

DESCRIPTION

Azeotropic Mixture of Fluoromethane and Hydrogen Chloride and Process for Purifying Fluoromethane

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FIELD OF THE INVENTION

The present invention relates to an azeotropic mixture of fluoromethane (hereinafter sometimes referred to as " CH_3F " or "HFC-41") and hydrogen chloride (hereinafter sometimes referred to as " HCl "), a process for purifying fluoromethane and uses thereof.

BACKGROUND OF THE INVENTION

Hydrofluorocarbons (HFC) are characterized by having an ozone depletion coefficient of 0 and, for example, HFC-41, difluoromethane (CH_2F_2) and trifluoromethane (CHF_3) are useful compounds as an etching gas for semiconductors.

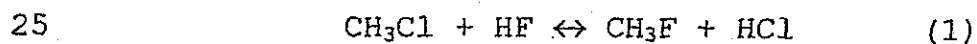
HFCs used as an etching gas for semiconductors are demanded to have high purity and particularly, the concentration of the acid component (e.g., hydrogen chloride, hydrogen fluoride) is demanded to be preferably 1.0 wt ppm or less, more preferably 0.5 wt ppm or less.

To satisfy these requirements, a large number of methods for producing high-purity HFCs have been proposed, but not so many methods have been proposed for the production of HFC-41. This is mainly because the method

in general of fluorinating a halogenated hydrocarbon with HF is, for example, bad in the reaction efficiency and accompanied with production of many by-products due to side reactions such as decomposition reaction.

5 In such an environment, Patent Document 1 (JP-B-4-7330) discloses a method of producing HFC-41 by reacting methyl alcohol and hydrogen fluoride (hereinafter sometimes referred to as "HF") in the gas phase with use of a fluorination catalyst (chromium fluoride) under the
10 condition of 100 to 500°C. However, this method has a problem that water produced as a by-product brings about corrosion of the fluorination catalyst and reaction apparatus.

 Also, Patent Document 2 (JP-A-60-13726) discloses a
15 method of producing HFC-41 by reacting methyl chloride (CH₃Cl) and HF in the gas phase with use of a fluorination catalyst (chromium fluoride) under the condition that the reaction temperature is 100 to 400°C. However, this method is disadvantageous in that an
20 equilibrium reaction represented by the following formula 1 takes place and since HFC-41 (boiling point under atmospheric pressure: -78.5°C) and hydrogen chloride (boiling point under atmospheric pressure: -84.9°C) are close in the boiling point, their separation is difficult.



[Patent Document 2] JP-A-60-13726

OBJECT OF THE INVENTION

An object of the present invention is to provide a
5 method for efficiently producing high-purity HFC-41 which
can be used as an etching gas for semiconductors.

SUMMARY OF THE INVENTION

As a result of intensive investigations to solve
10 those problems, the present inventors have newly found
that HFC-41 and HCl form a maximum azeotropic mixture.
Furthermore, it has been found that when a mixture
containing HFC-41 and HCl is distilled, HFC-41 containing
substantially no HCl (HCl concentration: 20 wt ppm or
15 less) can be obtained from the top of a distillation
column and also that when the obtained HFC-41 is
contacted with water and/or a treating agent containing
an alkali, high-purity HFC-41 having an HCl concentration
of 1.0 wt ppm or less can be obtained. The present
20 invention has been accomplished based on these findings.

The present invention relates to an azeotropic
mixture of HFC-41 and HCl, a process for purifying HFC-41
and uses thereof, which are described in [1] to [7] below.

[1] An azeotropic mixture of fluoromethane and
25 hydrogen chloride.

[2] A process for purifying fluoromethane,
comprising distilling a mixture containing fluoromethane

and hydrogen chloride to distill out fluoromethane from the top of a distillation column and obtain an azeotropic mixture of fluoromethane and hydrogen chloride from the bottom of the distillation column.

5 [3] The process for purifying fluoromethane as described in [2], wherein the distillation is performed under an operating pressure of 0.1 to 10.0 MPa.

