetrachloride may include optimizing operating conditions of the disproportionation reactor to maximize production of dichlorosilane.

The method may further include controlling a composition of the disproportionation reactor feed comprising trichlorosilane and silane such that the ratio of chlorine to silicon in the disproportionation reactor feed may range between about 1:1 and about 3:1.

The method may further include controlling a composition of the disproportionation reactor feed comprising trichlorosilane and silane such that the ratio of chlorine to silicon in the disproportionation reactor feed may range between about 1:1 and about 2.5:1.

The method may further include controlling a composition of the disproportionation reactor feed comprising trichlorosilane and silane such that the ratio of chlorine to silicon in the disproportionation reactor feed may range between about 1:1 and about 2:1.

The method may further include controlling a composition of the disproportionation reactor feed comprising trichlorosilane and silane such that the ratio of chlorine to silicon in the disproportionation reactor feed may range between about 1.25:1 and about 1.75:1.

The method may further include controlling a composition of the disproportionation reactor feed comprising trichlorosilane and silane such that
The ratio of chlorine to silicon in the disproportionation reactor feed may range between about 1.75:1 and about 2.25:1.

The method may further include controlling a composition of the disproportionation reactor feed comprising trichlorosilane and silane such that the ratio of chlorine to silicon in the disproportionation reactor feed may be about 1.5:1.

The method may further include controlling a composition of the disproportionation reactor feed comprising trichlorosilane and silane such that the ratio of chlorine to silicon in the disproportionation reactor feed may be about 2:1.

The method may further include separating silicon tetrachloride from a product of the disproportionation reactor in a post-disproportionation reactor silicon tetrachloride separator to yield a post-disproportionation reactor silicon tetrachloride-depleted stream and a post-disproportionation reactor silicon tetrachloride-rich stream. The method may further include separating dichlorosilane from trichlorosilane in the post-disproportionation reactor silicon tetrachloride-depleted stream by a post-disproportionation reactor dichlorosilane/trichlorosilane separator to yield a post-disproportionation reactor dichlorosilane-rich material and a post-disproportionation reactor trichlorosilane-rich material. The post-disproportionation reactor dichlorosilane-rich material may be essentially pure dichlorosilane.

The method may further include determining dichlorosilane concentration in the post-disproportionation reactor dichlorosilane-rich material.

The method may further include determining trichlorosilane concentration in the post-disproportionation reactor trichlorosilane-rich material.

The method may further include storing the post-disproportionation reactor dichlorosilane-rich material in a dichlorosilane storage system.

The method may further include storing the post-disproportionation reactor trichlorosilane-rich material in a trichlorosilane storage system.
The method may further include mixing the dichlorosilane-rich material with the trichlorosilane-rich material to yield a chemical vapor deposition reactor feed; and supplying the feed to the chemical vapor deposition reactor. Mixing the dichlorosilane-rich material with the trichlorosilane-rich material may include mixing dichlorosilane-rich material from the dichlorosilane storage system. Mixing the dichlorosilane-rich material with the trichlorosilane-rich material may include mixing trichlorosilane-rich material from the trichlorosilane storage system. Mixing the dichlorosilane-rich material with the trichlorosilane-rich material to yield a chemical vapor deposition reactor feed may include adjusting a ratio of chlorine to silicon in the chemical vapor deposition reactor feed.

The method may further include supplying the post-disproportionation reactor dichlorosilane-rich material directly to the chemical vapor deposition reactor.

The method may further include supplying the post-disproportionation reactor trichlorosilane-rich material directly to the chemical vapor deposition reactor.

The method may further include mixing the post-disproportionation reactor dichlorosilane-rich material and the post-disproportionation reactor trichlorosilane-rich material; and supplying the mixture of post-disproportionation reactor dichlorosilane-rich material and post-disproportionation reactor trichlorosilane-rich material to the CVD reactor.

The method may further include mixing the post-disproportionation reactor trichlorosilane-rich material with silane; and supplying the mixture of post-disproportionation reactor trichlorosilane-rich material and silane to the disproportionation reactor.

A method may be summarized as including producing and supplying silane and processing the silane according to methods claimed herein.
BRIEF DESCRIPTION OF SEVERAL VIEWS OF THE DRAWINGS

In the drawings, identical reference numbers identify similar elements or acts. The sizes and relative positions of elements in the drawings are not necessarily drawn to scale. For example, the shapes of various elements and angles are not drawn to scale, and some of these elements are arbitrarily enlarged and positioned to improve drawing legibility. Further, the particular shapes of the elements, as drawn, are not intended to convey any information regarding the actual shape of the particular elements, and have been solely selected for ease of recognition in the drawings.

Figure 1A is a schematic view of a system for preparing silicon including recycling of reaction byproducts according to one illustrated embodiment.

Figure 1B is a schematic view of a portion of the system of Figure 1A for preparing silicon further including an alternative for removing hydrogen chloride byproduct according to one illustrated embodiment.

Figure 1C is a schematic view of a portion of the system of Figure 1A for preparing silicon further including separating and recycling chlorosilane byproducts according to one illustrated embodiment.

Figure 1D is a schematic view of a portion of the system of Figure 1A for preparing silicon further including an alternative for removing hydrogen chloride byproduct according to one illustrated embodiment.

Figure 1E is a schematic view of a portion of the system of Figure 1A for preparing silicon further including reacting hydrogen chloride with silane in a separate reactor.

Figure 1F is a schematic view of a portion of the system of Figure 1A for preparing silicon further including reacting make-up hydrogen chloride with make-up silane in a separate reactor.

Figure 1G is a schematic view of a portion of the system of Figure 1A for preparing silicon further including reacting hydrogen chloride in an in situ reactor at the exit from the chemical vapor deposition reactor.
Figure 1H is a schematic view of a portion of the system of Figure 1A for preparing silicon further including reacting hydrogen chloride with silane in the exit from the chemical vapor deposition reactor.

Figure 1I is a schematic view of a portion of the system of Figure 1A for preparing silicon further including separating and disposing of dichlorosilane.

Figure 1J is a schematic view of a portion of the system of Figure 1A for preparing silicon wherein the system is designed to operate in vapor phase according to one illustrated embodiment.

Figure 1K is a schematic view of a portion of the system of Figure 1A for preparing silicon further including separating and disposing of chlorinated phosphorus materials.

Figure 1L is a schematic view of a portion of the system of Figure 1A for preparing silicon further including separating and using dichlorosilane.

Figure 2 is a schematic view of a portion of a system for preparing silicon including reacting in an in situ reactor hydrogen chloride in the effluent from a chemical vapor deposition reactor.

Figure 3 is a schematic view of a system for preparing silicon including preparing, separating and using dichlorosilane.

Figure 4 is a plot showing molar flow of byproducts as a function of outgas temperature in a post-CVD reactor in situ hydrogen chloride reactor at reaction equilibrium.

DETAILED DESCRIPTION

In the following description, certain specific details are included to provide a thorough understanding of various disclosed embodiments. One skilled in the relevant art, however, will recognize that embodiments may be practiced without one or more of these specific details, or with other methods, components, materials, etc. In other instances, well-known structures associated with systems for making silicon including, but not limited to, interior structures of mixers, separators, vaporizers, and recombination reactors, have
not been shown or described in detail to avoid unnecessarily obscuring descriptions of the embodiments.

Unless the context requires otherwise, throughout the specification and claims which follow, the word "comprise" and variations thereof, such as, "comprises" and "comprising" are to be construed in an open, inclusive sense, that is, as "including, but not limited to."

Reference throughout this specification to "one embodiment," or "an embodiment," or "another embodiment," or "some embodiments," or "certain embodiments" means that a particular referent feature, structure, or characteristic described in connection with the embodiment is included in at least one embodiment. Thus, the appearance of the phrases "in one embodiment," or "in an embodiment," or "in another embodiment," or "in some embodiments," or "in certain embodiments" in various places throughout this specification are not necessarily all referring to the same embodiment.

Furthermore, the particular features, structures, or characteristics may be combined in any suitable manner in one or more embodiments.

It should be noted that, as used in this specification and the appended claims, the singular forms "a," "an," and "the" include plural referents unless the content clearly dictates otherwise. Thus, for example, reference to a chlorosilane includes a single species of chlorosilane, but may also include multiple species of chlorosilanes. It should also be noted that the term "or" is generally employed as including "and/or" unless the content clearly dictates otherwise.

As used herein, the term "silane" refers to SiH₄. As used herein, the term "silanes" is used generically to refer to silane and/or any derivatives thereof. As used herein, the term "chlorosilane" refers to a silane derivative wherein one or more hydrogen has been substituted by chlorine. The term "chlorosilanes" refers to one or more species of chlorosilane. Chlorosilanes are exemplified by monochlorosilane (SiH₃Cl or MCS); dichlorosilane (SiH₂Cl₂ or DCS); trichlorosilane (SiHCl₃ or TCS); or tetrachlorosilane, also referred to as silicon tetrachloride (SiCl₄ or STC). The melting point and boiling point of
silanes increases with the number of chlorines in the molecule. Thus, for example, silane is a gas at standard temperature and pressure, while silicon tetrachloride is a liquid.

As used herein, unless specified otherwise, the term "chlorine" refers to atomic chlorine, *i.e.*, chlorine having the formula Cl, not molecular chlorine, *i.e.*, chlorine having the formula Cl₂. As used herein, the term "silicon" refers to atomic silicon, *i.e.*, silicon having the formula Si.

As used herein, the term "chemical vapor deposition reactor" or "CVD reactor" refers to a Siemens-type or "hot wire" reactor. The terms "chemical vapor deposition reactor" and "CVD reactor" may be used interchangeably.

Unless otherwise specified, the terms "silicon" and "polysilicon" are used interchangeably herein when referring to the silicon product of the methods and systems disclosed herein.

Unless otherwise specified, concentrations expressed herein as percentages should be understood to mean that the concentrations are in mole percent.

The headings provided herein are for convenience only and do not interpret the scope or meaning of the embodiments.

Figure 1A shows an exemplary embodiment of a configuration of a system for preparing silicon by chemical vapor deposition wherein reaction byproducts are continuously recycled and used as reactants within the system. Figures 1B-1L show exemplary embodiments of portions of a system for preparation of silicon by chemical vapor deposition wherein the embodiments relate to optional processes for recycling and/or removal of various byproducts produced in the chemical vapor deposition reactor.

System components that are the same throughout the figures are identified by the same number labels. System components that may have similar functions but are not the same from one figure to another are identified by different number labels. A shape or form provided for any particular
component of the systems shown in the figures is not intended to interpret or limit the particular component.

Figure 1A shows a schematic view of a system 100 for preparation of silicon including recycling and use of certain reaction byproducts. Although the description herein of Figure 1A may generally refer to certain of the reactants and byproducts as being in liquid phase, it is to be understood that the reactants and byproducts may exist in part or all of the system 100 in vapor or gas phase, or as a combination of liquid and vapor or gas phases, depending on the conditions or requirements of operation and on the characteristics of any particular reactant or byproduct. It will be readily understood to one of skill in the art that in operation certain reactants and/or byproducts at particular locations within the system 100 will necessarily exist in vapor or gas phase. Similarly, it will be understood that in operation certain reactants and/or byproducts at particular locations within the system 100 will necessarily exist in liquid phase. In certain embodiments, it may be advantageous to control conditions such that all gaseous materials are kept in solution to yield a uniform liquid phase. For example, the pressure within the system may be maintained at a level high enough to keep all gaseous materials in solution. In other conditions, it may be advantageous to alter conditions such that certain gaseous materials may be released from solution. For example, gaseous materials may be released from a liquid phase within a certain portion of the system by lowering the pressure of that portion of the system.

In embodiments of system 100 such as that exemplified in Figure 1A and described herein, silane and silicon tetrachloride are combined in a pre-disproportionation reactor silane/chlorosilane mixer 106 to yield a feed mixture to a disproportionation reactor 114. In certain embodiments wherein the reaction mixture in the disproportionation reactor 114 is intended to be a liquid at operating temperatures of the reactor 114, the feed pressures for the silane and silicon tetrachloride are each controlled to be sufficiently high to maintain the resulting mixture as a liquid. In such embodiments, silane and silicon tetrachloride are supplied to mixer 106 and mixtures of these reactants are
supplied to reactor 114 at pressures high enough to maintain the mixture supplied to the disproportionation reactor as a liquid under the desired operating temperature of the disproportionation reactor. In certain such embodiments, the pressure applied to the individual reactants and to the mixture supplied to the reactor 114 may be maintained under a pressure of about 50 psig above the bubble point of the reactants or the mixture. For example, when the disproportionation reactor 114 is intended to operate at a temperature of about 60°C, the pressure exerted on the mixture of reactants may be maintained in a range of about 150 psig to about 400 psig.

In certain embodiments, silane supplied as a liquid may be pre-vaporized and then added to the silicon tetrachloride as a vapor, which may be absorbed into the liquid silicon tetrachloride. In such embodiments, a static mixer, or some other mixing device, may mix the silane vapor with the liquid silicon tetrachloride. In such embodiments, when the disproportionation reactor is operated with the materials in liquid phase, the silane vapor must be completely absorbed into the liquid phase so that there is only a single phase within the reactor.

As necessary, the silicon tetrachloride feed may be heated or cooled to maintain the temperature of the mixture being fed to the reactor at the desired level, e.g., 60°C.

As illustrated in the particular embodiment of Figure 1A, conduit 101 supplies silane to an optional pump 102. In certain embodiments, conduit 101 may supply silane as a liquid at cold temperatures, e.g., -30°C. For example, the silane may be supplied under sufficient pressure to maintain the silane in liquid form under the conditions at which conduit 101 supplies the silane to pump 102. In one such embodiment, pressure exerted by pump 102 may be such as to liquefy the silane stream and/or maintain the silane in a liquid state under the conditions at which the system is operated. For example, in one embodiment, the pressure may be such as to maintain the silane in a liquid state at a temperature ranging between about 40°C and about 90°C. In another embodiment, the pressure may be such as to maintain the silane in a
liquid state at a temperature ranging between about 45°C and about 80°C. In yet another embodiment, the pressure may be such as to maintain the silane in a liquid state at a temperature ranging between about 50°C and about 70°C. In a further embodiment, the pressure may be such as to maintain the silane in a liquid state at a temperature ranging between about 55°C and about 65°C. In a particular such embodiment, the pressure may be such as to maintain the silane in a liquid state at a temperature of about 60°C. In one such embodiment, pump 102 may exert pressure within the range of about 10 psig to about 500 psig. In another such embodiment, pump 102 may exert pressure within the range of about 50 psig to about 300 psig. In yet another such embodiment, pump 102 may exert pressure within the range of about 100 psig to about 200 psig. In a further such embodiment, pump 102 may exert pressure at about 180 psig.

In certain embodiments, system 100 may not include pump 102. In such embodiments, a silane storage sphere or cylinder may supply silane liquid or vapor directly to system 100. In other embodiments of system 100 operating without pump 102, a silane storage vessel may supply liquid silane to a heat exchanger to vaporize the silane. Silane vapor from the vapor space of a silane storage vessel or from a heat exchanger may be supplied at an elevated pressure, e.g., 300 psig. Silane vapor mixes readily with liquid chlorosilanes.

Within certain embodiments, as discussed above and elsewhere herein, system 100 may operate with some or all of the reactants in gaseous or vapor phase. In certain such embodiments, some portions of system 100 may operate with reactants in gaseous or vapor phase, while other portions of the system may operate with reactants in liquid phase.

Pump 102 when present may represent any type of pumping system or apparatus suitable for delivery of materials or fluids in a vapor or liquid phase. In certain embodiments, pump 102 must be of a type suitable to adequately pressurize silane such that the silane remains in a liquid form at conditions under which silane is supplied to system 100 and under which
system 100 operates. In other embodiments, pump 102 may supply silane vapor to system 100. For example, pump 102 may be a piston-type pump in which a piston operates to drive or supply fluid at a controlled rate into system 100 wherein the fluid may be either a liquid or a vapor. As a further example, pump 102 may be a pressurized metering-type pump in which pressure drives fluid and a metering mechanism controls flow rate.

Pump 102 pumps silane via conduit 104 to pre-disproportionation reactor silane/chlorosilane mixer 106. In addition, conduit 163 delivers silicon tetrachloride to pre-disproportionation reactor silane/chlorosilane mixer 106.

Silicon tetrachloride delivered via conduit 163 may include silicon tetrachloride that has been produced as a byproduct during certain aspects of the operation of system 100, as further discussed below. Such silicon tetrachloride may be referred to as recycled silicon tetrachloride. The silicon tetrachloride provided via conduit 163 may include other reaction byproducts produced during operation of system 100, for example monochlorosilane, dichlorosilane, trichlorosilane and hydrogen chloride. These may be referred to as recycled monochlorosilane, recycled dichlorosilane, recycled trichlorosilane and recycled hydrogen chloride. The silicon tetrachloride provided via conduit 163 may further include additional silicon tetrachloride that has been added to adjust the molar ratio of chlorine to silicon in the mixture of reactants within pre-disproportionation reactor silane/chlorosilane mixer 106, as further discussed elsewhere herein. Such silicon tetrachloride that is added to adjust the quantity of silicon tetrachloride delivered via conduit 163 and thus the molar ratio of chlorine to silicon in the reactants in pre-disproportionation reactor silane/chlorosilane mixer 106 may be referred to as "make-up" silicon tetrachloride. In certain embodiments, trichlorosilane may also be added to aid in adjusting the molar ratio of chlorine to silicon in the reactants. Such trichlorosilane may be referred to as "make-up" trichlorosilane. In other embodiments, pure hydrogen chloride may be reacted with silane to aid in adjusting the molar ratio of chlorine to silicon in the reactants. Such pure hydrogen chloride may be referred to as "make-up" hydrogen chloride. In
certain embodiments the target molar ratio of chlorine to silicon may be in the range of between about 2:1 and about 3.9:1. In other embodiments the target molar ratio may be in the range of between about 2.5:1 and about 3.5:1. In yet other embodiments the target molar ratio may be in the range of between about 2.8:1 and about 3.3:1. In still other embodiments the target molar ratio may be in the range of between about 3:1 and about 3.2:1. In one embodiment the target molar ratio may be about 2.8:1. In another embodiment the target molar ratio may be about 3:1. In yet another embodiment the target molar ratio may be about 3.2:1. In yet another embodiment, the target molar ratio may be about 3.3:1. Silicon tetrachloride supplied as make-up silicon tetrachloride is typically highly purified. Trichlorosilane supplied as make-up trichlorosilane is also typically highly purified.

In certain embodiments, pre-disproportionation reactor silane/chlorosilane mixer 106 may be one of any of a variety of mixers suitable for mixing liquid fluids. In other embodiments, pre-disproportionation reactor silane/chlorosilane mixer 106 may be selected from any of a variety of mixers suitable for mixing fluids in a vapor or gaseous state. In certain embodiments, such mixers may be static mixers. In other embodiments, such mixers may be dynamic mixers.

