

**METHOD OF PRODUCING ULTRA HIGH PURITY MONOSILANE AND
APPARATUS THEREFOR**

The present invention relates to a method of producing ultra high purity monosilane and apparatus therefor, and particularly to an ultra high purity monosilane producing method which comprises liquefying and rectifying a feed monosilane gas, thereby producing high pressure monosilane gas and high pressure monosilane liquid, each having an ultra high purity, which are free from hydrogen having a boiling point lower than that of monosilane and chlorides having boiling points higher than that of monosilane, and an apparatus therefor.

Monosilane gas is generally indispensable for the manufacture of ultra LSIs, solar batteries, photosensitive materials and the like.

A known method for producing monosilane gas is that disclosed in the official gazette of Japanese Patent Publication N° 3,806/1989.

Such monosilane gas preferably should have a high purity, for instance, of 99.9999 % or more. However, a preferred method for producing such high purity monosilane gas and a preferred unit therefor have not yet been developed.

The present invention is intended to achieve the aforementioned purpose.

The ultra high purity monosilane producing method according to the present invention is characterized by comprising: pressurizing, cooling down and gas-liquid separating a feed monosilane gas; introducing the separated gas to the middle stage of a lower rectification column and

rectifying the pressurized gas in the lower rectification column; introducing the gas resulted from this rectification to the middle stage of an upper rectification column and rectifying the same gas there; and taking out a high pressure monosilane gas product or liquid monosilane product having an ultra high purity which is resulted from this rectification, from the bottom portion of said upper rectification column.

The ultra high purity monosilane producing method according to the present invention is characterized by further comprising: a step of warming the liquid reservoired in the bottom portion of said lower rectification column by means of a reboiler, whereby low boiling point components contained in said liquid are gasified so as to be recovered to the lower rectification column.

The ultra high purity monosilane producing unit according to the present invention is characterized by comprising: a lower rectification column with a reboiler-condenser disposed in its top portion and a condenser for cooling use disposed below the reboiler condenser; an upper rectification column with a condenser for cooling use disposed in its top portion, the bottom portion of the upper column being opposite the reboiler-condenser of said lower rectification column; means for cooling each of said condensers for cooling use; means for pressurizing, cooling down, and gas-liquid separating a feed monosilane gas; means for introducing the pressurized feed gas obtained by the above means into said lower rectification column; and means for introducing the gas rectified in said lower rectification column into said upper rectification column; wherein a high pressure gaseous monosilane product or liquid monosilane product having an ultra high purity is taken out of the bottom portion of said upper rectification column.

Now referring to the drawings, an embodiment of the present invention will be described.

In the present invention, an impure monosilane gas is used as a feed.

The composition of a feed monosilane gas used in the embodiment of the present invention and the boiling points of its components are as shown in Table 1.

TABLE 1

Composition of Feed Monosilane Gas	%	Boiling Points (°C at 1 atm)
Hydrogen (H ₂)	16.0	-252.9
Monosilane (SiH ₄)	69.2	-111.5
Monochlorosilane (SiH ₃ Cl)	4.1	-30.4
Dichlorosilane (SiH ₂ Cl ₂)	9.9	8.2
Trichlorosilane (SiHCl ₃)	0.8	31.8

In the present invention, a double rectification column is composed of a lower rectification column 1 and an upper rectification column 2, where a reboiler-condenser RC is disposed in the top portion of said lower rectification column 1 and a condenser for cooling use C₁ is disposed under this reboiler-condenser RC. Besides, condensers for cooling use C₂ and C₃ are disposed in the top portion of said upper rectification column 2.

For instance, a feed monosilane gas having the composition given in Table 1 is introduced at a temperature of about 0 °C and a pressure of about 2.5 kg/cm²G to a compressor 3 through a pipe P₁, where it is warmed to a temperature of about 40 °C and pressurized to about 30 Kg/cm²G. Then, the feed gas is introduced to a cooler 4 through a pipe P₂ so as to be cooled down to a temperature of about -20 °C while maintaining its high pressure, and its

heavy fraction is consequentially liquefied. The resulting gas-liquid mixture is thereafter introduced to a gas-liquid separator 5 through a pipe P_3 , where the heavy fraction is separated as a liquid. This liquid part will be returned for reuse to the feed system from the bottom portion of the gas-liquid separator 5 by way of a pipe P_4 , a valve V_1 and a pipe P_5 .

The gas remaining in the gas-liquid separator 5 is introduced at a temperature of about $-20\text{ }^{\circ}\text{C}$ and a pressure of about $30\text{ kg/cm}^2\text{G}$ between the rectifying portion a and rectifying portion b disposed respectively in the lower portion and middle portion of the lower rectification column 1 through a pipe P_6 , and passed through rectifying portion b. Then, a part of the gas passed through the said rectifying portion b is condensed and liquefied in the condenser C_1 for cooling use which has been cooled at about $-34\text{ }^{\circ}\text{C}$ by a refrigerant F_1 coming through a pipe P_7 , and the resulting liquid is caused to flow down in the rectifying portion b as a reflux liquid so as to be subjected to gas-liquid contact with a rising gas.

As a result, the heavy fraction in the liquid passing through the rectifying portion b is concentrated and the light fraction in the gas also passing there is concentrated. The liquid which has flowed down through the rectifying portion b is further passed through the rectifying portion a, and reservoired in the bottom portion of the rectification column 1.

This reservoired liquid is passed through a pipe P_8 and a pipe P_9 and introduced to a reboiler R_1 heated by a heating source (warm water) F_2 so as to be evaporated, and the resulting gas is taken out therefrom through a pipe P_{10} and introduced below the rectifying portion a.

After the refrigerant F_1 cools said condenser for cooling use C_1 , it will be taken out of a pipe P_{11} so as to be used in circulation.

