### Title: HIGH PRESSURE PLASMA HYDROGENATION OF SILICON TETRACLORIDE

A method for the plasma hydrogenation of SiCl₄. A high pressure plasma (16) is utilized to effect a reaction of H₂ (44) and SiCl₄ (42) to form HSICl₃ and other hydrogenated silicon chlorides which can be separated from H₂ and HCl by-product by passing the output gases from reactor (50) to condensation apparatus (56).
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HIGH PRESSURE PLASMA HYDROGENATION OF
SILICON TETRACHLORIDE

BACKGROUND OF THE INVENTION

This invention relates in general to a method for the hydrogenation of silicon tetrachloride and more specifically to a high pressure plasma (HPP) method for the hydrogenation of silicon tetrachloride to produce trichlorosilane.

Trichlorosilane is the most widely used silicon source gas for the production of polycrystalline silicon. SiHCl₃ is reduced with hydrogen at an elevated temperature to deposit pure polycrystalline silicon. By-products of this reaction are unreacted SiHCl₃, SiCl₄, HCl, other chlorosilanes and polymeric chlorosilanes. Less than about one third of the input SiHCl₃ is converted to silicon and about two thirds is converted to SiCl₄. The SiCl₄ cannot be used efficiently for polysilicon growth and thus is essentially a low-value waste product. Attempts have been made to convert silicon tetrachloride to trichlorosilane; that is, to convert the waste material SiCl₄ to a useful starting material SiHCl₃. In one such attempt, SiCl₄ is converted to SiHCl₃ in a hydrogen reaction at high temperatures (1000-1200°C) and at high reactor pressures (typically 30-50 atmospheres). In this conversion, however, conversion efficiency and throughput are too low to be practical. Another problem encountered is that of silicon deposition in the hydrogenation reactor during the conversion.

Accordingly, a need existed for a method of converting silicon tetrachloride to trichlorosilane in order to reduce the cost of starting materials and thereby to reduce the cost of polycrystalline silicon. It is therefore an object of this invention to provide an efficient method for converting silicon tetrachloride to trichlorosilane.
It is a further object of this invention to provide a high pressure plasma method for the hydrogenation of silicon tetrachloride. It is still another object of the invention to provide a method for the hydrogenation of silicon tetrachloride capable of high throughput and without silicon deposition during the conversion process.

SUMMARY OF THE INVENTION

The foregoing objects are achieved in the invention through the use of a high pressure plasma (HPP) for the hydrogenation of silicon tetrachloride. Hydrogen and silicon tetrachloride are reacted in the presence of a high pressure RF plasma to form SiHCl₃, SiH₂Cl₂, and HCl by the reaction

\[ \text{HPP} \quad \text{H}_2 + \text{SiCl}_4 \rightarrow \text{SiHCl}_3 + \text{SiH}_2\text{Cl}_2 + \text{HCl} \]

The process is optimized to enhance the production of SiHCl₃. Details of the invention will be further appreciated after a consideration of the following detailed description of the invention taken in connection with the drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 illustrates an apparatus for practice of the invention;

FIG. 2 illustrates a high pressure plasma module for impedance matching and for introduction of reactant gases; and

FIG. 3 illustrates in cross-section a high pressure plasma nozzle assembly.
A plasma can be defined as an approximately neutral cloud of charged particles. The plasma may be formed, for example, by an electric glow discharge in a strong electric field. The types and characteristics of plasmas can vary widely; two types commonly of interest are the low pressure and high pressure plasmas. The boundary line which distinguishes between the two types of plasma is a pressure of about 13.3 KPa, but for practical purposes the high pressure plasma (HPP) is typically produced at a pressure of about one atmosphere (101 KPa). An important distinction between low pressure and high pressure plasma relates to temperature: in a low pressure plasma the electron temperature can be much greater than the gas temperature; in contrast, the conditions found in a high pressure plasma lead to thermal equilibrium in which the electron and gas temperatures are nearly identical. The gas temperature in the high pressure plasma can typically reach 3000-5000°K.

FIG. 1 illustrates an apparatus suitable for practice of the invention. The apparatus comprises an RF generator 10 operating at 13.56 MHz, an impedance matching module 12 and a dual flow nozzle 14 for sustaining a high pressure RF plasma beam 16. The power rating of the RF generator is selected for the particular application. While the exact frequency of the generator is not critical to the invention, this particular frequency is chosen in accordance with FCC regulations. A co-axial cable 18 connects the RF generator to the impedance matching module.