After pre-disproportionation reactor silane/chlorosilane mixer 106 mixes silane provided via conduit 104 and silicon tetrachloride provided via conduit 163, conduit 108 supplies the resulting mixture from pre-disproportionation reactor silane/chlorosilane mixer 106 to pre-disproportionation reactor temperature controller 110. Pre-disproportionation reactor temperature controller 110 heats the mixture comprising silane and silicon tetrachloride supplied via conduit 108 to a temperature ranging from about 40°C to about 90°C. In certain such embodiments, the pre-disproportionation reactor temperature controller 110 heats the mixture supplied via conduit 108 to a temperature ranging from about 45°C to about 80°C. In other such embodiments, the pre-disproportionation reactor temperature controller 110 heats the mixture supplied via conduit 108 to a temperature
ranging from about 50°C to about 70°C. In yet other such embodiments, the pre-disproportionation reactor temperature controller 110 heats the mixture supplied via conduit 108 to a temperature ranging from about 55°C to about 65°C. In particular such embodiments, the temperature to which the mixture supplied via conduit 108 is heated may be about 60°C. Conduit 112 supplies the heated mixture comprising silane and silicon tetrachloride from heater 110 to disproportionation reactor 114. The mixture comprising recycled silicon tetrachloride is also likely to include with the silicon tetrachloride certain other recycled chlorosilanes, including dichlorosilane. The mixture comprising recycled silicon tetrachloride may also include recycled hydrogen chloride. Disproportionation reactor 114 includes a catalyst suitable for catalyzing reactions among silane and certain of the chlorosilanes leading to rearrangement of the molecules to yield in particular trichlorosilane. Catalysts that have been used include activated charcoal, various polymeric ion exchange resins, and certain metals, e.g., copper. Catalytic ion exchange resins include those having tertiary amines or quaternary ammonium groups.

Using polymeric ion exchange resins as catalysts in the disproportionation reactor may require in certain embodiments maintaining the heated mixture delivered via conduit 112 at a temperature between about 55°C and about 80°C. In other embodiments, the temperature of the heated mixture delivered via conduit 112 may be maintained between about 60°C and about 70°C. In yet other embodiments, the temperature of the heated mixture delivered via conduit 112 is maintained at about 60°C.

Alternatively, using other types of catalysts, e.g., metallic catalysts, in the disproportionation reactor may in certain embodiments allow temperatures in the disproportionation reactor as high as at least about 300°C.

The output of the disproportionation reactor delivered via conduit 116 includes trichlorosilane, as well as silicon tetrachloride and dichlorosilane. However, it includes only very low levels of silane, since the silane is converted within the disproportionation reactor 114 to the various chlorosilanes, such as dichlorosilane and trichlorosilane. For example, in one embodiment wherein
the chlorine to silicon ratio is maintained at 3.2:1 and the temperature within the
disproportionation reactor is maintained at 60°C, levels of silane and monochlorosilane in the disproportionation reactor product may be, respectively, $2 \times 10^{-5}$ and $7 \times 10^{-4}$ mole fractions. As noted above and as discussed elsewhere herein, silicon tetrachloride was added to the reaction mixture supplied to the disproportionation reactor 114 to maintain a molar ratio of silicon to chlorine within the reaction mixture suitable to drive disproportionation reactions within the reactor to optimally yield trichlorosilane. Such reaction mixtures typically thus include an excess of silicon tetrachloride and accordingly the mixture of reaction products delivered from the disproportionation reactor 114 via conduit 116 may retain an excess of silicon tetrachloride. In certain embodiments of the operation of system 100 as described herein, relative amounts of the various chlorosilanes in the reaction products from the disproportionation reactor 114 may be as follows: about 10% dichlorosilane; about 80% trichlorosilane; about 10% silicon tetrachloride. Adjusting the chlorine-to-silicon molar ratio may have a large effect on the levels of dichlorosilane in the reaction products. For example, in certain embodiments, increasing the molar ratio from 3:1 to 3.1:1 may decrease the amount of dichlorosilane from about 10% to about 6% of the total chlorosilanes. Increasing the molar ratio to 3.2:1 may further decrease the amount of dichlorosilane to about 3.8% of the total chlorosilanes. Increasing the molar ratio to 3.3:1 may still further decrease the amount of dichlorosilanes to about 2.0% of the total chlorosilanes. Thus, the levels of dichlorosilane in the disproportionation reaction products are surprisingly very sensitive to the molar ratio of chlorine to silicon in the reactants.

Pressure in the disproportionation reactor may be controlled by a back pressure control valve. When activated to adjust the pressure within the reactor, the valve may conveniently release material to an in-process storage tank. As appropriate, material from this tank may be supplied back into the system for processing within the reactor.
Conduit 116 delivers the mixture of reaction products from the disproportionation reactor 114 to a post-disproportionation reactor silicon tetrachloride separator 118 which separates and removes excess silicon tetrachloride from the reaction mixture. Conduit 120 transports the excess silicon tetrachloride from post-disproportionation reactor silicon tetrachloride separator 118 for recycling as further discussed below. When recycled, as discussed elsewhere herein, silicon tetrachloride provided from post-disproportionation reactor silicon tetrachloride separator 118 via conduit 120 may be mixed with make-up silicon tetrachloride and silicon tetrachloride from other sources within system 100. Post-disproportionation reactor silicon tetrachloride separator 118 may take any of a variety of forms of separators for silanes and/or chlorosilanes, for example, an apparatus suitable for distillation.

After post-disproportionation reactor silicon tetrachloride separator 118 removes excess silicon tetrachloride, conduit 122 transports the mixture of the remaining products of the reactions in the disproportionation reactor 114 from post-disproportionation reactor silicon tetrachloride separator 118 to a pre-CVD reactor vaporizer 128. The materials transported via conduit 122 typically include primarily trichlorosilane, with lesser amounts of dichlorosilane and only low amounts of silane and silicon tetrachloride. Heat is applied within pre-CVD reactor vaporizer 128 to the mixture supplied by conduit 122 to convert the mixture to a vapor. In certain embodiments, products may be removed from post-disproportionation reactor silicon tetrachloride separator 118 directly as a vapor, thus obviating the need for pre-CVD reactor vaporizer 128.

Conduit 130 transports the vaporized mixture to pre-CVD reactor mixer 132. As with the feed via conduit 122 to pre-CVD reactor vaporizer 128, the vaporized mixture transported from vaporizer 128 to mixer 132 via conduit 130 typically includes primarily trichlorosilane with lesser amounts of dichlorosilane and low amounts of silane and silicon tetrachloride. Dichlorosilane in the mixture transported by conduit 130 may be controlled at a level predetermined to be optimal for production of polysilicon. The level of dichlorosilane in conduit 130 may be controlled by adjusting the ratio of chlorine
to silicon in the material in conduit 108. Control of the ratio can be conveniently accomplished by adjusting the content of the material carried by conduit 163 and the relative rate at which the contents of conduits 163 and 104 are supplied to mixer 106.

Hydrogen gas is also supplied to pre-CVD reactor mixer 132. The hydrogen, which is supplied via conduit 152, may be hydrogen recovered from other locations within the process. For example, the hydrogen may be recovered and recycled following reactions within the chemical vapor deposition reactor, as described below. As necessary, hydrogen gas may also be provided from an external source (not shown) to pre-CVD reactor mixer 132.

Conduit 134 transports the vapor mixture from pre-CVD reactor mixer 132, comprising primarily trichlorosilane vapor and hydrogen gas, to CVD reactor 136. CVD reactor 136 includes a substrate on which silica may be deposited. CVD reactor 136 produces silicon as a result of various reactions taking place among trichlorosilane, hydrogen, and various other reactants or intermediates that occur within the CVD apparatus. Reactions taking place within the CVD reactor may include, but are not limited to, one or more of the following:

\[
\begin{align*}
\text{SiHCl}_3 + H_2 &\rightarrow \text{Si} + 3 \text{HCl} \\
4 \text{SiHCl}_3 &\leftrightarrow 3 \text{SiCl}_4 + 2H_2 + \text{Si} \\
\text{SiHCl}_3 + \text{HCl} &\leftrightarrow \text{SiCl}_4 + H_2 \\
\text{SiHCl}_3 &\leftrightarrow \text{SiCl}_2 + \text{HCl} \\
\text{SiH}_2\text{Cl}_2 &\rightarrow \text{Si} + 2 \text{HCl} \\
\text{SiH}_2\text{Cl}_2 + \text{SiCl}_4 &\leftrightarrow 2 \text{SiHCl}_3 \\
\text{SiH}_4 &\rightarrow \text{Si} + 2 H_2
\end{align*}
\]

The process of depositing silicon on the substrate in CVD reactor 136 is referred to as the Siemens or "hot wire" process. This process of producing silicon typically occurs at temperatures in excess of 600°C. The Siemens process thus requires high energy input, most of which is dissipated as heat.
Because of the cost associated with the high energy requirements for operation of the CVD reactor, the energy savings realized elsewhere in the system for producing silicon according to the novel processes described herein provide economic advantages that help to compensate for the costs associated with operation of the CVD reactor.

Silicon product 138 is removed from CVD reactor 136. Reactants and reaction byproducts remaining in CVD reactor 136 after the deposition reaction(s) are released from CVD reactor 136 as a mixture of gaseous materials and transported via conduit 140. The mixture of gaseous materials removed via conduit 140 may include, but is not limited to, one or more of hydrogen, hydrogen chloride, monochlorosilane, dichlorosilane, trichlorosilane, silicon tetrachloride, and oily contaminants, including polysilyl compounds. The oily contaminants in the gaseous mixture may be present in a form, for example, of a vapor or an aerosol.

The oily contaminants are preferably removed from the gaseous mixture. In one embodiment, as the temperature of the gaseous materials exiting the CVD reactor decreases, the oily contaminants condense, thereby removing the contaminants from the gaseous mixture. Such condensed contaminants may thus be regularly removed from the system as fluid oily condensates. In another embodiment, excess reactants and chlorosilane byproducts may be removed by distillation from higher boiling materials such as the oily contaminants. In certain embodiments, distillation may be performed using a distillation column. In other embodiments, distillation may be carried out with gas distillation membranes.

In the embodiment illustrated in Figure 1A, conduit 140 transports the gaseous mixture to a post-CVD reactor first cooler 142. Conduit 143 transports the cooled material to post-CVD decanter 169. Post-CVD decanter 169 separates lower boiling materials, e.g., hydrogen, hydrogen chloride and lower boiling silanes, from higher boiling materials, e.g., silicon tetrachloride, trichlorosilane and dichlorosilane. Post-CVD decanter 169 may be of any design suitable for use in separating the higher boiling and lower boiling...
materials from one another. For example, in one embodiment post-CVD
decanter 169 may include a distillation apparatus. In another embodiment, 5
post-CVD decanter 169 may include a separation column bed wherein lower
boiling materials rise to flow from the top and higher boiling materials flow from
the bottom. Conduit 145 transports the higher boiling silanes for processing
with like materials later in the process, as described below. Conduit 171
transports the lower boiling materials to post-CVD reactor compressor 144.
Post-CVD reactor compressor 144 pressurizes the gaseous mixture supplied by
conduit 171 to convert the gaseous mixture to a mixture of liquid chlorosilanes
with hydrogen and hydrogen chloride gases and chlorosilane vapors. Conduit
147 transports this two-phase vapor-liquid mixture to a post-CVD reactor
second cooler 146. Post-CVD reactor second cooler 146 further liquefies
higher boiling materials from the vapor phase of the two-phase mixture to
optimize subsequent removal of higher boiling silanes from the mixture.
Conduit 148 transports this mixture to a post-CVD reactor hydrogen separator
150. Post-CVD reactor hydrogen separator 150 may be of any design suitable
for use in removal of hydrogen gas from the two-phase gas/liquid mixture of
chlorosilanes within which the hydrogen gas is suspended or dissolved. In one
embodiment, for example, the hydrogen gas may be allowed to outgas from the
two-phase gas/liquid mixture delivered via conduit 148 and to selectively diffuse
through a hydrogen-specific separation membrane, for example a polymer
membrane, a metallic membrane, or a carbon membrane designed and used
for that purpose. Alternatively, in another embodiment, the hydrogen gas may
be removed by distillation. The hydrogen gas so removed may be further
purified by passing it through an absorption bed containing various absorbents,
*e.g.*, activated carbon. The hydrogen removed in post-CVD reactor hydrogen
separator 150 from the liquid mixture delivered via conduit 148 is transported as
recycled hydrogen via conduit 152 to pre-CVD reactor mixer 132. Pre-CVD
reactor mixer 132, as described above, mixes the recycled hydrogen with
chlorosilanes, primarily trichlorosilane, to be fed to CVD reactor 136 for further
production of silicon. In certain embodiments, excess hydrogen within system
100 may be removed, as necessary, from post-CVD reactor hydrogen separator 150 via conduit 153 to a hydrogen storage system.

Certain embodiments of system 100 may have multiple series of separator, condenser and cooling apparatus in order to optimize efficiency of separation of the lower and higher boiling materials from the byproducts from the CVD reactor. Other embodiments of system 100 may have only certain of the separator, condenser, and cooling apparatus elements added to or removed from the system. Yet other embodiments may have one or more of the separator, condenser or cooling apparatus advantageously positioned elsewhere in the system for optimal handling of the higher and lower boiling byproducts produced by the system.

In certain embodiments illustrated in Figure 1A, conduit 160 transports to pre-disproportionation reactor chlorosilane mixer 162 a liquid mixture of byproducts from CVD reactor 136 from which hydrogen has been removed in post-CVD reactor hydrogen separator 150. In some embodiments, conduit 145 from post-CVD reactor first cooler 142 may transport higher boiling chlorosilanes to conduit 160 for combination and transport with such materials from post-CVD reactor hydrogen separator 150 to pre-disproportionation reactor chlorosilane mixer 162. Hydrogen chloride may advantageously remain in the liquid mixture of chlorosilanes supplied via conduit 160 to pre-disproportionation reactor chlorosilane mixer 162.

In certain embodiments, conduit 160 may alternatively transport directly to post-disproportionation reactor silicon tetrachloride separator 118 the liquid mixture of byproducts from CVD reactor 136 from which hydrogen has been removed. In such embodiments, conduit 120 can transport silicon tetrachloride to pre-disproportionation reactor chlorosilane mixer 162 for recycling, as discussed above. Conduit 122 can transport the silicon tetrachloride-depleted mixture ultimately back to CVD reactor 136.

In certain embodiments, the contents of conduit 160 include primarily a mixture of chlorosilanes and hydrogen chloride. In some embodiments, as described above and elsewhere herein, the liquid mixture
transported by conduit 160 may contain essentially no hydrogen. In other embodiments, the contents of conduit 160 may contain at least a portion of the hydrogen originally present in the contents of conduit 148. In yet other embodiments, the contents of conduit 160 may contain most or at least a portion of the hydrogen chloride originally present in the contents of conduit 148. In still other embodiments, the liquid mixture transported by conduit 160 may contain essentially no hydrogen chloride. Alternatives for the disposition of hydrogen and hydrogen chloride are described elsewhere herein. In addition to the chlorosilanes transported to pre-disproportionation reactor chlorosilane mixer 162 by conduit 160, conduit 120, as discussed above, also provides recycled silicon tetrachloride from post-disproportionation reactor silicon tetrachloride separator 118 to pre-disproportionation reactor chlorosilane mixer 162.

The composition of the contents of pre-disproportionation reactor chlorosilane mixer 162 to which material has been supplied from conduit 160 and conduit 120 may be analyzed to determine the levels of the chlorosilanes within the contents of pre-disproportionation reactor chlorosilane mixer 162. In particular, the amount of chlorine and silicon within the contents of pre-disproportionation reactor chlorosilane mixer 162, including chlorine derived from hydrogen chloride, may be advantageously determined by analysis. As further discussed below and elsewhere herein, the novel method for optimally recycling all or at least most of the silicon tetrachloride, as well as the hydrogen chloride, produced as byproducts during the chemical vapor deposition reactions in system 100 requires careful control of the ratio of chlorine to silicon in the reactants delivered to disproportionation reactor 114. Such careful control of the ratio of chlorine to silicon effectively controls the relative amounts particularly of trichlorosilane and dichlorosilane produced in disproportionation reactor 114. Accordingly, based on the amounts of chlorine and silicon determined in the contents of pre-disproportionation reactor chlorosilane mixer 162, it is possible to calculate an amount of further silicon tetrachloride to be added to the contents of pre-disproportionation reactor chlorosilane mixer 162.
and thus also an amount of silane to be added to the mixture comprising silicon tetrachloride upon delivery of the mixture from pre-disproportionation reactor chlorosilane mixer 162 to pre-disproportionation reactor silane/chlorosilane mixer 106. Based on such calculations, conduit 164 may supply a metered amount of pure silicon tetrachloride as make-up silicon tetrachloride to the contents of pre-disproportionation reactor chlorosilane mixer 162 to optimize the amounts of chlorine and silicon in the contents of pre-disproportionation reactor chlorosilane mixer 162 and ultimately the chlorine-to-silicon ratio in the feed prepared in and supplied from pre-disproportionation reactor silane/chlorosilane mixer 106. Upon transport of the contents of pre-disproportionation reactor chlorosilane mixer 162 via conduit 163 to pre-disproportionation reactor silane/chlorosilane mixer 106 and addition of silane via conduit 104 to pre-disproportionation reactor silane/chlorosilane mixer 106 to initiate the process for preparation of silicon, as discussed above, the target chlorine content of the mixture within pre-disproportionation reactor chlorosilane mixer 162 is such that the chlorine-to-silicon molar ratio represents a mixture of reactants that is optimal for maximizing the production of trichlorosilane in disproportionation reactor 114 and minimizing or controlling the production of lower boiling chlorosilanes, particularly dichlorosilane. In some embodiments, the chlorine-to-silicon molar ratio corresponding to the mixture of reactants in pre-disproportionation reactor silane/chlorosilane mixer 106 ranges from about 2:1 to about 3.8:1. In certain such embodiments, the chlorine-to-silicon molar ratio ranges from about 3.1:1 to about 3.5:1. In some such embodiments, the chlorine-to-silicon molar ratio ranges from about 3.2:1 to about 3.3:1. In other such embodiments, the chlorine-to-silicon molar ratio is about 3.2:1. In still other such embodiments, the chlorine-to-silicon molar ratio is about 3.3:1. In certain embodiments, other chlorosilanes, such as dichlorosilane or trichlorosilane may be advantageously added to the contents of pre-disproportionation reactor chlorosilane mixer 162 and/or pre-disproportionation reactor silane/chlorosilane mixer 106 to assist in precisely adjusting the chlorine-to-silicon ratio of the feed to disproportionation reactor 114.
In certain embodiments, as an alternative to or in addition to adding make-up silicon tetrachloride to the contents of pre-disproportionation reactor chlorosilane mixer 162, the same effect may be achieved by adding pure tetrachlorosilane to pre-CVD reactor mixer 132. In such embodiments, the addition of pure tetrachlorosilane to pre-CVD reactor mixer 132 increases the production of silicon tetrachloride in chemical vapor deposition reactor 136. This additional silicon tetrachloride ultimately flows to pre-disproportionation reactor chlorosilane mixer 162, as discussed above, thus having an effect similar to the addition of pure make-up silicon tetrachloride directly to pre-disproportionation reactor chlorosilane mixer 162.