The gas introduced below said rectifying portion a from said pipe P_{10} rises through the rectifying portion a, where it is rectified in a gas-liquid contact with the liquid flowing down through the rectifying portion a. Furthermore, the gas which has risen through the rectifying portion a rises through the rectifying portion b after joining the gas coming from said pipe P_6 . Then, a part of the gas is liquefied in the condenser for cooling use C_1 so as to be used as a reflux liquid in the rectifying portion b, and the remaining part thereof rises through a rectifying portion c disposed in the upper portion of said lower rectification column 1 and introduced to the reboiler-condenser RC, where almost all of a part of monosilane in the same gas and high boiling point materials including monochlorosilane are liquefied and the resulting liquid is used as a reflux liquid in the rectifying portion c, rectifying portion b and rectifying portion a. At the same time, liquid monosilane reservoired in the bottom portion of said upper rectification column 2 at a position adjacent the reboiler-condenser RC and low boiling point materials such as hydrogen contained in the liquid monosilane are evaporated, thereby increasing the purity of the liquid monosilane.

Then, the gas which has not been liquefied in the reboiler-condenser RC is taken out of its top portion through a pipe P_{12} , slightly reduced in pressure by means of a valve V_2 , and introduced between a rectifying portion d and rectifying portion e respectively disposed in the lower portion and middle portion of the upper rectification column 2. Thus, the mixed gas of monosilane and hydrogen introduced in said upper rectification column 2 is passed through the rectifying portion e and cooled down by means of the condensers for cooling use C_3 and C_2 so that monosilane is

liquefied. The liquefied monosilane is caused to flow down through the rectifying portion e and rectifying portion d, wherein the liquid monosilane becomes a reflux liquid in the rectifying portion e and rectifying portion d. This reflux liquid is rectified in contact with the gas rising from below, and reservoiried at a pressure of about 30 kg/cm²G as high purity monosilane in the bottom portion of said upper rectification column 2 opposite the reboiler-condenser RC. From this portion, a high pressure gaseous monosilane product having an ultra high purity will be taken out through a pipe P₁₃ and a valve V₃ and a high pressure liquid monosilane product having an ultra high purity will be also taken out through a pipe P₁₄ and a valve V₄.

Hydrogen gas, not liquefied in the condensers for cooling use C₃ and C₂, is taken out of the top portion of said upper rectification column 2 through a pipe P₁₅, regulated in pressure by means of a valve V₅ and discharged as waste gas.

To said condenser for cooling use C₂, liquid nitrogen F₃ is introduced as a refrigerant through a pipe P₁₆. After the liquid nitrogen is evaporated in the condenser for cooling use C₂, it is taken out thereof through a pipe P₁₇, reduced in pressure by means of a valve V₆, and then used again as a refrigerant in the condenser for cooling use C₃. The resulting warmed nitrogen gas is taken out through a pipe P₁₈. Other refrigerants having a temperature of below -80 °C or less, such as liquefied ethylene or liquefied methane, can be used as the refrigerant in the condenser for cooling use C₂.

In addition, valve V₇ is inserted between the pipes P₅ and P₈, which will be opened when a part of the liquid reservoiried in the bottom portion of said lower rectification column 1 is desired to return to the feed system as required.

The ultra high purity monosilane producing method and unit according to the present invention are highly advantageous as mentioned above, i.e. capable of easily and continuously obtaining high pressure monosilane gas and high pressure liquid monosilane, each having an ultra high purity, and capable of making the whole of the producing plant compact because its dimensions are satisfactorily reduced in accordance with an extent of higher pressure, as compared with a producing plant for low pressure monosilane gas.

Fig. 1 is an explanatory view of an installation for carrying out the ultra high purity monosilane producing method and unit according to the present invention.

**CLAIMS:**

1. A method of producing ultra high purity monosilane which comprises:

pressurizing, and partially condensing a feed monosilane gas;

separating the gas and liquid phases of the partially condensed feed monosilane;

introducing the gas phase to the middle stage of a lower rectification column (1) and rectifying the gas phase therein;

introducing a gas produced by this rectification to an upper rectification column (2) and rectifying the same gas there; and

removing a high pressure monosilane gas product or liquid monosilane product having an ultra high purity which produced by this rectification, from the bottom portion of said upper rectification column.

2. A method as claimed in claim 1, which comprises: warming a liquid reservoir in the bottom portion of said lower rectification column (1) by means of a reboiler (R_1), whereby low boiling point components contained in said liquid are gasified so as to be recovered to the lower rectification column.

3. A method as claimed in claim 1 or 2, comprising providing refrigerant to a cooling means (C_1) at an intermediate level of said lower column (1).

4. An ultra high purity monosilane producing apparatus which comprises:

a lower rectification column (1) with a reboiler-condenser (RC) disposed in its top portion;

an upper rectification column (2) with a condenser (C_2) for cooling use disposed in its top portion, the bottom



portion of the upper column facing the reboiler-condenser (RC) of said lower rectification column;

means for cooling each of said condensers (C_1 , C_2) for cooling use;

means for pressurizing (3), cooling (4), and partially condensing separating a feed monosilane gas;

means (5) for separating the gas and liquid phases of said partially condensed gas;

means (P_6) for introducing the gas phase into said lower rectification column (1); and

means (P_{12}) for introducing the gas rectified in said lower rectification column into said upper rectification column (2);

wherein a high pressure gaseous monosilane product or liquid monosilane product having an ultra high purity is taken out of the bottom portion of said upper rectification column (2).

5. An apparatus as claimed in claim 4, comprising a cooling means (C_1) disposed in said lower column between the point of introduction of the gas phase and the reboiler-condenser (RC).

6. An apparatus as claimed in claim 5 wherein said cooling means (C_1) is a condenser.