The impedance-matching module is illustrated in FIG. 2. The module is a π network and consists of a tubular coil 20 and two variable capacitors 22 and 24 connected between the input and output of the coil, respectively, and ground. Coil 20 is made of two concentric tubes 26, 28 as shown in cross section in FIG. 2a and provides for...
conveying separate inner and outer gas streams, respectively, through the RF circuit. The output of generator 10 is connected to the input side of the π network by coaxial cable 18. The concentric tubes of coil 20 can be made of any material that is a good electrical conductor and that is unreactive with SiCl₄. Stainless steel coated with copper on its outer surface, for example, is suitable for the coil material. The copper coating reduces ohmic losses in the coil. When the π network is tuned for resonance, the voltage at the output 30 of the network reaches a maximum, a voltage sufficient to create and maintain a high pressure plasma at the tip of the nozzle.

The dual-flow high pressure plasma nozzle is illustrated in more detail in the cross-sectional view of FIG. 3. Output 30 of coil 20 having concentric inner and outer tubes 26, 28, conveying two different gas streams, is attached to nozzle 14. The nozzle is comprised of a metal shell 32 made of stainless steel or other metal that is resistant to the chlorosilane ambient. An inner electrode 34 is formed of a refractory metal such as molybdenum or tungsten. An insulator sheath 36 forms the end of the nozzle. The sheath is formed of an insulator such as boron nitride which has high dielectric strength at the RF frequency and is resistant to the chlorosilane ambient. One of the reactant gases is conveyed through inner tube 26 to inner electrode 34. A second gas is conveyed through outer tube 28 and then through a plurality of ports 38, or openings, which are bored through metal shell 32 and which are arranged concentrically about opening 40 into which inner tube 26 and inner electrode 34 are positioned. The nozzle thus permits the isolation of the two gas streams until they exit at the tip of the nozzle.

FIG. 1 also illustrates a gas control system for controlling input amounts of the silicon tetrachloride and hydrogen reactants. Sources of the silicon tetrachloride, hydrogen, and an inert gas such as helium are shown at 42,
44, 46, respectively. The gases are conveyed to a gas control system 48 which comprises appropriate valves and mass flow controllers for the safe and precise control of the reactant flows. A mole ratio of H₂ to SiCl₄ of between 4 and 5 is preferred to optimize the SiCl₄ to SiHCl₃ conversion efficiency. A mole ratio of 4.2, for example, results in a conversion efficiency of about 50%. Mole ratios higher than about 5 can be used to further increase the conversion efficiency, but the higher mole ratios tend to lead to some silicon production in addition to the trichlorosilane production. The gases are conveyed from the gas controller to the impedance matching module where they enter the inner and outer tubes of coil 20.

The high pressure plasma reaction takes place within a reactor 50. The reactor is simply a quartz tube 52, sealed at the ends by end seals 53 and 54. The end seals serve the purpose of sealing the quartz tube and controlling the ambient within the reactor. Dimensions of the quartz tube are not critical; a diameter about four times the length of the plasma beam and a length of about ten times the diameter is satisfactory.

The exact pressure within the reactor depends on the flow rate of reactants, the RF power of the plasma beam (because of gas expansion by heating) and the resistance of the gas flow line exiting the reactor. Control of the pressure at any one specific value is not required. The reactor is not evacuated, however, and thus the pressure within the reactor is consequently above one atmosphere.

Reaction products resulting from the high pressure plasma hydrogenation exit the reactor through end seal 53. The total output of the system comprises unreacted SiCl₄ and H₂ and the reaction products SiHCl₃, SiH₂Cl₂, and HCl. This gas mixture is separated by conventional techniques and the unreacted SiCl₄ and H₂ are recycled through the process. This separation can be accomplished, for example, by passing the output gases first through a
condensation apparatus 56 at -78°C. At this temperature all of the SiCl₄, SiHCl₃, SiH₂Cl₂, and some of the HCl will be condensed. The condensate is distilled to separate the individual components. Most of the HCl and all of the H₂ pass through the condensation apparatus and into a carbon adsorption bed 58. HCl is adsorbed in the bed while the H₂ passes through the bed and is recycled. The HCl is subsequently boiled from the carbon bed and the bed regenerated. The SiH₂Cl₂ is valuable elsewhere, e.g. for use in the epitaxial growth of silicon.