In certain embodiments, when establishing concentrations of reactants within the mixture to be delivered from pre-disproportionation reactor silane/chlorosilane mixer 106 as the feed to disproportionation reactor 114, a further consideration relates to providing reactants at a level that may more efficiently drive equilibrium of a targeted reaction toward completion. For example, in the reaction of silicon tetrachloride with silane in disproportionation reactor 114, providing an excess of silicon tetrachloride beyond calculated stoichiometric amounts may drive the formation of tetrachlorosilane more effectively toward completion. To this end increased amounts of silicon tetrachloride may be added to pre-disproportionation reactor chlorosilane mixer 162. The increased amounts of silicon tetrachloride may thus drive the reaction within reactor 114 more effectively toward higher levels of tetrachlorosilane relative to the other chlorosilanes. Such considerations related to manipulating reaction equilibria to optimize product yields may apply elsewhere within system 100 as well.

In certain embodiments, monochlorosilane, dichlorosilane and/or tetrachlorosilane may be added to the silicon tetrachloride, e.g., by adding one or more of these chlorosilanes to pre-disproportionation reactor chlorosilane mixer 162, to act as reaction initiator(s) in disproportionation reactor 114. In certain such embodiments, a molar ratio of one or more of these chlorosilanes to silicon tetrachloride may range from about 0:1 to about 2.5:1. In yet other such
embodiments, a molar ratio may range from about 0.1:1 to about 1:1. In still other such embodiments, a molar ratio may be about 1:2. In such embodiments, when mixing monochlorosilane, dichlorosilane and/or trichlorosilane with silicon tetrachloride, the mixtures are prepared so as to maintain an optimal ratio of chlorine to silicon in the disproportionation reactor feed after addition of silane to the mixture of silicon tetrachloride, other chlorosilane(s) and hydrogen chloride.

System 100 for producing silicon as described herein and as shown schematically in Figure 1A is particularly suited for handling increased levels of silicon tetrachloride supplied to the disproportionation reactor, as described above, since silicon tetrachloride that remains following reactions within disproportionation reactor 114 is separated from the reaction products in post-disproportionation reactor silicon tetrachloride separator 118 and recycled for further use within the system by transport via conduit 120 to pre-disproportionation reactor chlorosilane mixer 162. More generally, system 100 is specifically designed to efficiently use byproducts of the reactions that take place during the production of silicon. In particular, the operation of system 100 does not require isolation, removal and/or reprocessing of at least most of the byproducts resulting from the various reactions taking place because the byproducts are efficiently recycled and used within the system. Although separation of certain of the excess reactants and/or reaction byproducts from one another at various locations within the system may be desirable, such processing can easily and efficiently be carried out during operation of the system and provides a much more cost effective approach than those taken within existing systems, which require isolation, removal and/or reprocessing of materials, particularly reaction byproducts. Recycling of byproducts as described herein further results in particularly efficient conversion of the reactants and byproducts to maximize the yield of silicon. That is, the silicon-containing byproducts, in particular silicon tetrachloride and dichlorosilane, continue to be cycled through the system and thus silicon contained within these byproducts is ultimately recoverable as usable silicon, the desired
product. Further, not only does operation of the system for production of silicon as described herein improve efficiency and cost effectiveness of the process over existing production systems and processes, but it also overcomes environmental issues related to the disposal of certain byproducts such as silicon tetrachloride, hydrogen chloride, and dichlorosilane.

Hydrogen chloride produced as a byproduct of the reactions in CVD reactor 136 may be cycled back through the system and mixed with other reactants, including silane in pre-disproportionation reactor silane/chlorosilane mixer 106 and chlorosilanes throughout the process. The hydrogen chloride byproduct from CVD reactor 136 may thus participate in maintaining the chlorine balance within the system. The hydrogen chloride must remain dissolved in the liquid mixture of chlorosilanes as it flows through the system from post-CVD reactor hydrogen separator 150. Reaction of hydrogen chloride with silane added via conduit 104 into mixer 106 may yield trichlorosilane, for example by the following reaction:

$$\text{SiH}_4 + 3\text{HCl} \rightarrow \text{SiHCl}_3 + 3\text{H}_2$$

Exemplary reactions of hydrogen chloride with chlorosilanes are shown elsewhere herein. Reactions of silane, as well as various silane derivatives, with hydrogen chloride may be very exothermic. However, the relative levels of hydrogen chloride byproduct in the fluid and thus the amount of heat produced by reaction with silane and any other reactants compared to the volume of flow through the system may advantageously be such that the system may readily dissipate the heat by the mixing the liquid within and flowing the liquid through pre-disproportionation reactor silane/chlorosilane mixer 106. Alternatively, the facility may include cooling systems, e.g., heat exchangers, at one or more locations within and/or between pre-disproportionation reactor silane/chlorosilane mixer 106 and disproportionation reactor 114, as appropriate. Such may allow cooling of the stream either stepwise or at a single location in this portion of the process. As discussed elsewhere herein,
the resins used in disproportionation reactor 114 become unstable at elevated
temperatures. Thus process controllers must maintain the temperature of the
feed to disproportionation reactor 114 at less than 80°C, preferably no higher
than 70°C, more preferably between about 60°C and about 70°C. Heat
withdrawn from the fluid stream during cooling may be used in other aspects of
the process requiring heat.

In addition to the heat generated by the reaction of hydrogen
chloride with silane, the reaction also produces hydrogen gas as a byproduct.
Reactants must be supplied to disproportionation reactor 114 substantially as a
single phase. Thus a facility designed to recycle hydrogen chloride by keeping
it in the process flow may require application of pressure to the fluid at least
between pre-disproportionation reactor silane/chlorosilane mixer 106 and the
outlet of disproportionation reactor 114 sufficient to keep much or substantially
all of the hydrogen dissolved in the fluid. For example, pressure within this
portion of the system may be set at or below 2500 psig, particularly between
about 1500 psig and about 2500 psig, more particularly between about 1800
psig and about 2200 psig. The pressure should be optimally set at the lowest
level necessary to maintain the process fluid within disproportionation reactor
114 as a single phase. At other locations within the facility, where desired, a
decrease in pressure may allow release of any hydrogen remaining dissolved in
the fluid.

Figure 1B shows an optional aspect of system 100 of Figure 1A
related to removing hydrogen chloride from the liquid mixture of chlorosilanes in
which it is suspended or dissolved. Elements of Figure 1B that are identical or
similar to elements shown in Figure 1A are identified by the same numbers.
Although the hydrogen chloride may advantageously remain in the liquid
mixture of chlorosilanes supplied via conduit 160 to pre-disproportionation
reactor chlorosilane mixer 162 as discussed above regarding Figure 1A, it may
be desirable in other circumstances to remove the hydrogen chloride. In one
embodiment as illustrated in Figure 1B, conduit 154 transports the liquid
mixture containing hydrogen chloride and chlorosilanes from post-CVD reactor
hydrogen separator 150 to post-CVD reactor hydrogen chloride separator 156. Post-CVD reactor hydrogen chloride separator 156 may be of any design suitable to remove hydrogen chloride gas from the chlorosilanes. For example, post-CVD reactor hydrogen chloride separator 156 may allow the hydrogen chloride gas to outgas from the liquid mixture delivered via conduit 154 to post-CVD reactor hydrogen chloride separator 156. In one embodiment, the hydrogen chloride gas may then selectively move across a gas-permeable membrane. In another embodiment, the hydrogen chloride gas may move through a hydrogen chloride-specific membrane. In yet another embodiment, the hydrogen chloride gas may be separated as a low-boiling product from a distillation column. After passage through or recovery from either such membrane or such distillation column, conduit 158 may transport the hydrogen chloride gas to a hydrogen gas distribution and/or storage system (not shown). Such a distribution system may cycle the hydrogen chloride gas recovered in this manner back into the processes disclosed herein for further processing. The silicon production processes disclosed herein provide particularly surprising opportunities for recycling the hydrogen chloride produced during the processes, as discussed elsewhere herein. Alternatively, stored hydrogen chloride gas may be transported to and used in a trichlorosilane production facility. In yet other alternatives, the stored hydrogen chloride gas may be further purified, particularly for removal of residual chlorosilanes, and marketed for various uses requiring high-purity hydrogen chloride gas. For example, the hydrogen chloride gas from conduit 158 may flow through a carbon adsorption bed to remove residual chlorosilanes. Alternatively, the hydrogen chloride gas may flow over a heat exchanger containing liquid nitrogen to remove the chlorosilanes by condensation. In either such process, the chlorosilanes may be recovered and cycled back into a system for making polysilicon, such as that described herein. In at least one embodiment, the separated hydrogen chloride may, if necessary, be appropriately discarded or disposed of rather than recycled or recovered and purified.
In certain embodiments of system 100, post-CVD reactor hydrogen chloride separator 156 may only partially remove hydrogen chloride from the contents of conduit 154. In other embodiments, post-CVD system 100 may not even include post-CVD reactor hydrogen chloride separator 156, as described elsewhere herein.

As an alternative to removing hydrogen chloride by post-CVD reactor hydrogen chloride separator 156 as described above, post-CVD reactor hydrogen separator 150 may be designed and operated to separate both hydrogen and some or all of the hydrogen chloride from the mixture of byproducts delivered to post-CVD reactor hydrogen separator 150. In one such embodiment, the gaseous mixture of hydrogen and hydrogen chloride may be passed through a bed of carbon, e.g., activated carbon, to remove the hydrogen chloride from the hydrogen. In another embodiment, a heat exchanger containing a coolant such as liquid nitrogen may condense the hydrogen chloride from the gaseous mixture by cooling the mixture to the dew point of hydrogen chloride. In another embodiment, a combination of absorptive distillation and stripping may remove the hydrogen chloride from the hydrogen in the mixture.

Although hydrogen chloride may be removed in various ways, retaining the hydrogen chloride in the mixture of chlorosilanes, as further discusses elsewhere herein, eliminates the requirement for equipment to separately process hydrogen chloride and may also aid in maintaining chlorine balance appropriate for optimal operation of the polysilicon production system.

In certain embodiments, hydrogen chloride byproduct from CVD reactor 136 may be only partially retained within the process flow and thus only partially recycled in this manner. In certain such embodiments, post-CVD reactor hydrogen chloride separator 156 may remove a portion of the hydrogen chloride for other uses, leaving the remaining hydrogen chloride in the process stream. For example, process controllers may set the amount of hydrogen chloride to be recycled at a level appropriate to maintain an optimal chlorine-to-silicon ratio within the various reactants being fed to the disproportionation.
reactor 114. Hydrogen chloride that is not thus recycled may be removed from the process shown. Thus, in certain embodiments, post-CVD reactor hydrogen chloride separator 156 may only partially remove hydrogen chloride. In other embodiments, post-CVD reactor hydrogen chloride separator 156 may remove little, if any, of the hydrogen chloride. The disposition of hydrogen and hydrogen chloride within various embodiments of system 100 is further described elsewhere herein.

Figure 1C shows an optional aspect of system 100 of Figure 1A related to further processes for recycling chlorosilane reaction byproducts released from CVD reactor 136. Elements of Figure 1C that are identical or similar to elements shown in Figure 1A are identified by the same numbers. In one embodiment, as shown in Figure 1C, conduit 172 transports hydrogen chloride (if not otherwise removed) and the chlorosilane byproducts, including silicon tetrachloride, trichlorosilane and dichlorosilane, from post-CVD reactor hydrogen chloride separator 156 to post-CVD reactor chlorosilane separator 174. In another embodiment, the system may not include post-CVD reactor hydrogen chloride separator 156. In such embodiment, hydrogen chloride and the chlorosilane byproducts are transported directly from post-CVD reactor hydrogen separator 150 to post-CVD reactor chlorosilane separator 174.

Post-CVD reactor chlorosilane separator 174 may advantageously separate dichlorosilane and trichlorosilane from silicon tetrachloride. Following separation in post-CVD reactor chlorosilane separator 174, conduit 180 transports dichlorosilane and trichlorosilane to dichlorosilane/trichlorosilane separator 182. Dichlorosilane/trichlorosilane separator 182 may advantageously separate dichlorosilane from trichlorosilane. Conduit 186 transports trichlorosilane from dichlorosilane/trichlorosilane separator 182 to pre-CVD reactor vaporizer 128, thus to be recycled for deposition of polysilicon in CVD reactor 136. Conduit 184 transports the dichlorosilane from dichlorosilane/trichlorosilane separator 182 to post-CVD reactor chlorosilane mixer 178. Post-CVD reactor chlorosilane mixer 178 mixes the dichlorosilane with the silicon tetrachloride-containing contents of conduit
176. Conduit 160 transports the mixture comprising dichlorosilane and silicon tetrachloride from post-CVD reactor chlorosilane mixer 178 for recycling into system 100, as described above and shown in Figure 1A. In certain embodiments, as appropriate, delivery of dichlorosilane to post-CVD reactor chlorosilane mixer 178 via conduit 184 for combination with the silicon tetrachloride-containing contents of conduit 176 may be controlled so as to yield levels of dichlorosilane and/or ratios of chlorine to silicon that will provide mixtures of the chlorosilanes optimal for reaction in disproportionation reactor 114 when combined with silane. As described above, before combination of the mixture of chlorosilanes being transported by conduit 160 with silane, additional silicon tetrachloride may be added to the mixture in order to adjust the levels of reactants and the chlorine-to-silicon molar ratio in the mixture to produce and deliver optimal levels of trichlorosilane from disproportionation reactor 114 to CVD reactor 136 in Figure 1A.

In certain embodiments, system 100 may not include conduit 184 and post-CVD reactor chlorosilane mixer 178. In such embodiments of system 100, dichlorosilane separated by dichlorosilane/trichlorosilane separator 182 may be transferred to a dichlorosilane storage system. Dichlorosilane so stored may be added to the mixture of chlorosilanes supplied to the disproportionation reactor 114 and/or directly to the chemical vapor deposition reactor 136 to assist in controlling the level of reactants, in particular the ratio of chlorine to silicon, during operation of the system as discussed elsewhere herein. Alternatively, stored dichlorosilane may be provided or marketed for other uses or appropriately disposed of.

Figure 1D shows an optional aspect of system 100 of Figure 1A related to an alternative process for recycling hydrogen and removing hydrogen chloride from the gaseous byproducts of the reactions in CVD reactor 136. Elements of Figure 1D that are identical or similar to elements shown in Figure 1A are identified by the same numbers. Conduit 140 transports reaction byproducts and excess reactants from the CVD reactor 136, as in Figure 1A, to post-CVD reactor first cooler 142. Conduit 143 transports the cooled material
to post-CVD decanter 169. Conduit 145 transports higher boiling silanes for processing with such materials later in the process, as described elsewhere herein. Conduit 171 transports the lower boiling byproducts and reactants from post-CVD decanter 169 to post-CVD reactor compressor 144. Conduit 147 transports a two-phase vapor-liquid mixture produced by post-CVD reactor compressor 144 to post-CVD reactor second cooler 146. Conduit 148 transports the vapor-liquid mixture of by-products and reactants from post-CVD reactor second cooler 146 to post-CVD reactor hydrogen/hydrogen chloride separator 188. Post-CVD reactor hydrogen/hydrogen chloride separator 188 removes hydrogen and hydrogen chloride gases from chlorosilane byproducts and excess reactants. Conduit 191 transports the mixture of hydrogen and hydrogen chloride to pre-CVD reactor hydrogen/hydrogen chloride separator 192, in which hydrogen is separated from hydrogen chloride. Conduit 196 transports the hydrogen from pre-CVD reactor hydrogen/hydrogen chloride separator 192 to pre-CVD reactor mixer 132 which mixes the hydrogen with chlorosilanes, primarily trichlorosilane, for delivery via conduit 134 to CVD reactor 136 as disclosed and discussed above. The hydrogen is thus cycled back into system 100 for the production of silicon in the CVD reactor. Conduit 194 transports the hydrogen chloride from pre-CVD reactor hydrogen/hydrogen chloride separator 192 to a hydrogen chloride storage system. As discussed elsewhere herein, the hydrogen chloride may be transferred to a trichlorosilane production facility, may be diverted and separately reacted with silane or dichlorosilane, may be marketed, or may be discarded.

Figure 1E shows an optional aspect of system 100 of Figure 1A related to separately combining hydrogen chloride produced as a byproduct in CVD reactor 136 with silane to produce chlorosilanes. Elements of Figure 1E that correspond to elements shown in Figure 1A are identified by the same numbers. As described elsewhere herein and as shown in Figure 1A, conduit 154 transports CVD reactor byproducts from which hydrogen has been removed to post-CVD reactor hydrogen chloride separator 156. Post-CVD reactor hydrogen chloride separator 156 separates hydrogen chloride from the
CVD reactor byproducts. In Figure 1E conduit 157 transports hydrogen chloride from post-CVD reactor hydrogen chloride separator 156 to a pre-disproportionation reactor silane/hydrogen chloride reactor 159. Pre-disproportionation reactor silane/hydrogen chloride reactor 159 receives silane via conduit 155. As appropriate, hydrogen chloride supplied to pre-disproportionation reactor silane/hydrogen chloride reactor 159 may come from various other sources as well, including both within the polysilicon production facility and elsewhere. Pre-disproportionation reactor silane/hydrogen chloride reactor 159 reacts hydrogen chloride with silane to produce chlorosilanes. In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may advantageously produce primarily trichlorosilane and dichlorosilane. In other embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may produce primarily silicon tetrachloride. Conduit 161 transports the chlorosilanes from pre-disproportionation reactor silane/hydrogen chloride reactor 159 to pre-disproportionation reactor chlorosilane mixer 162. Alternatively, chlorosilanes from pre-disproportionation reactor 159 may be transported directly to post-disproportionation reactor silicon tetrachloride separator 118 shown in Figure 1A. Because the chlorosilanes supplied to pre-disproportionation reactor chlorosilane mixer 162 from pre-disproportionation reactor silane/hydrogen chloride reactor 159 comprise elemental silicon and chlorine, the supplied chlorosilanes may thus contribute to operating the processes described herein with optimal ratios of these elements. The levels of various chlorosilanes provided from pre-disproportionation reactor silane/hydrogen chloride reactor 159 via conduit 161 to pre-disproportionation reactor chlorosilane mixer 162, together with recycled chlorosilanes provided from other sources within the system, may limit the amount of make-up silicon tetrachloride required for operation at optimal silicon-to-chlorine ratios, as discussed above regarding system 100 of Figure 1A.

The output of pre-disproportionation reactor silane/hydrogen chloride reactor 159 may pass through a cooling system, such as one or more
heat exchangers, to decrease the temperature of the output. The heat exchangers may supply heat removed from the output reaction mixture of pre-disproportionation reactor silane/hydrogen chloride reactor 159 back to pre-disproportionation reactor silane/hydrogen chloride reactor 159 or to other locations within the facility requiring heat. For example, heat may be supplied to various separators, in particular distillers.

In certain embodiments, the one or more heat exchangers may be located within the pre-disproportionation reactor silane/hydrogen chloride reactor 159. In other embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may consist of multiple reactors in series with heat exchangers or other specialized cooling elements positioned between each of the multiple reactors. In such embodiments, reactors and cooling elements may be positioned alternating respectively in series.

