

DESCRIPTION

Title of the Invention: SEMICONDUCTOR CHEMICAL SOLUTION AND
METHOD FOR PRODUCING SEMICONDUCTOR CHEMICAL SOLUTION

TECHNICAL FIELD

[0001]

The present invention relates to a semiconductor process chemical liquid and a method for producing a semiconductor process chemical liquid.

BACKGROUND ART

[0002]

A conventional semiconductor manufacturing process includes washing a substrate such as a semiconductor substrate or a glass substrate with a semiconductor process chemical liquid, followed by drying the substrate. Isopropyl alcohol has been used as such a semiconductor process chemical liquid, for example.

[0003]

Patent Document 1 discloses a method for producing isopropyl alcohol by direct hydration of propylene. Although propylene and water are made to react in a reactor in this case, the proportions of propylene and water in the reactor is 1,300 to 2,100 parts by mass of water relative to 100 parts by mass of propylene, where the residence time of water in the reactor is more than 20 minutes and 50 minutes or less.

Citation List

Patent Document

[0004]

Patent Document 1: PCT International Publication No.
WO2017/217279

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0005]

However, the isopropyl alcohol production method disclosed in Patent Document 1 will produce tert-butyl alcohol (2-methyl-2-propyl alcohol) and ethyl alcohol as by-products when using a raw material gas with a high propylene purity. Therefore, there is a demand for the production of a semiconductor process chemical liquid with reduced contents of tert-butyl alcohol and ethyl alcohol.

[0006]

Unfortunately, it is very difficult to reduce, by distillation, the contents of tert-butyl alcohol and ethyl alcohol in the semiconductor process chemical liquid, since tert-butyl alcohol and ethyl alcohol have only small differences in boiling point from isopropyl alcohol and can form azeotropes with isopropyl alcohol.

[0007]

There is a concern that any residue of tert-butyl alcohol as an impurity from using a semiconductor process chemical liquid containing tert-butyl alcohol may adversely affect

semiconductor devices. Tert-butyl alcohol, which has a melting point of 26°C and is solid at room temperature, is considered likely to remain as a residue.

[0008]

It is an object of the present invention to provide a semiconductor process chemical liquid with reduced contents of tert-butyl alcohol and ethyl alcohol, as well as a method for producing a semiconductor process chemical liquid capable of reducing the contents of tert-butyl alcohol and ethyl alcohol.

Means for Solving the Problems

[0009]

(1) A semiconductor process chemical liquid consists essentially of isopropyl alcohol, in which a content of a tert-butyl alcohol is at most 1,000 ppb by mass, and a content of ethyl alcohol is at most 1,000 ppb by mass.

[0010]

(2) In the semiconductor process chemical liquid, a content of a six-carbon alcohol is at most 1 ppb by mass.

[0011]

(3) A method for producing a semiconductor process chemical liquid consisting essentially of isopropyl alcohol includes: a step of reacting a raw material water and a raw material gas containing propylene and having an isobutene content of at most 1 ppm by volume and an ethylene content of at most 1 ppm by volume, by feeding to a continuous reactor, in which, a gas phase and a liquid phase exist upon the reacting, and the continuous reactor discharges a gas

component from the gas phase, a mass ratio of the raw material gas relative to the raw material water fed to the continuous reactor is 0.01 or more and 0.20 or less, a residence time of the raw material water inside the continuous reactor, which is a ratio of volume (L) of the liquid phase relative to a feed rate (L/min) of the raw material water fed to the continuous reactor, is 10 minutes or more and 25 minutes or less, a residence time of the gas component inside the continuous reactor, which is a ratio of volume (L) of the gas phase relative to a discharge rate (L/min) of the gas component discharged from the continuous reactor, is 10 minutes or more and 150 minutes or less, and a volume ratio of a discharge amount of the gas component discharged from the continuous reactor relative to a feed amount of the raw material gas fed to the continuous reactor is 0.03 or more and 0.30 or less.

[0012]

(4) The method for producing a semiconductor process chemical liquid according to aspect (3), further includes the steps of: recovering a crude isopropyl alcohol aqueous solution from the liquid phase; and distilling the crude isopropyl alcohol aqueous solution in a high-boiling distillation column.

[0013]

(5) In the method for producing a semiconductor process chemical liquid according to aspect (3) or (4), the raw material gas has a propylene content of 99% by volume or more.

[0014]

(6) In the method for producing a semiconductor process chemical liquid according to any one of aspects (3) to (5), the continuous reactor has an internal temperature of 200°C or more and 300°C or less and an internal pressure of 150 atm or more and 280 atm or less.