The following general example illustrates the practice of the invention. The reactor is purged with helium or other inert gas to remove all air from the system. Hydrogen is introduced into both the inner and outer gas streams of the dual-walled coil at the impedance matching network. The RF generator is turned on and the power is increased to a level which is suitable for creating a plasma. The input and output capacitors of the π network are tuned to resonance. The creation of a plasma beam at the dual-flow nozzle and a low reflected power measured at the RF generator are indications of resonance.

After the plasma is created, SiCl₄ is gradually introduced into the inner gas stream while gradually reducing the H₂ flow in that stream. Changing the gas from hydrogen to silicon tetrachloride affects the tuning of the network; it is therefore necessary to simultaneously retune the impedance matching network to sustain the plasma. When all of the hydrogen in the inner gas stream is replaced by silicon tetrachloride the flow rates of the two gases are adjusted to obtain the desired flow rates and mole ratio of the reactants. Alternatively, the H₂ can be introduced through the inner stream and SiCl₄ through the outer.

The two reactants exit the high pressure plasma nozzle and react. The extremely high temperatures resulting from the plasma favor the hydrogenation reaction with little or
no catenation of molecules. Silicon tetrachloride is thus hydrogenated to form trichlorosilane and dichlorosilane with little formation of potentially detonable chlorosilane polymers. In comparison, a hydrogenation reaction carried out in low pressure plasmas tends to produce these detonable chlorosilane polymers in considerable quantities.

An in-line gas chromatograph is used to analyze the output gases from the high pressure plasma reactor so that the conversion efficiency can be instantaneously and continuously determined and monitored. Using the gas chromatograph data, the RF power is adjusted to optimize the conversion efficiency. As the RF power is increased the conversion efficiency is found to increase, reach a maximum, and then decrease. The power level for optimum conversion efficiency depends, however, on the input reactant mole ratio and flow rate. For optimum performance, therefore, the RF power level is adjusted for the particular mole ratio and flow rate and those variables are then precisely maintained.

The following more detailed example further illustrates the practice of the invention. Using a high pressure plasma apparatus as described above, the impedance matching module is adjusted and a plasma initiated. The outer gas stream is adjusted to 2 liters per minute of hydrogen. Silicon tetrachloride is introduced in the inner gas stream by bubbling 4 liters per minute of hydrogen through silicon tetrachloride maintained at room temperature. The mole ratio of hydrogen to silicon tetrachloride is about 4.2. The RF power is adjusted to about 1.7 KW. The hydrogenation is allowed to continue for about 6.5 minutes and the silicon-bearing reaction products are analyzed to be, in volume percent, about 50.1% SiCl$_4$, 41.3% SiHCl$_3$ and about 8.6% SiH$_2$Cl$_2$. Approximately 50% by volume of the input SiCl$_4$ is converted to either SiHCl$_3$ or SiH$_2$Cl$_2$. Excellent mass balance of the
input SiCl₄ and H₂, with the products SiCl₄,
SiHCl₃, SiH₂Cl₂ and HCl collected from the exhaust of
the HPP reactor is observed (after correcting for unreacted
H₂), indicating that the amount of polymeric material
formed is negligible.

There has thus been provided, in accordance with the
invention, a method for the hydrogenation without
catenation of silicon tetrachloride. This hydrogenation
is achieved by the high pressure plasma reaction of
hydrogen and silicon tetrachloride. The high pressure
plasma results in high conversion efficiency and high
throughput because of the high temperature encountered in
the plasma. An additional benefit of the high pressure
plasma, in contrast to low pressure plasma, is the lessened
equipment requirements accruing from working near
atmospheric pressure as opposed to a vacuum environment.

While the invention has been described and illustrated
with regard to specific examples, it is not intended that
the invention be so limited. It will be appreciated, for
example, that the dual-flow coil and plasma nozzle can be
constructed of materials and have configurations other than
those illustrated. Further, the flow rates and powers used
are optimized for the particular apparatus configuration
used and will, in general, be a function of the specific
reactor designs.