 [4] The process for purifying fluoromethane as described in [2] or [3], wherein the concentration of
10 hydrogen chloride contained in the fluoromethane distilled out from the top of the distillation column is 20 wt ppm or less.

 [5] The process for purifying fluoromethane as described in any one of [2] to [4], which comprises a
15 step of bringing the fluoromethane distilled out from the top of the distillation column into contact with water and/or a treating agent containing an alkali to remove the acid component containing hydrogen chloride.

 [6] A fluoromethane product comprising
20 fluoromethane obtained by the process described in any one of [2] to [5], wherein the fluoromethane has a hydrogen chloride concentration of 1.0 wt ppm or less.

 [7] An etching gas comprising the fluoromethane product described in [6].

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EFFECT OF THE INVENTION

According to the present invention, HCl can be

efficiently separated from a mixture containing HFC-41 and HCl by utilizing an azeotropic phenomenon between HFC-41 and HCl, and high-purity HFC-41 can be obtained.

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DETAILED DESCRIPTION OF THE INVENTION

The azeotropic mixture of HFC-41 and HCl, the purification method of HFC-41 and uses thereof according to the present invention are described in detail below.

HFC-41 and HCl form an azeotropic mixture. Under
10 atmospheric pressure, the boiling point of HFC-41 is -78.5°C , the boiling point of HCl is -84.9°C and the boiling point of an azeotropic mixture thereof is about -73°C , therefore, HFC-41 and HCl form a maximum azeotropic mixture. The azeotropic composition under
15 atmospheric pressure is such that HFC-41 is about 55 mol% and HCl is about 45 mol%. Also, under other pressures, for example, under 2.0 MPa, the boiling point of the azeotropic mixture is about 4°C and the azeotropic composition is such that HFC-41 is about 53 mol% and HCl
20 is about 47 mol%.

In this way, a maximum azeotropic mixture is present in the two-component system of HFC-41 and HCl and therefore, even if a mixture of HFC-41 and HCl is distilled under atmospheric pressure, the molar ratio
25 (HFC-41/HCl) of HFC-41 and HCl cannot be concentrated to about 55/45 or more.

The process for purifying fluoromethane of the

present invention is characterized in that when the concentration of HCl in a mixture of HFC-41 and HCl is smaller than that in the azeotropic composition, a mixture containing HFC-41 and HCl is distilled to distill
5 out HFC-41 from the top of a distillation column and obtain an azeotropic mixture of HFC-41 and HCl from the bottom of the distillation column. According to the process of the present invention, HFC-41 containing substantially no HCl, specifically, HFC-41 having an HCl
10 concentration of 20 wt ppm or less, can be efficiently obtained. In the case where the concentration of HCl in a mixture of HFC-41 and HCl is larger than that in the azeotropic composition, the HCl concentration must be previously decreased by water washing or the like.

15 The distillation apparatus which can be used in such a distillation operation may be sufficient if it has a function necessary for normal distillation, but a rectification apparatus such as plate column and packed column is preferably used. The distillation can be
20 performed by either continuous distillation or batch distillation.

The operating conditions of distillation are not limited and various modes can be employed according to utility and required quality, but from the aspect of
25 preventing excessive drop in the top temperature of the distillation column, the operating pressure is preferably from 0.1 to 10 MPa, more preferably from 0.5 to 5 MPa.

In this case, the top temperature falls in the range from about -80 to 60°C.

The concentration of HCl contained in HFC-41 distilled out from the top of the distillation column by
5 distilling a mixture of HFC-41 and HCl as above is usually 20 wt ppm or less. However, in use as an etching gas for semiconductors, the concentration of the acid component (e.g., HCl, HF) is demanded, as described above, to be preferably 1.0 wt ppm or less, more preferably 0.5
10 wt ppm or less.