Effects of the Invention

[0015]

The present invention can provide a semiconductor process chemical liquid with reduced contents of tert-butyl alcohol and ethyl alcohol, as well as a method for producing a semiconductor process chemical liquid with reduced contents of tert-butyl alcohol and ethyl alcohol.

BRIEF DESCRIPTION OF THE DRAWINGS

[0016]

FIG. 1 is a diagram illustrating an example of a reaction step in a method for producing a semiconductor process chemical liquid according to an embodiment.

PREFERRED MODE FOR CARRYING OUT THE INVENTION

[0017]

Hereinafter, embodiments of the present invention will be described with reference to the drawing.

[0018]

Method for Producing Semiconductor Process Chemical Liquid

The present embodiment is directed to a method for producing a semiconductor process chemical liquid consisting

essentially of isopropyl alcohol, the method including reacting a raw material gas and the raw material water by feeding to the continuous reactor (hereinafter referred to as reaction step). The method for producing a semiconductor process chemical liquid according to the present embodiment may further include a product recovery step, a purification step, and the like.

[0019]

Raw Material Gas

The raw material gas includes propylene, and the content of propylene is preferably of 99% by volume or more, and more preferably 99.9% by volume or more.

[0020]

As mentioned below, the raw material gas should be preferably as low as possible in isobutene and ethylene contents, since isobutene and ethylene can undergo hydration to form tert-butyl alcohol and ethyl alcohol, respectively. The raw material gas has an isobutene content of at most 1 ppm by volume. The raw material gas preferably has an isobutene content of at most 0.5 ppm by volume, and more preferably at most 0.1 ppm by volume. In addition, the raw material gas has an ethylene content of at most 1 ppm by volume. The raw material gas preferably has an ethylene content of at most 0.5 ppm by volume, and more preferably at most 0.1 ppm by volume. If necessary, the raw material gas may contain an inert gas such as nitrogen gas.

[0021]

As mentioned below, the raw material gas should be preferably as low as possible in a six-carbon alkene (alkene having six carbon atoms) content since the six-carbon alkene can undergo disproportionation to form isobutene and ethylene. The raw material gas preferably has a six-carbon alkene content of at most 1 ppm by volume, more preferably at most 0.5 ppm by volume, and even more preferably at most 0.1 ppm by volume.

[0022]

Raw Material Water

The raw material water includes water, but preferably further contains an acid catalyst. Examples of the acid catalyst include phosphotungstic acid, silicotungstic acid, and silicomolybdic acid. Two or more of them may be used in combination. When the raw material water contains an acid catalyst, the pH at 25°C of the raw material water is preferably 2.5 or more and 4.5 or less. If the raw material water has a pH at 25°C of 2.5 or more and 4.5 or less, it can provide a higher propylene conversion rate and a higher isopropyl alcohol selectivity.

[0023]

Reaction Step

An example of the reaction step will be described with reference to FIG. 1. When the raw material gas and the raw material water are supplied to a continuous reactor 1, a gas phase G, which includes the raw material gas, is present at the upper part of the continuous reactor 1, and a liquid phase

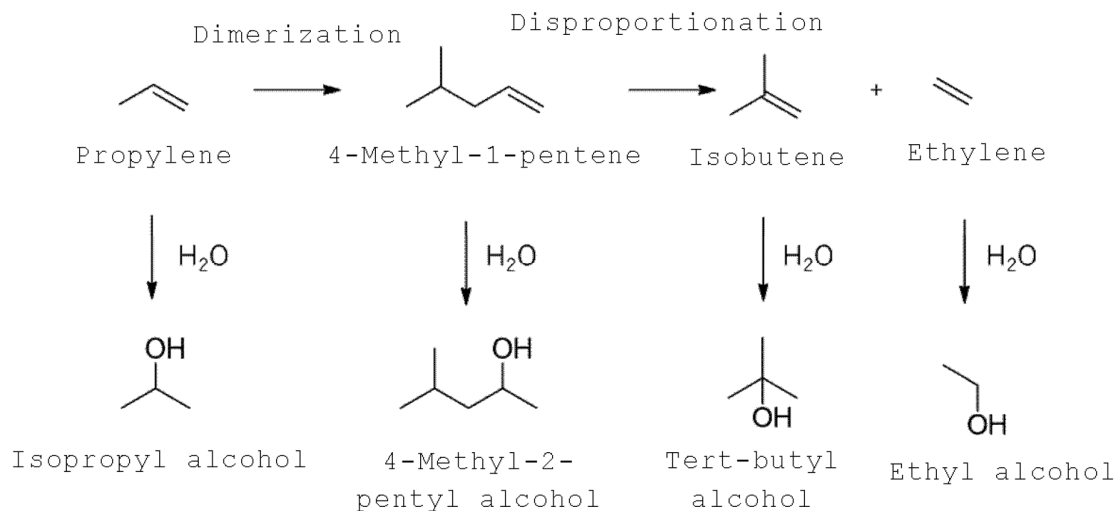
L, which includes the raw material water, is present at the lower part thereof. Herein, the liquid phase L contains the isopropyl alcohol formed in the reaction step. During the supply of the raw material gas and the raw material water to the continuous reactor 1, a control valve 2 is opened for discharge of gas components from the gas phase G. Thus, even when a raw material gas having high propylene purity is used, the time for which the raw material gas stays in the gas phase G becomes shorter, which will lead to suppression of propylene dimerization, a result of which the semiconductor process chemical liquid will have reduced contents of tert-butyl alcohol, ethyl alcohol, and six-carbon alcohols (alcohols having six carbon atoms).