Post-CVD reactor hydrogen chloride separator 156 may supply hydrogen chloride to pre-disproportionation reactor silane/hydrogen chloride reactor 159 in substantially pure form (although small amounts of silicon tetrachloride and/or trichlorosilane are acceptable). In certain embodiments, the silane provided to pre-disproportionation reactor silane/hydrogen chloride reactor 159 may represent a portion, e.g., 5-15%, of the silane that would otherwise feed to pre-disproportionation reactor silane/chlorosilane mixer 106 of system 100 shown in Figure 1A and described above.

Under operating conditions selected, pre-disproportionation reactor silane/hydrogen chloride reactor 159 operates at temperatures sufficiently high to completely convert the hydrogen chloride. In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may operate at a temperature greater than 100°C. In certain other embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may operate at a temperature greater than 200°C. In yet other embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may operate at a temperature ranging from about 300°C to about 600°C. Temperatures above 600°C may adversely affect the interior of pre-
disproportionation reactor silane/hydrogen chloride reactor 159, for example causing corrosion or loss of material strength.

Pre-disproportionation reactor silane/hydrogen chloride reactor 159 may operate in the presence or absence of a catalyst. A catalyst, if used, may be in the form of a copper wire or a copper-infused substrate. The substrate may be ultrapure silicon, thereby introducing no contaminants into the product(s) of the reactor.

Conduit 161 may transport the product(s) of the reaction in pre-disproportionation reactor silane/hydrogen chloride reactor 159 to pre-disproportionation reactor chlorosilane mixer 162 as a vapor. If added as a vapor, the temperature of the liquid to which the vapor is added, for example in pre-disproportionation reactor chlorosilane mixer 162, may be adjusted so that the vapor supplied by conduit 161 condenses and combines with the liquid. As described elsewhere herein regarding system 100 in Figure 1A, the liquid supplied to mixer 162 is primarily chlorosilanes. In one embodiment, rather than conduit 161 supplying the product(s) of pre-disproportionation reactor silane/hydrogen chloride reactor 159 to pre-disproportionation reactor chlorosilane mixer 162 as a vapor, the product(s) of the reaction in pre-disproportionation reactor silane/hydrogen chloride reactor 159 may alternatively be condensed to a liquid before being supplied to pre-disproportionation reactor chlorosilane mixer 162, for example by exposure to a heat exchanger cooled by any cooling medium suitable for the task. Alternatively, the liquid or vapor products from pre-disproportionation reactor silane/hydrogen chloride reactor 159 may be supplied directly to pre-disproportionation reactor silane/chlorosilane mixer 106.

During operation of pre-disproportionation reactor silane/hydrogen chloride reactor 159, the reaction yields hydrogen as a byproduct, as discussed elsewhere herein. In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 and/or conduit 161 may operate under pressure adequate to keep hydrogen in solution. In other embodiments, the reaction products from pre-disproportionation reactor silane/hydrogen chloride
reactor 159 may be directed back to post-CVD reactor hydrogen separator 150 to remove the hydrogen.

In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may advantageously operate with a stoichiometric molar excess of hydrogen chloride over silane. Under various embodiments of these conditions, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may preferably convert at least 60%, more preferably at least 70%, even more preferably at least 80%, still more preferably at least 90%, and most preferably 100% of the silicon provided by the silane to chlorosilanes. In certain embodiments pre-disproportionation reactor silane/hydrogen chloride reactor 159 converts at least most of the silane to dichlorosilane, trichlorosilane and silicon tetrachloride. In other embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 converts at least most of the silane to trichlorosilane and silicon tetrachloride. In most embodiments, there is little if any silane or monochlorosilane. Because there is a molar excess of hydrogen chloride over silane in pre-disproportionation reactor silane/hydrogen chloride reactor 159, the output of pre-disproportionation reactor silane/hydrogen chloride reactor 159 also contains unreacted hydrogen chloride. Additionally, the reactions in pre-disproportionation reactor silane/hydrogen chloride reactor 159 yield hydrogen gas.

In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may operate with a stoichiometric excess of silane over hydrogen chloride in order to quantitatively incorporate the chlorine from the hydrogen chloride into chlorosilanes. In certain such embodiments, the chlorosilanes produced in pre-disproportionation reactor silane/hydrogen chloride reactor 159 may include primarily dichlorosilane and trichlorosilane. In other embodiments, the chlorosilanes produced in pre-disproportionation reactor silane/hydrogen chloride reactor 159 may include monochlorosilanes. In some embodiments, the output of pre-disproportionation...
reactor silane/hydrogen chloride reactor 159 to conduit 161 may include unreacted silane.

In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may operate with hydrogen chloride and silane supplied to pre-disproportionation reactor silane/hydrogen chloride reactor 159 at levels such that neither is at a stoichiometric excess over the other. That is, under such conditions, essentially all of the silicon supplied in the silane and essentially all of the chlorine supplied in the hydrogen chloride react within pre-disproportionation reactor silane/hydrogen chloride reactor 159 to form chlorosilanes. In such embodiments, the output of pre-disproportionation reactor silane/hydrogen chloride reactor 159 may include essentially no silane and essentially no hydrogen chloride. In certain such embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may convert the silicon and the chlorine to dichlorosilane, trichlorosilane and silicon tetrachloride. In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may convert the silicon and the chlorine primarily to dichlorosilane and trichlorosilane. In certain such embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may convert the silicon and the chlorine primarily to trichlorosilane. In other such embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may convert the silicon and the chlorine primarily to dichlorosilane. In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may yield only low levels of monochlorosilane. For example, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may yield only 1-2 mole % of monochlorosilane, the remainder being chlorosilanes having higher ratios of chlorine to silicon.

Figure 1F shows an optional aspect of system 100 of Figure 1A related to separately combining make-up hydrogen chloride with make-up silane to produce chlorosilanes. In particular, Figure 1F shows an alternative to the aspect of system 100 shown in Figure 1E. Elements of Figure 1F that correspond to elements shown in Figures 1A and 1E are identified by the same
numbers. As described elsewhere herein and as shown in Figure 1A, conduit 160 transports to pre-disproportionation reactor chlorosilane mixer 162 a mixture of byproducts from CVD reactor 136 from which hydrogen has been removed in post-CVD reactor 150. In Figure 1E conduit 183 transports make-up hydrogen chloride to pre-disproportionation reactor silane/hydrogen chloride reactor 159. Conduit 155 transports make-up silane to pre-disproportionation reactor silane/hydrogen chloride reactor 159. The make-up hydrogen chloride and the make-up silane react in pre-disproportionation reactor silane/hydrogen chloride reactor 159 to produce chlorosilanes. In certain embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may advantageously produce primarily trichlorosilane and dichlorosilane. In other embodiments, pre-disproportionation reactor silane/hydrogen chloride reactor 159 may produce primarily silicon tetrachloride. Conduit 161 transports the chlorosilanes from pre-disproportionation reactor silane/hydrogen chloride reactor 159 to pre-disproportionation reactor chlorosilane mixer 162. Alternatively, chlorosilanes from pre-disproportionation reactor silane/hydrogen chloride reactor 159 may be transported directly to post-disproportionation reactor silicon tetrachloride separator 118, as shown in Figure 1A. As discussed elsewhere herein, because the chlorosilanes supplied to pre-disproportionation reactor chlorosilane mixer 162 from pre-disproportionation reactor silane/hydrogen chloride reactor 159 comprise elemental silicon and chlorine, the supplied chlorosilanes may thus contribute to operating the processes described herein with optimal ratios of these elements. The aspect shown in Figure 1F may provide an alternative to supplying make-up silicon tetrachloride to pre-disproportionation reactor chlorosilane mixer 162 via conduit 164 as described elsewhere herein.

Figure 1G shows an optional aspect of system 100 of Figure 1A related to in situ reaction of hydrogen chloride byproduct with chlorosilane byproducts from chemical vapor deposition reactor 136. In one such embodiment, the design of system 100 is such as to allow the in situ reaction to advantageously occur near the exit from the CVD reactor. Elements of Figure
1G that correspond to elements shown in Figure 1A are identified by the same numbers. As shown in Figure 1G and as described elsewhere herein, conduit 140 transports byproducts from CVD reactor 136. As described elsewhere herein, byproducts from the CVD reactor include hydrogen, hydrogen chloride, and various chlorosilanes.

The temperature of byproducts exiting from a CVD reactor 136 may range from about 800°C to about 1000°C. In certain processes for producing polysilicon in CVD reactors, the outgas byproducts from the CVD reactor may be rapidly cooled to a temperature of less than 150°C. However, recycling hydrogen chloride by in situ reaction of the hydrogen chloride byproduct with chlorosilane byproducts from the CVD reactor benefits from maintaining the temperature of the output from the CVD reactor at an elevated level. In certain such processes, the outgas byproducts may be cooled to a temperature ranging from about 300°C to about 400°C. In other such processes, the outgas byproducts may be cooled to a temperature ranging from about 400°C to about 700°C. In certain some such processes, the outgas byproducts may be cooled to a temperature ranging from about 400°C to about 500°C. Appropriate temperature control may be accomplished by heat interchange among effluent from and input to various reactors within system 100.

In certain embodiments, as shown in Figure 1G, conduit 140 transports the byproducts from CVD reactor 136 to an in situ hydrogen chloride reactor heat exchanger 135. In situ hydrogen chloride reactor heat exchanger 135 may transfer heat to the contents of conduit 140 to raise the temperature of the gaseous byproducts from CVD reactor 136 to a temperature sufficient for in situ reaction of the hydrogen chloride with the chlorosilanes, e.g., to about 500°C. Conduit 133, a continuation of conduit 140, or conduit 126 as discussed below, transports the gaseous byproduct mixture from in situ hydrogen chloride reactor heat exchanger 135 to post-CVD reactor in situ hydrogen chloride reactor 137. The reactions within the in situ reactor are somewhat exothermic, and thus the temperature may increase during reaction, e.g., by about 20°C to
about 25°C, or by about 40°C to about 50°C. Conduit 139 transports the reaction mixture to in situ hydrogen chloride reactor heat exchanger 135. In the embodiment shown in Figure 1G, in situ hydrogen chloride reactor heat exchanger 135 transfers heat from the reaction mixture leaving reactor 137 via conduit 139 to the reaction mixture entering reactor 137 via conduit 133. Conduit 141, the continuation of conduit 139, transports the reaction mixture from post-CVD reactor in situ hydrogen chloride reactor 137 through in situ hydrogen chloride reactor heat exchanger 135 to post-CVD reactor first cooler 142.

In some embodiments, it may be necessary to raise the temperature of the off-gas stream in conduit 140 from CVD reactor 136 to initiate the in situ reaction of hydrogen chloride with chlorosilanes. In such embodiments, conduit 140 may transport the off-gas stream to an optional start-up heater 131. When optional start-up heater 131 is used, conduit 126 transports the heated stream to the post-CVD reactor in situ hydrogen chloride reactor system.

In some embodiments, the temperature of the off-gas stream in conduit 140 from CVD reactor 136 may be greater than 500°C. In such embodiments, a waste heat boiler may be placed in conduit 140 to remove heat and lower the temperature to 500°C while generating steam for use elsewhere within or for export from system 100.

In some embodiments, a conduit 185 may advantageously deliver pure silane and/or pure hydrogen chloride to the mixture supplied from CVD reactor 136 to post-CVD in situ hydrogen chloride reactor 137. In such embodiments, supplying silane and/or hydrogen chloride may minimize the need for addition of pure silicon tetrachloride at other stages of the process as described elsewhere herein. In certain embodiments, small amounts of silane may be delivered to mixtures at other stages in the process, e.g., to the contents of conduit 141, to convert trace residual amounts of hydrogen chloride to chlorosilanes.
In one embodiment of the aspect of system 100 shown in Figure 1G, the byproduct mixture transported from CVD reactor 136 via conduit 140 may cool to about 300°C. In such embodiment, as an alternative to optional start-up heater 131, in situ hydrogen chloride reactor heat exchanger 135 may transfer sufficient heat to the contents of conduit 140 to raise the temperature of the byproduct mixture from about 300°C to about 500°C. In a particular such embodiment, the reaction within post-CVD reactor in situ hydrogen chloride reactor 137 may raise the temperature of the reaction mixture from about 500°C to about 522°C. Further in such embodiment, in situ hydrogen chloride reactor heat exchanger 135 may transfer heat from the reaction mixture transported from reactor 137 via conduit 139 to the byproduct mixture transported from CVD reactor 136 via conduit 140. The heat transferred may be sufficient to decrease the temperature of the reaction mixture exiting in situ hydrogen chloride reactor heat exchanger 135 via conduit 141 to about 322°C and to increase the temperature of the byproduct mixture exiting in situ hydrogen chloride reactor heat exchanger 135 by conduit 133 to about 500°C.

Reaction of hydrogen chloride with the chlorosilane byproducts within post-CVD reactor in situ hydrogen chloride reactor 137 depends on the residence time and temperature of the reaction mixture within the post-CVD reactor in situ hydrogen chloride reactor 137. The residence time must be sufficient to allow the reaction of hydrogen chloride within post-CVD reactor in situ hydrogen chloride reactor 137 to reach completion. The reactor 137 is thus designed to take into consideration the rate of flow and temperature of the byproduct mixture from CVD reactor 136 through post-CVD reactor in situ hydrogen chloride reactor 137 and to allow adequate residence time of the reaction mixture within reactor 137. Flow rate of byproduct mixture from the CVD reactor is typically a function of the system and thus is not readily controlled. Thus, residence time in the in situ hydrogen chloride reactor is most readily controlled by setting the volume of the in situ reactor. This may be most readily accomplished by increasing the number of in situ reactors as necessary,
acting either in parallel or in series, to provide a residence time appropriate for the reaction conditions within and the flow rate of the byproduct mixture.

In some embodiments when multiple reactors are used, reaction temperature may be different in different reactors. For example, the temperature in an initial reactor in a series may be higher that the temperature in a subsequent reactor. The initial reactor with the higher temperature may allow the bulk of the reaction to take place (faster kinetics) while a subsequent reactor with a lower temperature may be more suitable for the reaction to reach equilibrium.

In certain embodiments, reactions within post-CVD reactor in situ hydrogen chloride reactor 137 may require up to two minutes or more. In some embodiments, the reactions may require up to one minute. In other embodiments, the reactions may require between 30 seconds and one minute. In yet other embodiments, the reactions may require between 10 seconds and 30 seconds. In still other embodiments, the reactions may require between one second and 10 seconds. In certain embodiments, the reactions may require less than one second. In certain embodiments, a production plant may include one, two, three or four post-CVD reactor in situ hydrogen chloride reactors.

Figure 1H shows an optional aspect of system 100 of Figure 1A related to reacting hydrogen chloride with silane near the exit from chemical vapor deposition reactor 136. Elements of Figure 1H that correspond to elements shown in Figure 1A are identified by the same numbers. As shown in Figure 1H and as described elsewhere herein, conduit 140 transports byproducts from CVD reactor 136. In the embodiment shown in Figure 1H, conduit 140 transports the byproducts to a post-CVD reactor silane/hydrogen chloride reactor 149. Also as shown in Figure 1H and described elsewhere herein, post-CVD reactor hydrogen chloride separator 156 separates hydrogen chloride from byproducts of CVD reactor 136. Conduit 165 transports hydrogen chloride from post-CVD reactor hydrogen chloride separator 156 to post-CVD reactor silane/hydrogen chloride reactor 149. The contents of post-CVD reactor silane/hydrogen chloride reactor 149 include the byproducts of CVD reactor 136.
delivered by conduit 140. Conduit 167 transports silane to post-CVD reactor silane/hydrogen chloride reactor 149. The hydrogen chloride supplied via conduit 165 and the silane supplied via conduit 167 combine with the byproducts exiting from CVD reactor 136 via conduit 140. In certain embodiments, the amount of silane delivered via conduit 167 to post-CVD reactor silane/hydrogen chloride reactor 149 is stoichiometrically limited compared to the amount of hydrogen chloride in reactor 149, including the hydrogen chloride added via conduit 165. That is, after addition of hydrogen chloride and silane to post-CVD reactor silane/hydrogen chloride reactor 149, there is an excess of hydrogen chloride over silane within reactor 149.

In certain embodiments, the processes in post-CVD silane/hydrogen chloride reactor may be staged in various ways to optimize the outcome. In general, the bulk of the hydrogen chloride reacts in situ in a first stage, achieving 80-100% conversion. As appropriate, silane may then be added in small amounts to further convert any residual hydrogen chloride to chlorosilanes. Such staging of the process for converting hydrogen chloride to chlorosilanes in the outgas stream and careful control of silane addition may allow essentially complete reaction of the hydrogen chloride byproduct. Such staging and control may thus obviate the need for removal of hydrogen chloride by post-CVD hydrogen chloride separator 156 and cycling back to post-CVD silane/hydrogen chloride reactor 149 via conduit 165.

Rapid cooling of the chemical vapor deposition reactor outgas byproducts helps to limit the production of silicon tetrachloride which, in the absence of the recycling processes described herein, has generally required disposal. However, the reaction of silane with hydrogen chloride proceeds only slowly at such decreased temperatures. Thus recycling hydrogen chloride by reaction with silane in post-CVD reactor silane/hydrogen chloride reactor 149 may benefit from maintaining the temperature of the output from CVD reactor 136 at an elevated level. Selecting an optimal temperature for the contents of post-CVD reactor silane/hydrogen chloride reactor 149 must take into consideration the various reactions taking place. In particular, the temperature
is selected to maximize production of the preferred products from the reactions. Optimally, for the polysilicon production processes described herein, it may be desirable to establish conditions such that the output from post-CVD reactor silane/hydrogen chloride reactor 149 into the production system contains primarily trichlorosilane and silicon tetrachloride, with only limited amounts dichlorosilane, and minimal amounts of monochlorosilane, silane or hydrogen chloride. In a system capable of reacting all of the hydrogen chloride from the outgas byproducts, post-CVD reactor hydrogen chloride separator 156 is unnecessary. On the basis of calculations using equilibrium reactions, a temperature of about 300-600°C may be optimal for the contents of post-CVD reactor silane/hydrogen chloride reactor 149 during the reactions involving hydrogen chloride and silane (see Example 1 herein), with silane being added only to remove any residual hydrogen chloride. For such conditions, the output from CVD reactor 136 may be cooled from about 800-1 000°C to a temperature such that, after addition of the silane and hydrogen chloride, the temperature of the contents of post-CVD reactor silane/hydrogen chloride reactor 149 is less than about 600°C, more typically between about 400°C and about 500°C. In such embodiments, post-CVD reactor first cooler 142 or a similar cooling system may advantageously be positioned between CVD reactor 136 and post-CVD reactor silane/hydrogen chloride reactor 149. Alternatively or additionally, inlet and outlet streams of post-CVD silane/hydrogen chloride reactor 149 may advantageously pass through a heat exchanger. For example, as shown in Figure 1H, conduit 140 transports outgas byproduct mixture from CVD reactor 136 via an optional post-CVD silane/hydrogen chloride reactor heat exchanger 177 and conduit 179 to post-CVD silane/hydrogen chloride reactor 149. Conduit 181 transports the reaction products from post-CVD silane/hydrogen chloride reactor 149 via heat exchanger 177 and conduit 151. Heat exchanger 177, if used, may exchange heat between the inlet and outlet of post-CVD silane/hydrogen chloride reactor 149 or may exchange heat as appropriate among effluents from and input to various reactors within system 100. For example, temperature may be advantageously decreased to the desired level
by heat exchange with the vapor reactants entering the chemical vapor deposition reactor or by a waste heat boiler generating steam for use within or for export from system 100. Control of the reaction conditions may be based on analysis of residual hydrogen chloride in the contents of conduit 181.