Accordingly, the process for purifying fluoromethane of the present invention preferably comprises a step of bringing HFC-41 distilled out from the top into contact with water and/or a treating agent
15 containing an alkali to remove the acid component containing HCl. The alkali which can be used in this treating agent may be an aqueous alkali solution or an alkali-containing solid material (for example, soda lime). The treating agent is preferably water or an aqueous
20 alkali solution. The aqueous alkali solution is preferably an aqueous sodium hydroxide solution or an aqueous potassium hydroxide solution. The concentration of the aqueous alkali solution is preferably from 0.01 to 20%, more preferably from 0.1 to 10%. The contact time
25 is not particularly limited, but since the solubility of HFC-41 in water is slightly higher, the contact temperature is preferably in a low-temperature region,

specifically in the range from 5 to 40°C.

In this way, by brining HFC-41 distilled out from the top into contact with water and/or a treating agent containing an alkali, the concentration of HCl in HFC-41 can be decreased to 1.0 wt ppm or less. Depending on the treating agent used, the water concentration in HFC-41 may increase. In such a case, HFC-41 is contacted with molecular sieves (zeolite) or the like, whereby the water concentration can be decreased to 5 wt ppm or less.

10 The thus-purified HFC-41 contains the acid component (e.g., HCl, HF) only in a concentration of 1.0 wt ppm or less and high-purity HFC-41 can be obtained. The concentration of acid component in HFC-41 can be measured by an analyzer such as ion chromatography (IC).

15 Fig. 1 is a flow sheet showing one example of the fluoromethane purification apparatus which can be used in the method of the present invention. The process for purifying fluoromethane of the present invention is described in more detail by referring to Fig. 1.

20 CH_3Cl and HF are reacted in the gas phase at a reaction temperature of 250°C in the presence of a fluorination catalyst (for example, chromium fluoride) to obtain a reaction product containing HFC-41, HCl, CH_3Cl , HF and trace organic impurities. From the obtained
25 reaction product, methyl chloride and HF are removed, for example by distillation, to obtain a mixture (1) mainly containing HFC-41 and HCl.

The obtained mixture (1) is introduced into a distillation column (2) and a distillation operation is performed. From the bottom of this distillation column (2), an azeotropic mixture of HFC-41 and HCl is taken out as a bottom distillate (5) and a part thereof is returned as reboiling vapor (4) to the bottom of the distillation column. From the top of the distillation column (2), HFC-41 containing substantially no HCl is extracted as a top distillate (3). In this way, HCl can be efficiently removed from the mixture (1). Such an operation can be performed in the batch system but is preferably performed by continuous operation.

The theoretical plate number and actual plate number of the distillation column (2) and the reflux ratio are determined by taking account of separation conditions, column efficiency and the like, and the mixture (1) is preferably fed to a plate calculated to give least distillation of HCl out from the top.

When the top distillate (3) extracted from the top is introduced into an acid component treating unit (6) and contacted with, for example, an aqueous potassium hydroxide solution (5%), high-purity HFC-41 (7) more reduced in the acid component in HFC-41 can be obtained.

A single gas of the thus-obtained high-purity HFC-41 where the concentration of acid component (e.g., HCl, HF) is 1.0 wt ppm or less, or a mixed gas of this high-purity HFC-41 and another gas (for example, He, N₂, Ar, O₂

or NF_3) (hereinafter, these single gas and mixed gas both are referred to as a "fluoromethane product") can be used as an etching gas for use at the etching step in the production process of a semiconductor device.

5 More specifically, the etching gas comprising the fluoromethane product of the present invention can be used under various dry etching conditions such as plasma etching and microwave etching, for etching a thin film or the like formed by CVD, sputtering or vapor deposition in
10 the process of producing a semiconductor device such as LSI and TFT.

The gas which can be mixed with high-purity HFC-41 is not particularly limited and can be appropriately selected according to use. Not only one gas but also two
15 or more gases can be mixed with high-purity HFC-41. The amount mixed is also not particularly limited and can be appropriately adjusted according to use.

EXAMPLES

20 The present invention is described in greater detail below by referring to Example, but the present invention is not limited thereto.