[0024]

Although the reason therefor is not clear, it may be based on the following speculation. If the gas components are not discharged from the upper part of the continuous reactor 1 when using a raw material gas with a high propylene purity, propylene can easily undergo dimerization to form six-carbon alkenes such as 4-methyl-1-pentene. That can result in disproportionation of six-carbon alkenes to form isobutene and ethylene, which can then undergo hydration to form tert-butyl alcohol and ethyl alcohol (see the reaction mechanism below). In addition, six-carbon alkenes not having undergone disproportionation can undergo hydration to form six-carbon alcohols such as 4-methyl-2-pentyl alcohol.

[0025]

[Chem. 1]



[0026]

The mass ratio of the raw material gas relative to the raw material water fed to the continuous reactor 1 is 0.01 or more and 0.20 or less, preferably 0.02 or more and 0.07 or less, and more preferably 0.03 or more and 0.05 or less. If the mass ratio of the raw material gas relative to the raw material water fed to the continuous reactor 1 is less than 0.01, the semiconductor process chemical liquid productivity may decrease, and if it is more than 0.20, the resulting semiconductor process chemical liquid may have increased contents of tert-butyl alcohol, ethyl alcohol, and six-carbon alcohols.

[0027]

The volume ratio of the rate of discharge of the gas components from the continuous reactor 1 relative to the rate of feed of the raw material gas to the continuous reactor 1 is 0.03 or more and 0.30 or less, and preferably 0.11 or more and

0.16 or less. If the ratio of the rate of discharge of the gas components from the continuous reactor 1 relative to the rate of feed of the raw material gas to the continuous reactor 1 is less than 0.03, the resulting semiconductor process chemical liquid may have increased contents of tert-butyl alcohol, ethyl alcohol, and six-carbon alcohols, and if it is more than 0.30, the propylene conversion rate may decrease.

[0028]

The gas components being discharged from the continuous reactor 1 contains water from the raw material water, propylene from the raw material gas, impurities (e.g., propane) from the raw material gas, the main product (isopropyl alcohol), and by-products (e.g., hexene, isobutene, ethylene). Hexene includes 4-methyl-1-pentene and other isomers that can undergo disproportionation to form isobutene and ethylene. An increase in the contents of isobutene and ethylene in the gas components being discharged from the continuous reactor 1 may lead to an increase in the contents of tert-butyl alcohol and ethyl alcohol in the semiconductor process chemical liquid. Therefore, the content of isobutene in the gas components being discharged from the continuous reactor 1 is preferably 0.1 ppm by volume or more and 20 ppm by volume or less, and more preferably 1 ppm by volume or more and 8 ppm by volume or less. In addition, the content of ethylene in the gas components being discharged from the continuous reactor 1 is preferably 0.1 ppm by volume or more and 20 ppm by volume or less, and more preferably 1 ppm by

volume or more and 5 ppm by volume or less.

[0029]

The residence time of the raw material water inside the continuous reactor 1 is 10 minutes or more and 25 minutes or less, and preferably 12 minutes or more and 18 minutes or less. If the residence time of the raw material water inside the continuous reactor 1 is less than 10 minutes, the propylene conversion rate may decrease, and if it is more than 25 minutes, the resulting semiconductor process chemical liquid may have increased contents of tert-butyl alcohol, ethyl alcohol, and six-carbon alcohols.

[0030]

The residence time of the raw material water inside the continuous reactor 1 can be obtained from the formula:
(the volume (L) of the liquid phase L in the continuous reactor 1)/(the raw material water feed rate (L/min)).