The system as described may not require additional silane and/or hydrogen chloride as there may be sufficient chlorosilanes in the outgas byproducts to nearly completely react with hydrogen chloride in the outgas, e.g., at least 99% or even at least 99.6% of the hydrogen chloride. In the embodiment shown in Figure 1H, conduit 151 transports the products of post-CVD reactor silane/hydrogen chloride reactor 149 to post-CVD reactor first cooler 142. In other embodiments, the products of post-CVD reactor silane/hydrogen chloride reactor 149 may be transported directly to post-CVD reactor compressor 144. It will be readily understood by one of skill in the art that the positions of the cooling systems, compressor system and post-CVD reactor silane/hydrogen chloride reactor 149 relative to one another may vary depending on the temperature requirements for optimal reactions of the byproducts from CVD reactor 136.

Because silane is delivered to post-CVD reactor silane/hydrogen chloride reactor 149 at a level stoichiometrically limited compared to hydrogen chloride, the delivered silane may react essentially completely with the hydrogen chloride to form chlorosilanes within post-CVD reactor silane/hydrogen chloride reactor 149. In the embodiment shown in Figure 1H, the hydrogen chloride with which the silane reacts in post-CVD reactor silane/hydrogen chloride reactor 149 includes hydrogen chloride directly from chemical vapor deposition reactor 136 and from post-CVD reactor hydrogen chloride separator 156 via conduit 165. In certain embodiments, the system may include a small reactor to which very small amounts of silane may be added to allow conversion of small amounts of residual hydrogen chloride. Such a reactor may be termed a "hydrogen chloride trim reactor." In such embodiments, there may be no silane added to the initial reactor(s), only the subsequent reactor(s).
Transport of the reactants through post-CVD reactor silane/hydrogen chloride reactor 149 may be controlled to optimize the reaction of silane supplied via conduit 167 with hydrogen chloride in the contents of post-CVD reactor silane/hydrogen chloride reactor 149. In certain embodiments, flow within post-CVD reactor silane/hydrogen chloride reactor 149 may be controlled by the number and size of reactor elements within reactor 149 to allow optimal reaction within the contents of reactor 149. For example, flow through post-CVD reactor silane/hydrogen chloride reactor 149 may be controlled by the characteristics of the reactor elements such that the duration of time within reactor 149 is optimal for completion of the desired reactions. In certain embodiments, the reactions may require up to two minutes or more. In some embodiments, the reactions may require up to one minute. In other embodiments, the reactions may require between 30 seconds and one minute. In yet other embodiments, the reactions may require between 10 seconds and 30 seconds. In still other embodiments, the reactions may require between one second and 10 seconds. In certain embodiments, the reactions may require less than one second. Chlorosilanes produced by reaction of hydrogen chloride with silane in post-CVD reactor silane/hydrogen chloride reactor 149 may ultimately be cycled with the other chlorosilanes produced in chemical vapor deposition reactor 136 back to disproportionation reactor 114. Hydrogen chloride that is not converted to chlorosilanes within post-CVD reactor silane/hydrogen chloride reactor 149 may be retained in or separated from the contents of system 100, e.g., as shown in Figures 1A-1E.

Operating system 100 in such a manner as to optimally utilize hydrogen chloride as described above and elsewhere herein contributes to effectively maintaining the chlorine balance within the system. Chlorine balance may also be effectively controlled within the system by supplying trichlorosilane instead of silicon tetrachloride as a make-up chlorosilane when appropriate. For example, trichlorosilane may be added to pre-disproportionation reactor chlorosilane mixer 162, to pre-disproportionation reactor silane/chlorosilane mixer 106, or directly to CVD reactor 136 to control
the chlorine balance or the chlorine-to-silicon ratio of the feed supplied to chemical vapor deposition reactor 136. Alternatively or additionally, make-up hydrogen chloride and silane may be reacted in the in situ hydrogen chloride reactor to form chlorinated silanes.

Operating system 100 to optimally utilize hydrogen chloride as described herein also eliminates or at least limits the need to separate hydrogen chloride for recycle and eliminates or at least limits costs associated with building and operating facilities to process and store hydrogen chloride for sale or for use at other facilities.

Processes for recycling hydrogen chloride byproduct described herein, e.g., as shown in Figures 1E-1H, are not limited to use in embodiments of polysilicon production processes described herein. Such processes for recycling hydrogen chloride may be suitable for use in any polysilicon production facilities, systems, or processes, particularly those that are not typically designed to include hydrogen chloride as a reactant. For example, the processes for recycling hydrogen chloride described herein may be advantageously used in facilities or processes in which silicon tetrachloride, metallurgical grade silicon, and hydrogen are combined to produce trichlorosilane for the production of polysilicon. In-process conversion of hydrogen chloride to chlorosilanes as described herein allows maintenance of chlorine balance within a production facility without resorting to recycling hydrogen chloride within the system or transferring it to and reacting it within a separate metallurgical silicon reactor.

Figure 11 shows an optional aspect of system 100 of Figure 1A related to controlling levels of dichlorosilane during operation of the system. As discussed elsewhere herein, optimal operation of system 100, in particular production of polysilicon, may benefit from precise control of the level of dichlorosilane in the feed supplied via conduit 134 to CVD reactor 136. Typically a facility producing polysilicon by chemical vapor deposition may have an imbalance of dichlorosilane. Dichlorosilane originates from various sources within such an operation and is ultimately fed to the chemical vapor deposition
reactor. For example, the silicon tetrachloride thermal converters and the front end of the polysilicon production operation both make dichlorosilane. However, there is a limit to the amount of dichlorosilane that can be utilized within the chemical vapor deposition reactor. Excess dichlorosilane may thus exist downstream from the chemical vapor deposition reactor. In embodiments of the process illustrated schematically in Figure 1, dichlorosilane may be more effectively and efficiently used, and operation of aspects of system 100 as shown may eliminate or markedly decrease the requirement for disposal of dichlorosilane. Elements of Figure 11 that correspond to elements shown in Figure 1A are identified by the same numbers. In certain embodiments, as shown in Figure 1, conduit 116 delivers the mixture of reaction products from disproportionation reactor 114 to post-disproportionation reactor silicon tetrachloride separator 118. Removal of silicon tetrachloride from the reaction product mixture by separator 118 is described elsewhere herein. Conduit 121 delivers to post-disproportionation reactor dichlorosilane separator 117 the reaction product mixture from which silicon tetrachloride has been removed. Post-disproportionation reactor dichlorosilane separator 117 separates and removes dichlorosilane from the mixture of reaction products. Levels of dichlorosilane at various points within the process for producing polysilicon may be adjusted by use of dichlorosilane that has been separated from the reaction products of disproportionation reactor 114. Alternatively, conduit 123 may advantageously provide dichlorosilane from post-disproportionation reactor dichlorosilane separator 117 to pre-CVD reactor vaporizer 128, or optionally directly to pre-CVD reactor mixer 132, to precisely adjust the level of dichlorosilane in the feed via conduit 134 to CVD reactor 136. In another embodiment, conduit 113 may supply dichlorosilane from post-disproportionation reactor dichlorosilane separator 117 to pre-disproportionation reactor chlorosilane mixer 162. Mixer 162 may advantageously mix the dichlorosilane with silicon tetrachloride, other chlorosilanes and hydrogen chloride, if present, to optimally control the ratio of chlorine to silicon as well as the level of dichlorosilane in the feed to disproportionation reactor 114. In
certain embodiments, conduit 115 may, if necessary, transfer dichlorosilane from post-disproportionation reactor dichlorosilane separator 117 for storage and subsequent use, as needed. The system described herein for cycling dichlorosilane back into the processes for producing polysilicon efficiently utilizes dichlorosilane produced by reactions within the system. In certain embodiments, as necessary, any small amounts of excess dichlorosilane removed from post-disproportionation reactor dichlorosilane separator 117 via conduit 115 may be disposed of.

A polysilicon production facility may include multiple CVD reactors. Optimal requirements for the level of dichlorosilane in the feed to CVD reactors may be unique to each particular reactor within such a production operation. Supplying dichlorosilane from post-disproportionation reactor dichlorosilane separator 117 to the feed for each CVD reactor may thus be uniquely pre-programmed. The dichlorosilane may be supplied to each reactor in a programmed manner, thus allowing flexibility to precisely control the dichlorosilane level in the feed to any particular reactor and thus allowing optimal operation. The reaction rate and energy consumption within a given CVD reactor may be controlled at least in part by controlling the level of dichlorosilane fed to the reactor in this manner. In certain embodiments, adding dichlorosilane to the feed to the CVD reactor may not be necessary.

In certain embodiments, operation of the aspect of system 100 shown in Figure 11 may proceed in a non-time dependent manner. In such embodiments, disproportionation reactor 114 may be operated to maintain the level of dichlorosilane in the product of disproportionation reactor 114 at a constant predetermined level. The concentration of dichlorosilane in the product of disproportionation reactor 114 may be controlled, for example, to range from about 2% by weight to about 8% by weight (both on a silicon tetrachloride-free basis). In such embodiments, the dichlorosilane levels in the trichlorosilane feeds to all CVD reactors may be identical. In certain such embodiments, the level of dichlorosilane in the trichlorosilane feeds to the chemical vapor deposition reactors may be selected to be the highest possible
level that does not adversely affect the quality of the polysilicon produced. In certain such embodiments, the disproportionation reactor may first be controlled to produce a product that contains a low level of dichlorosilane for a period of time. This product may be delivered to and stored in a first storage tank. In such embodiments, the disproportionation reactor may then be controlled to produce a product that contains a high level of dichlorosilane for a period of time. This product may be delivered to and stored in a second storage tank. In such embodiments, the feed to any particular chemical vapor deposition reactor may then be produced by blending product from the first tank with product from the second tank. In such embodiments, the dichlorosilane level of feed supplied to any given chemical vapor deposition reactor may be blended differently from that supplied to any other chemical vapor deposition reactor. In such embodiments, the dichlorosilane level in the trichlorosilane feed supplied to any particular chemical vapor deposition reactor may not vary with time but may nevertheless be different from that supplied to any other chemical vapor deposition reactor.

The above approaches allow controlled and effective use of dichlorosilane produced in the disproportionation reactor. Thus there may be little, if any, excess dichlorosilane requiring disposal. Further, the use of dichlorosilane may be precisely controlled such that it may be converted to polysilicon without adversely affecting the quality of the resulting product.

Portions of system 100 that are described above as being operated with reactants and/or products in liquid phase may alternatively operate, when appropriate, under conditions such that reactants and/or products are in a vapor or gaseous phase at appropriate locations within the system. In certain embodiments of system 100 of Figure 1A, as shown in Figure 1J, silane and chlorosilanes may be supplied in vapor phase to pre-disproportionation reactor silane/chlorosilane mixer 106. Conduit 104 supplies silane as a vapor to pre-disproportionation reactor silane/chlorosilane mixer 106. In practice heat supplied from a heat exchanger elsewhere within the operation may vaporize the silane as further discussed elsewhere herein. In
certain embodiments as illustrated, conduits 120 and 160 supply chlorosilanes, including in particular silicon tetrachloride, to pre-disproportionation reactor chlorosilane mixer 162. Conduit 164 delivers additional silicon tetrachloride to pre-disproportionation reactor chlorosilane mixer 162, as described above, to adjust the molar ratio of chlorine to silicon in the mixture in pre-disproportionation reactor chlorosilane mixer 162 and thus as supplied to pre-disproportionation reactor silane/chlorosilane mixer 106. As described elsewhere herein, other chlorosilanes may also be advantageously added to adjust the chlorine-to-silicon molar ratio in mixer 162. Conduit 166 transports the mixture of chlorosilanes in pre-disproportionation reactor chlorosilane mixer 162 to a pre-disproportionation reactor vaporizer 168. Pre-disproportionation reactor vaporizer 168 vaporizes the mixture of chlorosilanes from pre-disproportionation reactor chlorosilane mixer 162. Conduit 170 supplies the vaporized mixture of chlorosilanes from pre-disproportionation reactor vaporizer 168 to pre-disproportionation reactor silane/chlorosilane mixer 106. As shown in Figure 1J, mixer 106 mixes the silane vapor supplied by conduit 104 and the vaporized chlorosilanes supplied via conduit 170. The contents of mixer 106 may also include other byproducts of the reactions in system 100, such as hydrogen and/or hydrogen chloride that may not have been removed from the process streams elsewhere within system 100. Conduit 108 feeds the mixture from pre-disproportionation reactor silane/chlorosilane mixer 106 into system 100 for processing as shown in Figure 1A and described elsewhere herein. Under such embodiments, vaporization of the materials and operation of this portion of the system must be carried out under pressures such that all components of the materials are in vapor phase within the range of temperatures at which disproportionation reactor 114 operates. That is, the system operates under conditions such that all reactants remain in a single phase except at locations within the system where separation and removal of certain components is desired. Conduit 108 supplies the vaporized mixture of silane and chlorosilanes to pre-disproportionation reactor temperature controller 110. Pre-disproportionation reactor temperature controller 110 heats the
vaporized reaction mixture at a controlled pressure to a selected temperature within the ranges as described above for operation of the system when reactants are in liquid phase. Conduit 112 transports the heated vapor to disproportionation reactor 114. Conduit 116 transports the vapor phase reaction products from disproportionation reactor 114 to post-disproportionation reactor silicon tetrachloride separator 118. Post-disproportionation reactor silicon tetrachloride separator 118 separates silicon tetrachloride from the reaction products and other excess reactants for recycling back into the system via conduit 120 to pre-disproportionation reactor chlorosilane mixer 162, as described above. From post-disproportionation reactor silicon tetrachloride separator 118, conduit 198 transports the vapor mixture of reaction products after removal of the silicon tetrachloride to pre-CVD reactor mixer 132. In addition, conduit 152 delivers hydrogen gas to pre-CVD reactor mixer 132, as described above. Pre-CVD reactor mixer 132 mixes the vapor mixture of reaction products delivered via conduit 198 and the hydrogen gas delivered via conduit 152. Conduit 134 delivers the vapor or gaseous mixture of reaction products and hydrogen from pre-CVD reactor mixer 132 to CVD reactor 136, as described above. Alternatively, recycled hydrogen may be fed separately to chemical vapor deposition reactor 136 and mixed with trichlorosilane within the reactor 136.

Figure 1K shows an optional aspect of system 100 of Figure 1A related to removal of phosphorus or other high boiling impurities from reactants within system 100. Phosphorus contaminants may be introduced into the reactants from various sources, for example, extracted from metal in the system or included within reactants such as silane, make-up silicon tetrachloride and/or make-up trichlorosilane. Such contaminants may, even at very low levels, adversely affect the quality of polysilicon produced by such a system. Phosphorus contaminants within reactants and/or products of system 100 may include low boiling phosphorus contaminants, such as PH₃ and PH₂Cl₂, and/or high boiling phosphorus contaminants, such as PHCl₂ and PCl₃. Elements of Figure 1K that correspond to elements shown in Figure 1A are identified by the
same numbers. Disproportionation reactor 114 may convert low boiling phosphorus contaminants to high boiling phosphorus contaminants. Conduit 116 transports the reaction products of disproportionation reactor 114, including high boiling phosphorus contaminants PHCl2 and PCI3, to post-disproportionation reactor silicon tetrachloride separator 118. As described above regarding Figure 1A, post-disproportionation reactor silicon tetrachloride separator 118 primarily separates silicon tetrachloride from trichlorosilane. However, under selected operating conditions, post-disproportionation reactor silicon tetrachloride separator 118 may also separate high boiling phosphorus contaminants from trichlorosilane. Under such conditions, conduit 125 transports the silicon tetrachloride and the high boiling phosphorus contaminants to high-boiling phosphorus separator 119. In certain embodiments under selected operating conditions, high-boiling phosphorus separator 119 may separate silicon tetrachloride and PHCl2 from PCI3. In other embodiments under other operating conditions, high-boiling phosphorus separator 119 may separate silicon tetrachloride from PCI3, or from PHCl2 and PCI3. PCI3, or PHCl2 and PCI3, may accumulate for collection from high-boiling phosphorus separator 119. Conduit 127 may remove and transport collected high boiling phosphorus contaminants to waste for disposal. With each pass, high-boiling phosphorus separator 119 may only partially remove the high boiling phosphorus contaminants from the silicon tetrachloride. Conduit 129 transports to pre-disproportionation reactor chlorosilane mixer 162 silicon tetrachloride and any high boiling phosphorus contaminants or other high boiling impurities, that have not been removed. The high boiling phosphorus contaminants in pre-disproportionation reactor chlorosilane mixer 162 again pass through disproportionation reactor 114, post-disproportionation reactor silicon tetrachloride separator 118 and high-boiling phosphorus separator 119. Disproportionation reactor 114 may further convert PHCl2 to higher-boiling PCI3. Repeated such cycles may ultimately convert and purge all of the phosphorus contaminants from the reactants and products of system 100 as PCI3. The system may remove in this manner levels of phosphorus as low as parts per
trillion. Operation of system 100 only includes this optional aspect if removal of phosphorus contaminants from feed materials to the CVD reactor is required.

In certain embodiments, high-boiling phosphorus separator 119 may be a distillation apparatus of relatively moderate size, e.g., having about 50 trays. In certain embodiments, post-disproportionation reactor silicon tetrachloride separator 118 may operate under relatively tight specifications regarding silicon tetrachloride. For example, post-disproportionation reactor silicon tetrachloride separator 118 may pass silicon tetrachloride at a level of 0.5 weight % or less via conduit 122 to the CVD reactor. In certain such embodiments, the level of silicon tetrachloride passed via conduit 122 may be 0.005 weight % or less. Within post-disproportionation reactor silicon tetrachloride separator 118, tight specifications that severely limit passage of silicon tetrachloride via conduit 122 toward chemical vapor deposition reactor 136 are conducive to passing PHCl₂ via conduit 125 to high-boiling phosphorus separator 119. Such tight specifications may lead to increased levels of trichlorosilane in the material passed from post-disproportionation reactor silicon tetrachloride separator 118 via conduit 125. Movement of trichlorosilane in this manner, however, is not an issue because such trichlorosilane will ultimately cycle back through disproportionation reactor 114. In certain embodiments, specifications of post-disproportionation reactor silicon tetrachloride separator 118 regarding silicon tetrachloride may be set more loosely, such that the level of silicon tetrachloride transported via conduit 122 may range between about 0.5 and 5 weight %.