<Analysis of Composition>

As for the bottom distillate, the gas distilled out
25 was passed into a gas cleaning bottle containing pure water as the absorbing solution, HCl in the gas distilled out was quantitated by neutralization-titrating the

absorbing solution with sodium hydroxide for volumetric analysis, HFC-41 was quantitated by measuring the volume of the gas at the outlet of gas cleaning bottle, and the compositional ratio was determined from results obtained.

5 As for the top distillate, the gas distilled out was passed into a gas cleaning bottle containing ultrapure water as the absorbing solution, Cl was quantitated by analyzing the absorbing solution by ion chromatography, HFC-41 was quantitated by measuring the
10 volume of the gas at the outlet of gas cleaning bottle, and the HCl concentration was determined from results obtained.

(Conditions for Measurement by Ion Chromatography)

Device: HIC-SP manufactured by Shimadzu Corporation

15 Column: Shodex IC SI-90 4E produced by Showa Denko K.K.

<Purification of Fluoromethane>

Using a distillation column equipped with a condenser and having a diameter of 150 mm ϕ and a theoretical plate number of 20 (actual plate number: 36),
20 a distillation operation was performed under an operating pressure of about 2.0 MPa by feeding a mixture comprising HFC-41 and HCl (composition: HFC-41/HCl=80/20 by mol) to 10th theoretical plate at ordinary temperature and at a rate of 34.4 g/h. The top temperature was controlled to
25 -5°C and distillates were extracted from the top and the bottom at 18.7 g/h and 15.7 g/h, respectively. In this distillation operation, the reflux ratio was controlled

to 10. After the inside of distillation column was stabilized, the bottom distillate was sampled and the composition was analyzed, as a result, the molar ratio of HFC-41 to HCl was 55/45 (HFC-41/HCl). Similarly, the top
5 distillate was sampled and the composition was analyzed, as a result, the concentration of HCl in HFC-41 was 10 wt ppm.

From these analysis results, it was revealed that HCl having a boiling point lower than that of HFC-41
10 (boiling point of HFC-41 under atmospheric pressure: -78.5°C > boiling point of HCl under atmospheric pressure: -84.9°C) is recovered at the bottom, and HFC-41 and HCl form a maximum azeotropic mixture.

Furthermore, the top distillate was contacted with
15 an aqueous 2% potassium hydroxide solution at a temperature of about 5°C and after cooling, collecting and sampling the solution, the concentration of HCl in HFC-41 was determined by ion chromatography, as a result, the HCl concentration was 0.5 wt ppm. Thus, high-purity
20 HFC-41 was obtained.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 shows a schematic view showing the fluoromethane purification apparatus which can be used in
25 the present invention.

[Description of Reference Numerals]

1 feed solution (mixture)

- 2 distillation column
- 3 top distillate
- 4 reboiling vapor
- 5 bottom distillate
- 5 6 acid component treating unit
- 7 high-purity fluoromethane

CLAIMS

1. An azeotropic mixture of fluoromethane and hydrogen chloride.

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2. A process for purifying fluoromethane, comprising distilling a mixture containing fluoromethane and hydrogen chloride to distill out fluoromethane from the top of a distillation column and obtain an azeotropic
10 mixture of fluoromethane and hydrogen chloride from the bottom of the distillation column.

3. The process for purifying fluoromethane as claimed in claim 2, wherein the distillation is performed
15 under an operating pressure of 0.1 to 10.0 MPa.

4. The process for purifying fluoromethane as claimed in claim 2 or 3, wherein the concentration of hydrogen chloride contained in the fluoromethane
20 distilled out from the top of the distillation column is 20 wt ppm or less.

5. The process for purifying fluoromethane as claimed in any one of claims 2 to 4, which comprises a
25 step of bringing the fluoromethane distilled out from the top of the distillation column into contact with water and/or a treating agent containing an alkali to remove

the acid component containing hydrogen chloride.

6. A fluoromethane product comprising fluoromethane obtained by the process claimed in any one of claims 2 to 5, wherein the fluoromethane has a hydrogen chloride concentration of 1.0 wt ppm or less.

7. An etching gas comprising the fluoromethane product claimed in claim 6.