Accordingly, it is intended that the invention embrace
all such variations and modifications as fall within the
scope of the appended claims.
CLAIMS

1. A method for producing SiHCl₃ which comprises: reacting H₂ and SiCl₄ in a high pressure plasma.

2. The method of claim 1 wherein the mole ratio of H₂ to SiCl₄ is in the range of 4 to 5 inclusive.

3. The method of claim 1 wherein said reacting of H₂ and SiCl₄ is done at a pressure in excess of about 13.3 KPa.

4. The method of claim 1 characterized by the essential absence of catenation.

5. The method of claim 1 wherein more than 30% of said SiCl₄ is converted to SiHCl₃.

6. A method for producing SiHCl₃ which comprises: introducing reactants comprising hydrogen and silicon tetrachloride into a volume and subjecting said reactants to a high pressure plasma.

7. The method of claim 6 wherein said reactants are introduced separately to said volume.

8. The method of claim 6 wherein the output of said step of subjecting said reactants to a high pressure plasma comprises unreacted hydrogen and silicon tetrachloride and reaction products trichlorosilane, dichlorosilane and hydrogen chloride.

9. The method of claim 8 wherein said output is separated by condensation.
10. A process for the hydrogenation of silicon tetrachloride in an apparatus capable of producing a high pressure plasma which comprises the steps of: initiating a plasma in the apparatus; introducing hydrogen to the plasma through a first means; introducing silicon tetrachloride to the plasma through a second means; and combining the hydrogen and silicon tetrachloride in the presence of said plasma.
1 (amended) A method for producing SiHCl₃ and SiH₂Cl₂ which comprises: creating a high pressure radio frequency hydrogen plasma at a pressure of about 100 KPa; and reacting H₂ and SiCl₄ in said high pressure radio frequency plasma to form SiHCl₃ and SiH₂Cl₂.

2. The method of claim 1 wherein the mole ratio of H₂ to SiCl₄ is in the range of 4 to 5 inclusive.

3 (cancelled)

4 (cancelled)

5 (cancelled)

6 (cancelled)

7 (amended) The method of claim 1 wherein said reactants are introduced separately to said volume.

8 (amended) The method of claim 1 wherein the output of said step of creating with said reactants a high pressure plasma comprises unreacted hydrogen and silicon tetrachloride and reaction products trichlorosilane, dichlorosilane and hydrogen chloride.

9. The method of claim 8 wherein said output is separated by condensation.
A process for the hydrogenation of silicon tetrachloride to form SiHCl$_3$ and SiH$_2$Cl$_2$ in an apparatus capable of producing a high pressure radio frequency plasma which comprises the steps of: initiating a high pressure radio frequency hydrogen plasma in the apparatus at a pressure of about 100 KPa; introducing hydrogen to the plasma through a first means; introducing silicon tetrachloride to the plasma through a second means; and combining the hydrogen and silicon tetrachloride in the presence of said plasma to form SiHCl$_3$ and SiH$_2$Cl$_2$.

A method for producing SiHCl$_3$ and SiH$_2$Cl$_2$ which comprises: creating in a volume a high pressure radio frequency hydrogen plasma at a pressure of about 100 KPa; introducing reactants comprising hydrogen and silicon tetrachloride to said volume; and creating with said reactants a high pressure radio frequency plasma, said reactants combining in said plasma to form SiHCl$_3$ and SiH$_2$Cl$_2$ without the production of substantial amounts of chlorosilane polymers.
INTERNATIONAL SEARCH REPORT

I. CLASSIFICATION OF SUBJECT MATTER

According to International Patent Classification (IPC) or to both National Classification and IPC

INT. CL. 3 COIB 33/107
US. CL. 204/164

II. FIELDS SEARCHED

Minimum Documentation Searched

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<th>Classification System</th>
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Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of Document</th>
<th>Relevance to Claim No.</th>
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<td>X</td>
<td>GB, A, 838,378, Published, 22 June 1960</td>
<td>1-10</td>
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<td>X</td>
<td>US, A, 4,102,985, Published, 25 July 1978, Harvey II</td>
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<td>A</td>
<td>US, A, 3,840,750, Published, 08 October 1974, Davis et al</td>
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IV. CERTIFICATION

Date of the Actual Completion of the International Search: 03 JULY 1981

Date of Mailing of this International Search Report: 24 JUL 1981

International Searching Authority: ISA/US

Signature of Authorized Officer: Jack Cooper