In certain embodiments, the specifications for design and operation of high-boiling phosphorus separator 119 may be set to remove well over half of the PCI3 in a single pass. In certain other embodiments, the specification for removal of PCI3 may be set more loosely, such that high-boiling phosphorus separator 119 removes no more than half of the PCI3 in a single pass. Even if set loosely, high-boiling phosphorus separator 119 will nevertheless remove the PCI₃ in subsequent passes.
Figure 1L shows an optional aspect of system 100 of Figure 1A related to separating and using dichlorosilane during operation of the system. As discussed elsewhere herein, optimal operation of system 100, in particular production of polysilicon, may benefit from precise control of the level of dichlorosilane in the feed supplied via conduit 134 to CVD reactor 136. During operation of a facility for producing polysilicon by chemical vapor deposition, dichlorosilane may originate from various sources. For example, the chlorosilanes transported from disproportionation reactor 114 include dichlorosilane. In system 100 shown in Figure 1A, as described above, dichlorosilane transported from disproportionation reactor 114 is ultimately fed to CVD reactor 136. Embodiments of the processes for producing polysilicon illustrated schematically in Figure 1L may allow removal and more effective, efficient and optimal use of dichlorosilane during the production processes. Elements of Figure 1L that correspond to elements shown in Figure 1A are identified by the same numbers.

In certain embodiments, as shown in Figure 1L, conduit 116 transports the mixture of reaction products from disproportionation reactor 114 to post-disproportionation reactor silicon tetrachloride separator 118. Removal of silicon tetrachloride from the reaction product mixture by separator 118 is described elsewhere herein. Conduit 1121 transports to post-disproportionation reactor trichlorosilane/dichlorosilane separator 1101 the reaction product mixture from which silicon tetrachloride has been removed. Separator 1101 yields dichlorosilane, or a dichlorosilane-rich mixture, and trichlorosilane, or a trichlorosilane-rich mixture. Conduit 1103 transports the dichlorosilane, or the dichlorosilane-rich mixture, from separator 1101 to dichlorosilane storage system 1107. In certain embodiments, conduit 1111 may transport dichlorosilane to pre-CVD reactor dichlorosilane/trichlorosilane mixer 1117. Dichlorosilane may be supplied via conduit 1109 for other uses within the system or elsewhere or it may be sold. In certain embodiments, the dichlorosilane or the dichlorosilane-rich mixture may be pure dichlorosilane.
In certain embodiments, conduit 1105 transports the trichlorosilane, or the trichlorosilane-rich mixture, from post-disproportionation reactor trichlorosilane/dichlorosilane separator 1101 to trichlorosilane storage system 1113. In certain embodiments, conduit 1115 may transport trichlorosilane to pre-CVD reactor dichlorosilane/trichlorosilane mixer 1117. In certain embodiments, trichlorosilane may be supplied from trichlorosilane storage system 1113 for other uses within the system or elsewhere or it may be sold. In certain embodiments, the trichlorosilane or the trichlorosilane-rich mixture may be pure trichlorosilane. Conduit 1119 may supply mixed dichlorosilane and trichlorosilane from dichlorosilane/trichlorosilane mixer 1117 to pre-CVD reactor vaporizer 128 as appropriate for optimal production of polysilicon within CVD reactor 136.

Figure 2 shows an exemplary embodiment of a configuration of a portion of a system for preparing polysilicon related to controlling levels of chlorosilanes within the system and reacting in situ hydrogen chloride and chlorosilane byproducts from a chemical vapor deposition reactor. Elements of Figure 2 that correspond to elements shown in Figures 1A and 1G are identified by numbers that begin with "2" rather than "1" but are otherwise identical. Although elements numbered in this manner are similar, one of skill in the art will readily recognize that the portion of a system shown in Figure 2 may function with appropriate materials fed to a chemical vapor deposition reactor from any source and are not necessarily related to the system for production of silicon described elsewhere herein and exemplified in Figures 1A-1K. In particular, conduit 203 may feed CVD reactor 236 from any source of appropriate reactants.

Byproducts from CVD reactor 236 may include hydrogen, hydrogen chloride and various chlorosilanes. As discussed above, the temperature of byproducts exiting from a CVD reactor may range from about 800°C to about 1000°C. In certain processes for producing polysilicon in CVD reactors, the outgas products from the CVD reactor may be cooled to a temperature ranging from about 300°C to about 400°C, or from about 400°C to
about 700°C, or from about 400°C to about 500°C. Appropriate temperature control may be accomplished by interchange of heat to or from various sources.

In certain embodiments, as exemplified in Figure 2, conduit 240 transports byproducts from CVD reactor 236 to an in situ hydrogen chloride reactor heat exchanger 235. In situ hydrogen chloride reactor heat exchanger 235 may transfer heat to the contents of conduit 240 to raise the temperature of the gaseous byproducts from CVD reactor 236 to a temperature sufficient for in situ reaction of hydrogen chloride with chlorosilanes, *e.g.*, about 500°C. Conduit 233, a continuation of conduit 240, or conduit 226 as discussed below, transports the gaseous byproduct mixture from in situ hydrogen chloride heat exchanger 235 to post-CVD reactor in situ hydrogen chloride reactor 237. Conduit 239 transports the reaction mixture from post-CVD in situ hydrogen chloride reactor 237 to in situ hydrogen chloride reactor heat exchanger 235.

The reactions within in situ hydrogen chloride reactor 237 are somewhat exothermic. In situ hydrogen chloride reactor heat exchanger 235 transfers heat between the mixture exiting from reactor 237 via conduit 239 and the mixture supplied to reactor 237 via conduit 233, as described above regarding the embodiment shown in Figure 1G.

Conduit 241, the continuation of conduit 239, transports the reaction mixture from post-CVD reactor in situ hydrogen chloride reactor 237 to post-CVD reactor first cooler 242. Conduit 243 transports the cooled material to post-CVD first decanter 269. Post-CVD first decanter 269 separates lower boiling materials, *e.g.*, hydrogen, hydrogen chloride and lower boiling silanes, from higher boiling materials, *e.g.*, silicon tetrachloride, trichlorosilane and dichlorosilane. Post-CVD first decanter 269 may be of any design suitable for use in separating the higher boiling and lower boiling materials from one another. For example, in one embodiment post-CVD decanter 269 may include a distillation apparatus. In another embodiment, post-CVD decanter 269 may include a separation column bed wherein lower boiling materials rise to flow from the top and higher boiling materials flow from the bottom. Conduit 245 transports the higher boiling silanes for processing with like materials at
other points in polysilicon production processes. Conduit 271 transports the lower boiling materials to post-CVD reactor compressor 244. Post-CVD reactor compressor 244 pressurizes the gaseous mixture supplied by conduit 271 to convert the gaseous mixture to a mixture of liquid chlorosilanes with hydrogen and hydrogen chloride gases and chlorosilane vapors. Conduit 247 transports this two-phase vapor-liquid mixture to post-CVD reactor second cooler 246. Post-CVD reactor second cooler 246 further liquefies higher boiling materials from the vapor phase of the two-phase mixture to optimize subsequent removal of higher boiling silanes from the mixture. Conduit 248 transports the cooled material to post-CVD second decanter 273. Post-CVD second decanter 273 separates the lower boiling materials from the higher boiling materials. Conduit 275 transports the lower boiling materials to post-CVD silicon tetrachloride absorber/hydrogen separator 224. Post-CVD silicon tetrachloride absorber/hydrogen separator 224 contains an inert material, e.g., steel packing, and serves to allow downward flow of materials, in particular trichlorosilane, to decrease the content of silicon tetrachloride exiting from the post-CVD silicon tetrachloride absorber/hydrogen separator 224. Conduit 252 transports a vapor-phase mixture from post-CVD silicon tetrachloride absorber/hydrogen separator 224 to CVD reactor 236. Conduit 293 transports a liquid-phase mixture to silicon tetrachloride/trichlorosilane separator 295. Conduit 299 transports trichlorosilane-rich material from silicon tetrachloride/trichlorosilane separator 295 to CVD reactor 236. Conduit 299 includes a flow diverter/controller 287. Conduit 290 transports trichlorosilane-rich material from silicon tetrachloride/trichlorosilane separator 295 to post-CVD silicon tetrachloride absorber/hydrogen separator 224 as appropriate for optimal operation of the system. Flow diverter/controller 287 controls the relative flow of trichlorosilane-rich material via conduits 290 and 299.

Controlling the flow of trichlorosilane within the system shown in Figure 2 may allow efficient, cost-effective production of polysilicon by CVD reactor 236. For example, the amount of silicon tetrachloride produced, in particular that transported via conduit 252 back into CVD reactor 236, may be
controlled by feeding trichlorosilane to post-CVD silicon tetrachloride absorber/hydrogen separator 224 at a controlled temperature and rate. Under appropriate control of temperature and flow, the mixture transported by conduit 252 to CVD reactor 236 may include trichlorosilane-saturated hydrogen with only a minimal amount of silicon tetrachloride. In one embodiment, for example, the temperature of the trichlorosilane-rich material supplied by conduit 290 to post-CVD silicon tetrachloride absorber/hydrogen separator 224 may be about 35°C. Operation of the system shown in Figure 2 allows optimal management of silicon tetrachloride levels without requiring use of very cold temperatures typically used to remove this byproduct during polysilicon production processes.

In some embodiments, it may be necessary to raise the temperature of the off-gas stream in conduit 240 from CVD reactor 236 to initiate the in situ reaction of hydrogen chloride with chlorosilanes. In such embodiments, conduit 240 may transport the off-gas stream to an optional start-up heater 231. In such embodiments, conduit 226 transports the heated stream from optional start-up heater 231 to the post-CVD reactor in situ hydrogen chloride reactor system.

In some embodiments, the temperature of the off-gas stream in conduit 240 from the CVD reactor 236 may be greater than 500°C. In such embodiments, a waste heat boiler may be placed in conduit 240 to remove heat and lower the temperature to 500°C while generating steam for use within or for export from a system within which the elements of Figure 2 operate.

In some embodiments, a conduit 285 may advantageously deliver pure silane and/or pure hydrogen chloride to the mixture supplied from CVD reactor 236 to post-CVD in situ hydrogen chloride reactor 237. In such embodiments, supplying silane and/or hydrogen chloride may minimize the need for addition of pure silicon tetrachloride at other stages of a process such as that in system 100 as described elsewhere herein. In certain embodiments, only small amounts of silane may be delivered to mixtures at other stages in the
process, e.g., to the contents of conduit 241 to convert trace residual amounts of hydrogen chloride to chlorosilanes.

Although Figure 2 shows silicon tetrachloride/trichlorosilane separator 295 as an element of the unit depicted, it would also be understood by one of skill in the art that such an element could be operated separately, for example, with material being supplied to it for processing from any appropriate source.

Figure 3 shows an exemplary embodiment of a configuration of a portion of a system for preparing polysilicon in which the portion of the system that carries out the disproportionation reaction is optimized to produce and process dichlorosilane. Elements of Figure 3 that correspond to elements shown in Figures 1A and 1L are identified by numbers that begin with "3" rather than "1" but are otherwise identical. Although elements numbered in this manner are similar to elements described elsewhere herein, one of skill in the art will readily recognize that the portion of a system shown in Figure 3 may function with appropriate materials fed to a CVD reactor from any source and are not necessarily related to the system for production of silicon described elsewhere herein and exemplified in Figures 1A-1L. In particular, trichlorosilane, dichlorosilane and silane may be supplied from any appropriate source within or outside of the described system.

In certain embodiments, as exemplified in Figure 3, conduit 304 supplies silane and conduit 3133 supplies trichlorosilane to a pre-disproportionation reactor silane/chlorosilane mixer 306. Conduit 3135 may also supply trichlorosilane to pre-disproportionation reactor silane/chlorosilane mixer 306. Pre-disproportionation reactor silane/chlorosilane mixer 306 may be one of any of a variety of mixers described elsewhere herein for mixing silane and trichlorosilane for delivery to a disproportionation reactor.

In certain embodiments, the mixture of silane and trichlorosilane is established such as to maximize production of dichlorosilane in disproportionation reactor 314. In some embodiments, trichlorosilane and silane may be mixed in quantities to achieve a molar ratio of chlorine to silicon.
in a range between about 1:1 and about 3:1. In some such embodiments, the target molar ratio may be in the range between about 1:1 and about 2.5:1. In other such embodiments, the target molar ratio may be in the range between about 1:1 and about 2:1. In yet other such embodiments, the target molar ratio may be in the range between about 1.25:1 and about 1.75:1. In still other such embodiments, the target molar ratio may be in the range between about 1.75:1 and about 2.25:1. In certain embodiments, the target molar ratio may be about 1.5:1. In certain other embodiments, the target molar ratio may be about 2:1.

After pre-disproportionation reactor silane/trichlorosilane mixer 306 mixes silane provided via conduit 304 and trichlorosilane provided via conduit 3133 and/or conduit 3135, conduit 308 supplies the resulting mixture from pre-disproportionation reactor silane/trichlorosilane mixer 306 to pre-disproportionation reactor temperature controller 310. Pre-disproportionation reactor temperature controller 310 heats the mixture comprising silane and trichlorosilane supplied via conduit 308 to a temperature appropriate for reaction within disproportionation reactor 314, as described elsewhere herein.

Conduit 312 carries the heated mixture comprising silane and trichlorosilane from temperature controller 310 to disproportionation reactor 314. Conduit 316 transports the reaction mixture from disproportionation reactor 314 to post-disproportionation reactor silicon tetrachloride separator 318. The reaction mixture may include dichlorosilane, trichlorosilane and silicon tetrachloride. Silicon tetrachloride separator 318 removes silicon tetrachloride from the reaction mixture to yield a dichlorosilane-rich stream. Conduit 3121 transports the dichlorosilane-rich stream to post-disproportionation reactor dichlorosilane/trichlorosilane separator 3101. Separator 3101 yields dichlorosilane, or a dichlorosilane-rich mixture, and trichlorosilane, or a trichlorosilane-rich mixture. Conduit 3103 transports the dichlorosilane, or the dichlorosilane-rich mixture, to dichlorosilane storage system 3107. In certain embodiments, the dichlorosilane, or dichlorosilane-rich mixture, transported by conduit 3103 from post-disproportionation reactor dichlorosilane/trichlorosilane separator 3103 may be pure dichlorosilane. In
certain embodiments, conduit 3127 may transport the dichlorosilane, or the
dichlorosilane-rich mixture, directly to CVD reactor 336. In other embodiments,
conduit 3111 may transport the dichlorosilane to pre-CVD reactor
dichlorosilane/trichlorosilane mixer 3117. Dichlorosilane may be sold or
supplied for other uses via conduit 3109.

In certain embodiments, conduit 3105 transports the
trichlorosilane, or the trichlorosilane-rich mixture, from post-disproportionation
reactor dichlorosilane/trichlorosilane separator 3101 to trichlorosilane storage
system 3113. In certain embodiments, the trichlorosilane or the trichlorosilane-
rich mixture may be pure trichlorosilane. In certain embodiments, conduit 3131
may transport the trichlorosilane or the trichlorosilane-rich mixture, directly to
CVD reactor 336. In other embodiments, conduit 3115 may transport
trichlorosilane to pre-CVD reactor dichlorosilane/trichlorosilane mixer 3117. In
still other embodiments, conduit 3135 may transport trichlorosilane to pre-
disproportionation reactor silane/trichlorosilane mixer 306, as noted above. In
certain embodiments, trichlorosilane may be supplied from trichlorosilane
storage system 3113 via conduit 3125 for other purposes. Conduit 3129 may
supply mixed dichlorosilane and trichlorosilane from
dichlorosilane/trichlorosilane mixer 3117 to CVD reactor 336 as appropriate for
optimal production of polysilicon within reactor 136.

The systems and processes disclosed and discussed herein for
the production of silicon have marked advantages over systems and processes
currently employed.

The systems and processes are suitable for the production of
either semiconductor grade or solar grade silicon. The use of silane as a
starting material in the production process allows high purity silicon to be
produced more readily. Silane is much easier to purify. Because of its low
boiling point, it can be readily purified and during purification does not have the
tendency to carry along contaminants as may occur in the preparation and
purification of trichlorosilane as a starting material. Further, certain processes
for the production of trichlorosilane utilize carbon or graphite, which may carry
along into the product or react with chlorosilanes to form carbon-containing compounds.

The systems and processes disclosed herein for production of silicon provide large cost savings related to both building and operating production facilities. In particular, since silicon tetrachloride is recycled within the processes, rather than removed for external reprocessing via use of thermal conversion reactors into trichlorosilane, there is a savings of the very high costs associated with building and operating such facilities. In particular, savings of capital and operating can both be on the order of 20-40%.

The only materials generally requiring removal from the system, as described herein, are the silicon product itself. If desired for a particular purpose, hydrogen chloride gas and/or chlorosilanes, in particular dichlorosilane and/or silicon tetrachloride, may be removed for disposal or alternative uses during operation of the system. However, their removal is not required, nor is it even necessarily preferable.

The above description of illustrated embodiments, including what is described in the Abstract, is not intended to be exhaustive or to limit the embodiments to the precise forms disclosed. Although specific embodiments and examples are described above for illustrative purposes, various equivalent modifications can be made without departing from the spirit and scope of the disclosure, as will be recognized by those skilled in the relevant art. The teachings provided above of the various embodiments can be applied to other systems, methods and/or processes for producing silicon, not only the exemplary systems, methods and devices generally described above.

For instance, the detailed description above has set forth various embodiments of the systems, processes, methods and/or devices via the use of block diagrams, schematics, flow charts and examples. Insofar as such block diagrams, schematics, flow charts and examples contain one or more functions and/or operations, it will be understood by those skilled in the art that each function and/or operation within such block diagrams, schematics, flowcharts or examples can be implemented, individually and/or collectively, by a wide range
of system components, hardware, software, firmware, or virtually any combination thereof.

In certain embodiments, the systems used or devices produced may include fewer structures or components than in the particular embodiments described above. In other embodiments, the systems used or devices produced may include structures or components in addition to those described herein. In further embodiments, the systems used or devices produced may include structures or components that are arranged differently from those described herein. For example, in some embodiments, there may be additional heaters and/or mixers and/or separators in the system to provide effective control of temperature, pressure, or flow rate. Further, in implementation of procedures or methods described herein, there may be fewer operations, additional operations, or the operations may be performed in different order from those described herein. Removing, adding, or rearranging system or device components, or operational aspects of the processes or methods, would be well within the skill of one of ordinary skill in the relevant art in light of this disclosure.

The operation of methods and systems for making polysilicon described herein may be under the control of automated control systems. Such automated control systems may include one or more of appropriate sensors (e.g., flow sensors, pressure sensors, temperature sensors), actuators (e.g., motors, valves, solenoids, dampers), chemical analyzers and processor-based systems which execute instructions stored in processor-readable storage media to automatically control the various components and/or flow, pressure and/or temperature of materials based at least in part on data or information from the sensors, analyzers and/or user input.

Regarding control and operation of the systems and processes, or design of the systems and devices for making polysilicon, in certain embodiments the present subject matter may be implemented via Application Specific Integrated Circuits (ASICs). However, those skilled in the art will recognize that the embodiments disclosed herein, in whole or in part, can be
equivalently implemented in standard integrated circuits, as one or more computer programs running on one or more computers \((e.g.,\) as one or more programs running on one or more computer systems), as one or more programs running on one or more controllers \((e.g.,\) microcontrollers) as one or more programs running on one or more processors \((e.g.,\) microprocessors), as firmware, or as virtually any combination thereof. Accordingly, designing the circuitry and/or writing the code for the software and/or firmware would be well within the skill of one of ordinary skill in the art in light of this disclosure.

The present disclosure may be further illustrated by reference to the following example. This example is provided by way of illustration only and not by way of limitation.

**EXAMPLES**

**EXAMPLE 1**

**CHEMICAL VAPOR DEPOSITION REACTOR OUTGAS**

**MOLAR FLOW vs. TEMPERATURE**

Calculated Gibbs temperatures plotted against molar flow of reactants and byproducts in chemical vapor deposition reactor outgas to which silane and hydrogen chloride have been added are shown in Figure 4. The plotted results assume all reactions have reached equilibrium. The conditions used in the calculation include a molar excess of hydrogen chloride over added silane. The results do not show hydrogen, which is produce in quantities much larger than those shown. Including hydrogen within the calculations would change the shapes of the curves. Nevertheless, the calculated equilibrium results are considered to reflect dynamic conditions within the outgas of the CVD reactor.

The results demonstrate that between 400°C and 500°C the primary silicon- and/or chlorine-containing components of the outgas are trichlorosilane and silicon tetrachloride. The level of dichlorosilane is low.
compared to the trichlorosilane and silicon tetrachloride. Silane, monochlorosilane and hydrogen chloride are essentially absent. For example, the calculated results show that at 500C and 400C, respectively, 99.9% and 99.99% of the hydrogen chloride has reacted.

The various embodiments described herein above can be combined to provide further embodiments. Aspects of the embodiments can be modified, if necessary to employ concepts of various patents, applications and publications to provide yet further embodiments.

These and other changes can be made to the embodiments in light of the above-detailed description. In general, in the following claims, the terms used should not be construed to limit the claims to the specific embodiments disclosed in the specification and the claims, but should be construed to include all possible embodiments along with the full scope of equivalents to which such claims are entitled. Accordingly, the claims are not limited by the disclosure.
CLAIMS

What is claimed is:

1. A method of producing silicon, the method comprising:
   reacting a disproportionation reactor feed comprising silane and silicon tetrachloride by a disproportionation reactor;
   performing a chemical vapor deposition on a mixture from the disproportionation reactor by a chemical vapor deposition reactor to deposit silicon on a substrate within the chemical vapor deposition reactor; and
   recovering silicon from the chemical vapor deposition reactor.

2. The method of claim 1, further comprising:
   separating hydrogen from a byproduct mixture of the chemical vapor deposition comprising hydrogen and silicon tetrachloride to yield a composition comprising silicon tetrachloride;
   mixing the composition comprising silicon tetrachloride and a composition comprising silane by a pre-disproportionation reactor silane/chlorosilane mixer to yield the disproportionation reactor feed comprising silane and silicon tetrachloride;
   controlling the temperature of the disproportionation reactor feed comprising silane and silicon tetrachloride by a pre-disproportionation reactor temperature controller; and
   reacting the components of the disproportionation reactor feed comprising silane and silicon tetrachloride by the disproportionation reactor to form a disproportionation reaction product comprising dichlorosilane, trichlorosilane and silicon tetrachloride.

3. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes mixing a composition comprising dichlorosilane and a composition comprising silane.
4. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes mixing a composition comprising trichlorosilane and a composition comprising silane.

5. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes mixing a composition comprising hydrogen chloride and a composition comprising silane.

6. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes mixing a composition comprising liquid or vapor silane and a composition comprising liquid or vapor silicon tetrachloride.

7. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 10 psig to about 500 psig.

8. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 50 psig to about 300 psig.

9. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes
providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 150 psig to about 200 psig.

10. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure of about 180 psig.

11. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 500 psig to about 2500 psig.

12. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 1500 psig to about 2500 psig.

13. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor
silane/chlorosilane mixer and the disproportionation reactor at a pressure ranging from about 1800 psig to about 2200 psig.

14. The method of claim 2 wherein mixing the composition comprising silicon tetrachloride and a composition comprising silane includes providing the composition comprising silane and the composition comprising silicon tetrachloride to one or both of the pre-disproportionation reactor silane/chlorosilane mixer and the disproportionation reactor at a pressure of about 2000 psig

15. The method of claim 2 wherein the disproportionation reactor comprises a catalyst.

16. The method of claim 15 wherein the catalyst comprises a polymeric ion exchange resin.

17. The method of claim 15 wherein the catalyst comprises a metal.

18. The method of claim 15 wherein the catalyst comprises copper.

19. The method of claim 15 wherein the catalyst comprises copper-infused essentially pure silicon.

20. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range of from about 30°C to about 500°C.
21. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range from about 300°C to about 500°C.

22. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range from about 300°C to about 400°C.

23. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range from about 200°C to about 300°C.

24. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range from about 90°C to about 200°C.

25. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range of from about 30°C to about 90°C.

26. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range of from about 55°C to about 75°C.
27. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed in a range of from about 60°C to about 70°C.

28. The method of claim 2 wherein controlling the temperature of the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride includes controlling the temperature of the disproportionation reactor feed to about 60°C.

29. The method of claim 2, further comprising: controlling the composition of the composition comprising silicon tetrachloride or the rate at which the composition comprising silicon tetrachloride is supplied to the pre-disproportionation reactor silane/chlorosilane mixer such that the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride ranges between about 2:1 and about 3.9:1.

30. The method of claim 29 wherein the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride ranges between about 2.5:1 and about 3.5:1.

31. The method of claim 29 wherein the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride ranges between about 2.8:1 and about 3.3:1.

32. The method of claim 29 wherein the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride is about 2.8:1.
33. The method of claim 29 wherein the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride is about 3:1.

34. The method of claim 29 wherein the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride is about 3.2:1.

35. The method of claim 29 wherein the ratio of chlorine to silicon in the disproportionation reactor feed comprising the mixture of silane and silicon tetrachloride is about 3.3:1.

36. The method of claim 2, further comprising:
   separating silicon tetrachloride from a product of the disproportionation reaction in a post-disproportionation reactor silicon tetrachloride separator, to yield a post-disproportionation reactor silicon tetrachloride-rich stream and a post-disproportionation reactor trichlorosilane-rich stream.

37. The method of claim 36, further comprising:
   adjusting silicon tetrachloride content of the disproportionation reactor feed using the silicon tetrachloride separated from the product of the disproportionation reactor in the post-disproportionation reactor silicon tetrachloride separator.

38. The method of claim 2, further comprising:
   vaporizing a mixture comprising the disproportionation reaction product in a pre-CVD reactor vaporizer to yield a vaporized disproportionation reaction product;
mixing hydrogen with the vaporized disproportionation reaction product by a pre-CVD reactor mixer to yield a mixture of hydrogen and disproportionation reaction product; and

performing chemical vapor deposition on the mixture of hydrogen and disproportionation reaction product by the chemical vapor deposition reactor to deposit silicon on the substrate within the chemical vapor deposition reactor.

39. The method of claim 38 wherein mixing hydrogen with the vaporized disproportionation reaction product includes mixing hydrogen with the vaporized disproportionation reaction product by a pre-CVD reactor mixer.

40. The method of claim 38 wherein mixing hydrogen with the vaporized disproportionation reaction product includes mixing hydrogen with the vaporized disproportionation reaction product in the chemical vapor deposition reactor.

41. The method of claim 2, further comprising:
releasing from the chemical vapor deposition reactor an effluent mixture comprising hydrogen, silicon tetrachloride, and one or more of hydrogen chloride, dichlorosilane and trichlorosilane.

42. The method of claim 41, further comprising:
cooling by a post-CVD reactor first cooler the effluent mixture from the chemical vapor deposition reactor to yield a vapor-liquid two-phase mixture.

43. The method of claim 42, further comprising:
removing oily contaminants, including polysilyl materials, from the effluent mixture cooled by the first cooler.
44. The method of claim 42, further comprising:
separating by a post-CVD reactor decanter the vapor-liquid two-phase mixture from the first cooler to yield a vapor phase and a liquid phase.

45. The method of claim 44, further comprising:
converting the vapor phase from the decanter to a vapor-liquid two-phase mixture or a vapor phase by a post-CVD reactor compressor.

46. The method of claim 45, further comprising:
cooling by a post-CVD reactor second cooler the vapor-liquid two-phase mixture or the vapor phase from the compressor.

47. The method of claim 41, further comprising:
supplying the effluent mixture from the chemical vapor deposition reactor to a post-CVD reactor in situ hydrogen chloride reactor; and
converting hydrogen chloride in the effluent mixture from the chemical vapor deposition reactor to chlorosilanes by the post-CVD reactor in situ hydrogen chloride reactor.

48. The method of claim 47, further comprising:
heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor.

49. The method of claim 48 wherein heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger includes heating the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 200°C to about 700°C.
50. The method of claim 48 wherein heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger includes heating the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 300°C to about 600°C.

51. The method of claim 48 wherein heating the effluent mixture from the chemical vapor deposition reactor by an in situ hydrogen chloride reactor heat exchanger includes heating the effluent mixture from the chemical vapor deposition reactor to a temperature of about 500°C.

52. The method of claim 48 wherein the in situ hydrogen chloride reactor heat exchanger exchanges heat from an effluent from the post-CVD reactor in situ hydrogen chloride reactor to the effluent mixture from the chemical vapor deposition reactor before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor.

53. The method of claim 48, further comprising:

heating the effluent mixture from the chemical vapor deposition reactor by a post-CVD reactor startup heater before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor via the in situ hydrogen chloride reactor heat exchanger.

54. The method of claim 47 wherein a residence time of the effluent mixture from the chemical vapor deposition reactor within the post-CVD reactor in situ hydrogen chloride reactor is less than about 10 minutes.
55. The method of claim 47 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 5 minutes.

56. The method of claim 47 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 1 minute.

57. The method of claim 47 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 0.5 minute.

58. The method of claim 47 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 0.1 minute.

59. The method of claim 47, further comprising:
   cooling by a post-CVD reactor first cooler an effluent mixture from the post-CVD reactor in situ hydrogen chloride reactor to yield a vapor-liquid two-phase mixture;
   separating by a post-CVD reactor decanter the vapor-liquid two-phase mixture from the first cooler to yield a vapor phase and a liquid phase;
   converting the vapor phase from the decanter to a vapor-liquid two-phase mixture or a vapor phase by a post-CVD reactor compressor; and
   cooling the vapor-liquid two-phase mixture or the vapor phase from the compressor by a post-CVD reactor second cooler.

60. The method of claim 41, further comprising:
   separating hydrogen from the chemical vapor deposition reactor effluent mixture by a post-CVD reactor hydrogen separator to yield a post-CVD
reactor hydrogen-rich stream and a post-CVD reactor hydrogen-depleted stream.

61. The method of claim 60 wherein the concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream is less than 15 weight%.

62. The method of claim 60 wherein the concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream is less than 10 weight%.

63. The method of claim 60 wherein the concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream is less than 5 weight%.

64. The method of claim 60 wherein the concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream is less than 1 weight%.

65. The method of claim 60 wherein the concentration of silicon tetrachloride in the post-CVD reactor hydrogen-rich stream is less than 0.1 weight%.

66. The method of claim 60, further comprising:
mixing by a pre-CVD reactor mixer the post-CVD reactor hydrogen-rich stream with a post-disproportionation reactor trichlorosilane-rich stream from a post-disproportionation reactor silicon tetrachloride separator.

67. The method of claim 60, further comprising:
mixing the post-CVD reactor hydrogen-depleted stream and a post-disproportionation reactor silicon tetrachloride-rich stream from the post-
disproportionation reactor silicon tetrachloride separator by a pre-
disproportionation reactor chlorosilane mixer.

68. The method of claim 67, further comprising:
determining amounts of elemental silicon and elemental chlorine in
the post-CVD reactor hydrogen-depleted stream and in the post-
disproportionation reactor silicon tetrachloride-rich stream prior to mixing the
post-CVD reactor hydrogen-depleted stream and the post-disproportionation
reactor silicon tetrachloride-rich stream.

69. The method of claim 67, further comprising:
mixing by the pre-disproportionation reactor chlorosilane mixer
amounts of the post-CVD reactor hydrogen-depleted stream; the post-
disproportionation reactor silicon tetrachloride-rich stream; and, as required, a
feed of purified silicon tetrachloride, trichlorosilane, dichlorosilane, or a mixture
of one or more of purified silicon tetrachloride, trichlorosilane, or dichlorosilane;
and
controlling the amounts of elemental chlorine and elemental
silicon supplied from each source to maintain a selected ratio of chlorine to
silicon in the disproportionation reactor feed.

70. The method of claim 60, further comprising:
separating by a post-CVD reactor hydrogen chloride separator
hydrogen chloride from the post-CVD reactor hydrogen-depleted stream to yield
a post-CVD reactor hydrogen-depleted, hydrogen chloride-rich stream and a
post-CVD reactor hydrogen-depleted, hydrogen chloride-depleted stream.

71. The method of claim 70, further comprising:
transporting the post-CVD reactor hydrogen-depleted, hydrogen
chloride-rich stream from the post-CVD reactor hydrogen chloride separator to
a hydrogen chloride storage system.
72. The method of claim 70, further comprising:
transporting the post-CVD reactor hydrogen-depleted, hydrogen chloride-depleted stream from the post-CVD reactor hydrogen chloride separator to a pre-disproportionation reactor chlorosilane mixer.

73. The method of claim 70, further comprising:
separating by a post-CVD reactor chlorosilane separator silicon tetrachloride from dichlorosilane and trichlorosilane in the hydrogen-depleted, hydrogen chloride-depleted stream to yield a post-CVD reactor silicon tetrachloride-rich stream and a post-CVD reactor dichlorosilane-rich, trichlorosilane-rich stream.

74. The method of claim 73, further comprising:
separating the dichlorosilane from the trichlorosilane in the post-CVD reactor dichlorosilane-rich, trichlorosilane-rich stream by a dichlorosilane/trichlorosilane separator to yield a post-CVD reactor dichlorosilane-rich stream and a post-CVD reactor trichlorosilane-rich stream.

75. The method of claim 74, further comprising:
mixing the post-CVD reactor trichlorosilane-rich stream with a post-disproportionation reactor trichlorosilane-rich stream.

76. The method of claim 74, further comprising:
mixing the post-CVD reactor silicon tetrachloride-rich stream and the post-CVD reactor dichlorosilane-rich stream by a post-CVD reactor chlorosilane mixer.

77. The method of claim 76 wherein mixing the silicon tetrachloride-rich stream and the dichlorosilane-rich stream by a post-CVD reactor chlorosilane mixer includes selecting an amount of dichlorosilane and adding the amount of dichlorosilane to the post-CVD reactor chlorosilane mixer.
thereby controlling the concentration of dichlorosilane in the feed to the disproportionation reactor and the chemical vapor deposition reactor.

78. The method of claim 77 wherein controlling the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor includes controlling the ratio of chlorine to silicon in the feed to the disproportionation reactor.

79. The method of claim 78 wherein controlling the ratio of chlorine to silicon in the feed to the disproportionation reactor includes controlling one or more of make-up silicon tetrachloride, trichlorosilane, and dichlorosilane added to the feed to the disproportionation reactor.

80. The method of claim 74, further comprising:
   supplying dichlorosilane from the dichlorosilane/trichlorosilane separator to the chemical vapor deposition reactor.

81. The method of claim 80 wherein supplying dichlorosilane from the dichlorosilane/trichlorosilane separator to the chemical vapor deposition reactor includes adjusting the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor.

82. The method of claim 74, further comprising:
   storing all or a portion of the dichlorosilane in a dichlorosilane storage system or disposing of the dichlorosilane by a dichlorosilane disposal system.

83. The method of claim 41, further comprising:
   separating hydrogen and hydrogen chloride from the chemical vapor deposition reactor effluent mixture by a post-CVD reactor.
hydrogen/hydrogen chloride separator to yield a hydrogen/hydrogen chloride-rich stream and a hydrogen/hydrogen chloride-depleted stream; separating the hydrogen from the hydrogen chloride in the hydrogen/hydrogen chloride-rich stream by a pre-CVD reactor hydrogen/hydrogen chloride separator; and transporting the hydrogen chloride from the pre-CVD reactor hydrogen/hydrogen chloride separator to a hydrogen chloride storage system.

84. The method of claim 83, further comprising:
mixing by a pre-CVD reactor mixer the hydrogen from the pre-CVD reactor hydrogen/hydrogen chloride separator with a post-disproportionation reactor trichlorosilane-rich stream from the post-disproportionation reactor silicon tetrachloride separator.

85. The method of claim 70, further comprising:
feeding the hydrogen-depleted, hydrogen chloride-rich stream from the post-CVD reactor hydrogen chloride separator and silane to a pre-disproportionation reactor silane/hydrogen chloride reactor; and reacting the silane with the hydrogen chloride by the pre-disproportionation reactor silane/hydrogen chloride reactor to yield chlorosilanes including trichlorosilane and silicon tetrachloride.

86. The method of claim 85 wherein a temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor ranges between about 50°C and 700°C.

87. The method of claim 85 wherein a temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor ranges between about 100°C and about 600°C.
88. The method of claim 85 wherein a temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor ranges between about 300°C and about 500°C.

89. The method of claim 85 wherein a temperature within the pre-disproportionation reactor silane/hydrogen chloride reactor is about 500°C.

90. The method of claim 85 wherein a molar ratio of silane to hydrogen chloride in the feed to the pre-disproportionation reactor silane/hydrogen chloride reactor ranges from about 0:1 to about 2:1.

91. The method of claim 85 wherein a molar ratio of silane to hydrogen chloride ranges from about 0:1 to about 1.5:1.

92. The method of claim 85 wherein a molar ratio of silane to hydrogen chloride ranges from about 0:1 to about 1:1.

93. The method of claim 85 wherein a molar ratio of silane to hydrogen chloride is about 0.33:1.

94. The method of claim 85 wherein reacting the silane with the hydrogen chloride by a pre-disproportionation reactor silane/hydrogen chloride reactor includes reacting the silane with the hydrogen chloride in the presence of a metal-containing catalyst.

95. The method of claim 94 wherein the metal-containing catalyst comprises copper.

96. The method of claim 95 wherein the metal-containing catalyst comprises copper-infused essentially pure silicon.
97. The method of claim 85, further comprising:

mixing by the pre-disproportionation reactor chlorosilane mixer amounts of the post-CVD reactor hydrogen-depleted, hydrogen chloride-depleted stream; the chlorosilanes from the pre-disproportionation reactor silane/hydrogen chloride reactor; a silicon tetrachloride-rich stream from a post-disproportionation reactor silicon tetrachloride separator; and, as required, a feed of purified silicon tetrachloride, purified trichlorosilane, purified dichlorosilane, or a mixture of one or more of purified silicon tetrachloride, purified trichlorosilane, or purified dichlorosilane; and

controlling the amounts of elemental chlorine and elemental silicon supplied from each source to maintain a selected ratio of chlorine to silicon in the feed to the disproportionation reactor.

98. The method of claim 70, further comprising:

reacting by a post-CVD reactor silane/hydrogen chloride reactor the hydrogen-depleted, hydrogen chloride-rich stream from the post-CVD reactor hydrogen chloride separator with silane and the chemical vapor deposition reactor effluent mixture.

99. The method of claim 98, further comprising:

adjusting the temperature of the chemical vapor deposition reactor effluent mixture in the post-CVD reactor silane/hydrogen chloride reactor to between about 200°C and about 600°C prior to mixing the hydrogen-depleted, hydrogen chloride-rich stream with the silane and the chemical vapor deposition reactor effluent mixture in the post-CVD reactor silane/hydrogen chloride reactor.

100. The method of claim 99 wherein adjusting the temperature of the chemical vapor deposition reactor effluent in the post-CVD reactor silane/hydrogen chloride reactor includes adjusting the temperature by a post-CVD reactor heat exchanger.
101. The method of claim 99 wherein adjusting the temperature of the chemical vapor deposition reactor effluent mixture in the post-CVD reactor silane/hydrogen chloride reactor prior to mixing the hydrogen chloride with the silane and the chemical vapor deposition reactor effluent mixture includes adjusting the temperature to between about 400°C and about 500°C.

102. The method of claim 98 wherein a molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor silane/hydrogen chloride reactor ranges from about 0:1 to about 2:1.

103. The method of claim 102 wherein a molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor silane/hydrogen chloride reactor ranges from about 0:1 to about 1.5:1.

104. The method of claim 103 wherein a molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor silane/hydrogen chloride reactor ranges from about 0:1 to about 1:1.

105. The method of claim 104 wherein a molar ratio of silane to hydrogen chloride in the feed to the post-CVD reactor silane/hydrogen chloride reactor is about 0.33:1.

106. The method of claim 98, further comprising:

adjusting the flow in the post-CVD reactor silane/hydrogen chloride reactor such that a residence time of the hydrogen chloride-silane-CVD effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor is sufficient to allow complete reaction of the hydrogen chloride and the silane.

107. The method of claim 106 wherein the post-CVD reactor silane/hydrogen chloride reactor includes one or more reaction chambers of
sufficient total volume to provide a residence time appropriate to allow complete reaction of the hydrogen chloride and the silane.

108. The method of claim 107 wherein the residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor is less than about 10 minutes.

109. The method of claim 107 wherein the residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor is less than about 5 minutes.

110. The method of claim 107 wherein the residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor is less than about 1 minute.

111. The method of claim 107 wherein the residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor is less than about 0.5 minute.

112. The method of claim 107 wherein the residence time of the effluent mixture within the post-CVD reactor silane/hydrogen chloride reactor is less than about 0.1 minute.

113. The method of claim 36, further comprising:
separating dichlorosilane from the post-disproportionation reactor trichlorosilane-rich stream by a post-disproportionation reactor dichlorosilane separator to yield a post-disproportionation reactor dichlorosilane-rich stream.

114. The method of claim 113, further comprising:
determining dichlorosilane concentration in a feed to the chemical vapor deposition reactor; and
adjusting the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor.

115. The method of claim 114 wherein adjusting the concentration of dichlorosilane in the feed to the chemical vapor deposition reactor includes adding the post-disproportionation reactor dichlorosilane-rich stream to the feed to the chemical vapor deposition reactor.

116. The method of claim 114 wherein adjusting the concentration of dichlorosilane in the chemical vapor deposition reactor includes adding dichlorosilane separated from a chemical vapor deposition reactor effluent mixture from which hydrogen and hydrogen chloride have been removed.

117. The method of claim 2 wherein mixing a composition comprising silane and a composition comprising silicon tetrachloride includes mixing a composition comprising silane in a vapor phase, a liquid phase, or a vapor-liquid mixed phase and a composition comprising silicon tetrachloride in a vapor phase, a liquid phase, or a vapor-liquid mixed phase.

118. The method of claim 2, further comprising:
mixing one or more of monochlorosilane, dichlorosilane, and trichlorosilane with the disproportionation reactor feed by a pre-disproportionation reactor chlorosilane mixer prior to reacting the disproportionation reactor feed by the disproportionation reactor.

119. The method of claim 118 wherein a molar ratio of the one or more of monochlorosilane, dichlorosilane, and trichlorosilane to silicon tetrachloride ranges from about 0 to about 3:1.
120. The method of claim 118 wherein the molar ratio of the one or more of monochlorosilane, dichlorosilane, and trichlorosilane to silicon tetrachloride ranges from about 0 to about 2.5:1.

121. The method of claim 118 wherein the molar ratio of the one or more of monochlorosilane, dichlorosilane, and trichlorosilane to silicon tetrachloride ranges from about 0.1:1 to about 1:1.

122. The method of claim 118 wherein a molar ratio of the one or more of monochlorosilane, dichlorosilane, and trichlorosilane to silicon tetrachloride is about 0.5:1.

123. The method of claim 2, further comprising:
converting low boiling phosphorus contaminants to intermediate and high boiling phosphorus contaminants by the disproportionation reactor.

124. The method of claim 123 wherein low boiling phosphorus contaminants include PH₃ and PH₂Cl.

125. The method of claim 123 wherein intermediate boiling phosphorus contaminants include PHCl₂.

126. The method of claim 123 wherein high boiling phosphorus contaminants include PCl₃.

127. The method of claim 123, further comprising:
separating silicon tetrachloride and intermediate and high boiling phosphorus contaminants from low boiling phosphorus contaminants in a disproportionation reaction effluent by a post-disproportionation reactor silicon tetrachloride separator.
128. The method of claim 127, further comprising:
separating the high boiling phosphorus contaminants from the
silicon tetrachloride and the intermediate boiling phosphorus contaminants in a
high-boiling phosphorus separator.

129. The method of claim 128, further comprising:
discarding the high boiling phosphorus contaminants.

130. The method of claim 128, further comprising:
cycling the intermediate boiling phosphorus contaminants to the
disproportionation reactor; and
converting intermediate boiling phosphorus contaminants to high
boiling phosphorus contaminants by the disproportionation reactor.

131. The method of claim 36, further comprising:
separating dichlorosilane from trichlorosilane in the post-
disproportionation reactor trichlorosilane-rich stream by a post-
disproportionation reactor dichlorosilane/trichlorosilane separator to yield a
post-disproportionation reactor dichlorosilane-rich/trichlorosilane-depleted
material and a post-disproportionation reactor trichlorosilane-rich/dichlorosilane-
depleted material.

132. The method of claim 131, further comprising:
determining dichlorosilane concentration in the post-
disproportionation reactor dichlorosilane-rich/trichlorosilane-depleted material.

133. The method of claim 131, further comprising:
determining trichlorosilane concentration in the post-
disproportionation reactor trichlorosilane-rich/dichlorosilane-depleted material.
134. The method of claim 131 wherein the post-disproportionation reactor dichlorosilane-rich/trichlorosilane-depleted material is essentially pure dichlorosilane.

135. The method of claim 131, further comprising:

storing the dichlorosilane-rich/trichlorosilane-depleted material in a dichlorosilane storage system.

136. The method of claim 131, further comprising:

storing the trichlorosilane-rich/dichlorosilane-depleted material in a trichlorosilane storage system.

137. The method of claim 131, further comprising:

mixing the dichlorosilane-rich/trichlorosilane-depleted material with the trichlorosilane-rich/dichlorosilane-depleted material to yield a chemical vapor deposition reactor feed; and

supplying the feed to the chemical vapor deposition reactor.

138. The method of claim 137 wherein mixing the dichlorosilane-rich/trichlorosilane-depleted material with the trichlorosilane-rich/dichlorosilane-depleted material includes mixing dichlorosilane-rich/trichlorosilane-depleted material from the dichlorosilane storage system.

139. The method of claim 137 wherein mixing the dichlorosilane-rich/trichlorosilane-depleted material with the trichlorosilane-rich/dichlorosilane-depleted material includes mixing trichlorosilane-rich/dichlorosilane-depleted material from the trichlorosilane storage system.

140. The method of claim 137 wherein mixing the dichlorosilane-rich/trichlorosilane-depleted material with the trichlorosilane-rich/dichlorosilane-depleted material to yield a chemical vapor deposition
reactor feed includes adjusting a ratio of chlorine to silicon in the chemical vapor deposition reactor feed.

141. A method of producing silicon, the method comprising:
performing a chemical vapor deposition on a mixture comprising trichlorosilane by a chemical vapor deposition reactor;
recovering silicon from the chemical vapor deposition reactor;
releasing from the chemical vapor deposition reactor an effluent mixture comprising hydrogen, silicon tetrachloride, and one or more of hydrogen chloride, dichlorosilane, and trichlorosilane; and
converting hydrogen chloride in the effluent mixture from the chemical vapor deposition reactor to chlorosilanes by a post-CVD reactor in situ hydrogen chloride reactor.

142. The method of claim 141, further comprising:
controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a first post-CVD reactor heat exchanger before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor.

143. The method of claim 142 wherein controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a first post-CVD reactor heat exchanger includes controlling the temperature of the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 200°C to about 700°C.

144. The method of claim 142 wherein controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a first post-CVD reactor heat exchanger includes controlling the temperature of the effluent mixture from the chemical vapor deposition reactor to a temperature in a range of from about 300°C to about 600°C.
145. The method of claim 142 wherein controlling the temperature of the effluent mixture from the chemical vapor deposition reactor by a first post-CVD reactor heat exchanger includes controlling the temperature of the effluent mixture from the chemical vapor deposition reactor to a temperature of about 500°C.

146. The method of claim 142 wherein the first post-CVD reactor heat exchanger exchanges heat from an effluent from the post-CVD reactor in situ hydrogen chloride reactor to the effluent mixture from the chemical vapor deposition reactor before supplying the effluent mixture from the chemical vapor deposition reactor to the post-CVD reactor in situ hydrogen chloride reactor.

147. The method of claim 141 wherein a residence time of the effluent mixture from the chemical vapor deposition reactor within the post-CVD reactor in situ hydrogen chloride reactor is less than about 10 minutes.

148. The method of claim 141 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 5 minutes.

149. The method of claim 141 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 1 minute.

150. The method of claim 141 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 0.5 minute.
151. The method of claim 141 wherein a residence time of the effluent mixture within the post-CVD reactor in situ hydrogen chloride reactor is less than about 0.1 minute.

152. The method of claim 141, further comprising:
cooling by a first cooling system an effluent mixture from the post-CVD reactor in situ hydrogen chloride reactor.

153. The method of claim 152, further comprising:
converting the effluent mixture from the post-CVD reactor in situ hydrogen chloride reactor to a vapor-liquid two-phase mixture by a compressor system.

154. The method of claim 153, further comprising:
cooling the vapor-liquid two-phase mixture from the compressor system by a second cooling system.

155. The method of claim 154 wherein the second cooling system comprises a second post-CVD reactor heat exchanger.

156. The method of claim 154, further comprising:
separating hydrogen from the effluent mixture from the post-CVD reactor in situ hydrogen chloride reactor by a post-CVD reactor silicon tetrachloride absorber/hydrogen separator.

157. The method of claim 156, further comprising:
saturating with trichlorosilane the hydrogen separated by the post-CVD reactor silicon tetrachloride absorber/hydrogen separator.
158. The method of claim 156, further comprising:
mixing the hydrogen from the post-CVD reactor silicon
tetrachloride absorber/hydrogen separator with a feed to the chemical vapor
deposition reactor.

159. The method of claim 156, further comprising:
separating by a post-CVD reactor silicon
tetrachloride/trichlorosilane separator trichlorosilane from silicon tetrachloride in
the effluent mixture from the post-CVD reactor silicon tetrachloride
absorber/hydrogen separator.

160. The method of claim 159, further comprising:
feeding trichlorosilane from the silicon tetrachloride/trichlorosilane
separator to the silicon tetrachloride absorber/hydrogen separator; and
reacting the trichlorosilane with silicon tetrachloride in the silicon
tetrachloride absorber/hydrogen separator.

161. The method of claim 160, further comprising:
adjusting the temperature of the trichlorosilane prior to feeding the
trichlorosilane to the silicon tetrachloride absorber/hydrogen separator.

162. The method of claim 161 wherein adjusting the
temperature includes adjusting the temperature of the trichlorosilane to about
35°C.

163. The method of claim 159, further comprising:
mixing the trichlorosilane from the silicon
tetrachloride/trichlorosilane separator with a feed to the chemical vapor
deposition reactor.
164. The method of claim 159, further comprising:
cooling the trichlorosilane; and
venting vapor phase lower boiling materials from the trichlorosilane.

165. The method of claim 159, further comprising:
separating by a high-boiling phosphorus separator high boiling phosphorus contaminants including PCl$_3$ from the silicon tetrachloride.

166. The method of claim 159, further comprising:
mixing the trichlorosilane with a feed to the chemical vapor deposition reactors.

167. A method of producing silicon, the method comprising:
performing a chemical vapor deposition on a mixture comprising trichlorosilane by a chemical vapor deposition reactor;
recovering silicon from the chemical vapor deposition reactor;
releasing from the chemical vapor deposition reactor an effluent mixture comprising hydrogen, silicon tetrachloride, and one or more of hydrogen chloride, dichlorosilane, and trichlorosilane; and
cooling the effluent mixture from the chemical vapor deposition reactor by a first cooling system.

168. The method of claim 167, further comprising:
separating by a post-CVD reactor hydrogen separator hydrogen from the cooled effluent mixture from the chemical vapor deposition reactor; and
separating by a post-CVD reactor hydrogen chloride separator hydrogen chloride from the effluent mixture from the chemical vapor deposition reactor from which hydrogen has been removed by the post-CVD reactor hydrogen separator.
169. The method of claim 168, further comprising:
feeding the hydrogen chloride from the post-CVD reactor
hydrogen chloride separator and silane to a hydrogen chloride-silane reactor;
and
reacting the silane with the hydrogen chloride by the hydrogen chloride-silane reactor to produce chlorosilanes including trichlorosilane.

170. The method of claim 169, further comprising:
reacting by a post-CVD reactor silane/hydrogen chloride reactor
the hydrogen chloride from the post-CVD reactor hydrogen chloride separator
with silane and the chemical vapor deposition reactor effluent mixture.

171. A method of producing silicon, the method comprising:
reacting a disproportionation reactor feed comprising
trichlorosilane and silane by a disproportionation reactor to form a
disproportionation reactor product comprising dichlorosilane, trichlorosilane and
silicon tetrachloride;
performing a chemical vapor deposition on a mixture from the
disproportionation reactor by a chemical vapor deposition reactor to deposit
silicon on a substrate within the chemical vapor deposition reactor; and
recovering silicon from the chemical vapor deposition reactor.

172. The method of claim 171, further comprising:
controlling a composition of the disproportionation reactor feed
comprising trichlorosilane and silane such that the ratio of chlorine to silicon in
the disproportionation reactor feed ranges between about 1:1 and about 3:1.

173. The method of claim 171, further comprising:
controlling a composition of the disproportionation reactor feed
comprising trichlorosilane and silane such that the ratio of chlorine to silicon in
the disproportionation reactor feed ranges between about 1:1 and about 2.5:1.
174. The method of claim 171, further comprising:
controlling a composition of the disproportionation reactor feed
comprising trichlorosilane and silane such that the ratio of chlorine to silicon in
the disproportionation reactor feed ranges between about 1:1 and about 2:1.

175. The method of claim 171, further comprising:
controlling a composition of the disproportionation reactor feed
comprising trichlorosilane and silane such that the ratio of chlorine to silicon in
the disproportionation reactor feed ranges between about 1.25:1 and about
1.75:1.

176. The method of claim 171, further comprising:
controlling a composition of the disproportionation reactor feed
comprising trichlorosilane and silane such that the ratio of chlorine to silicon in
the disproportionation reactor feed ranges between about 1.75:1 and about
2.25:1.

177. The method of claim 171, further comprising:
controlling a composition of the disproportionation reactor feed
comprising trichlorosilane and silane such that the ratio of chlorine to silicon in
the disproportionation reactor feed is about 1.5:1.

178. The method of claim 171, further comprising:
controlling a composition of the disproportionation reactor feed
comprising trichlorosilane and silane such that the ratio of chlorine to silicon in
the disproportionation reactor feed is about 2:1.

179. The method of claim 171 wherein reacting a
disproportionation reactor feed to form a disproportionation reaction product
comprising dichlorosilane, trichlorosilane and silicon tetrachloride includes
optimizing operating conditions of the disproportionation reactor to maximize production of dichlorosilane.

180. The method of claim 179, further comprising:
separating silicon tetrachloride from a product of the disproportionation reactor in a post-disproportionation reactor silicon tetrachloride separator to yield a post-disproportionation reactor silicon tetrachloride-depleted stream and a post-disproportionation reactor silicon tetrachloride-rich stream.

181. The method of claim 180, further comprising:
separating dichlorosilane from trichlorosilane in the post-disproportionation reactor silicon tetrachloride-depleted stream by a post-disproportionation reactor dichlorosilane/trichlorosilane separator to yield a post-disproportionation reactor dichlorosilane-rich material and a post-disproportionation reactor trichlorosilane-rich material.

182. The method of claim 181, further comprising:
determining dichlorosilane concentration in the post-disproportionation reactor dichlorosilane-rich material.

183. The method of claim 181, further comprising:
determining trichlorosilane concentration in the post-disproportionation reactor trichlorosilane-rich material.

184. The method of claim 181 wherein the post-disproportionation reactor dichlorosilane-rich material is essentially pure dichlorosilane.

185. The method of claim 181, further comprising:
storing the post-disproportionation reactor dichlorosilane-rich material in a dichlorosilane storage system.

186. The method of claim 181, further comprising:
storing the post-disproportionation reactor trichlorosilane-rich material in a trichlorosilane storage system.

187. The method of claim 181, further comprising:
mixing the dichlorosilane-rich material with the trichlorosilane-rich material to yield a chemical vapor deposition reactor feed; and
supplying the feed to the chemical vapor deposition reactor.

188. The method of claim 187 wherein mixing the dichlorosilane-rich material with the trichlorosilane-rich material includes mixing dichlorosilane-rich material from the dichlorosilane storage system.

189. The method of claim 187 wherein mixing the dichlorosilane-rich material with the trichlorosilane-rich material includes mixing trichlorosilane-rich material from the trichlorosilane storage system.

190. The method of claim 187 wherein mixing the dichlorosilane-rich material with the trichlorosilane-rich material to yield a chemical vapor deposition reactor feed includes adjusting a ratio of chlorine to silicon in the chemical vapor deposition reactor feed.

191. The method of claim 181, further comprising:
supplying the post-disproportionation reactor dichlorosilane-rich material directly to the chemical vapor deposition reactor.

192. The method of claim 181, further comprising:
supplying the post-disproportionation reactor trichlorosilane-rich material directly to the chemical vapor deposition reactor.

193. The method of claim 181, further comprising:
imixing the post-disproportionation reactor dichlorosilane-rich material and the post-disproportionation reactor trichlorosilane-rich material; and
supplying the mixture of post-disproportionation reactor dichlorosilane-rich material and post-disproportionation reactor trichlorosilane-rich material to the CVD reactor.

194. The method of claim 181, further comprising:
imixing the post-disproportionation reactor trichlorosilane-rich material with silane; and
supplying the mixture of post-disproportionation reactor trichlorosilane-rich material and silane to the disproportionation reactor.

195. A method of producing silicon, comprising:
producing and supplying silane; and
processing the silane according to methods claimed herein.
FIG. 1H
FIG. 4