[0031]

The residence time of gas components inside the continuous reactor 1 is 10 minutes or more and 150 minutes or less, and preferably 30 minutes or more and 100 minutes or less. If the residence time of the gas components inside the continuous reactor 1 is less than 10 minutes, the propylene conversion rate may decrease, and if it is more than 150 minutes, the resulting semiconductor process chemical liquid may have increased contents of tert-butyl alcohol, ethyl alcohol, and six-carbon alcohols.

[0032]

The residence time of the gas components inside the continuous reactor 1 can be obtained from the formula:
(the volume (L) of the gas phase G in the continuous reactor 1)/(the discharge rate (L/min) of the gas components).
Although the reaction is performed at high temperature and high pressure in the continuous reactor 1, the discharge rate of the gas components from the continuous reactor 1 with such temperature and pressure can be determined by analyzing the liquid phase and the gas phase obtained after the temperature and pressure of the gas components discharged from the continuous reactor 1 are set to 25°C and 101 kPa (absolute pressure), respectively.

[0033]

The continuous reactor 1 preferably has an internal temperature of 200°C or more and 300°C or less, and more preferably 250°C or more and 280°C or less. When the temperature in the continuous reactor is 200°C or more, the propylene conversion rate increases, and when the temperature is 300°C or less, the resulting semiconductor process chemical liquid can have reduced contents of tert-butyl alcohol, ethyl alcohol, and six-carbon alcohols.

[0034]

The continuous reactor 1 preferably has an internal pressure of 150 atm or more and 280 atm or less, and more preferably 200 atm or more and 255 atm or less. When the pressure inside the continuous reactor 1 is 150 atm or more, the propylene conversion rate increases, and when 280 atm or

less, the resulting semiconductor process chemical liquid can have reduced contents of tert-butyl alcohol, ethyl alcohol, and six-carbon alcohols.

[0035]

The propylene conversion rate is preferably 85% or more and 97% or less and more preferably 92% or more and 95% or less. The isopropyl alcohol selectivity is preferably 99% or more and 99.9% or less, and more preferably 99.5% or more and 99.8% or less.

[0036]

The propylene conversion rate may be calculated from the amount of propylene fed to the continuous reactor 1 and the amount of propylene discharged outside the system. Examples of the propylene discharged to outside the system may include the propylene discharged through the control valve 2 (see FIG. 1) from the gas phase G of the continuous reactor 1, and the propylene discharged to outside rather than being returned to the reaction step from the product recovery step and purification step described below.

[0037]

Product Recovery Step

The liquid components including the raw material water and isopropyl alcohol produced in the reaction step are discharged from the liquid phase L of the continuous reactor 1, and transported to a product recovery column. At this time, by setting the temperature and pressure inside of the recovery column to predetermined ranges, respectively, propylene

dissolved in the water included in the liquid components is separated, whereby a crude isopropyl alcohol aqueous solution is recovered. Herein, the temperature of the product recovery column is preferably 80°C or more and 200°C or less, and more preferably 100°C or more and 150°C or less. In addition, the pressure of the product recovery column is preferably of 100 kPa or more and 5,000 kPa or less (absolute pressure), and more preferably 500 kPa or more and 2,000 kPa or less (absolute pressure).

[0038]

The separated propylene may be collected in a drum and reused as a raw material gas. The crude isopropyl alcohol aqueous solution preferably has an isopropyl alcohol content of 1% by mass or more and 20% by mass or less, and more preferably 3% by mass or more and 8% by mass or less.

[0039]

As mentioned above, when using a raw material gas with a high propylene purity in a conventional isopropyl alcohol production method, tert-butyl alcohol and ethyl alcohol will be produced as by-products. It is very difficult to separate tert-butyl alcohol and ethyl alcohol by distillation in the purification step described below, since tert-butyl alcohol and ethyl alcohol have only small differences in boiling point from isopropyl alcohol, and thus form azeotropes with isopropyl alcohol. However, according to an embodiment, the control of the residence time of the raw material water in the continuous reactor 1 and the residence time of the gas

components in the continuous reactor 1 can reduce the production of tert-butyl alcohol and ethyl alcohol as by-products. Thus, the mass ratio of each of tert-butyl alcohol and ethyl alcohol relative to isopropyl alcohol in the crude isopropyl alcohol aqueous solution can be reduced to 1,000 ppb or less, and can also be reduced to 500 ppb or less. In view of the cost and yield of the reaction step and the purification step, the mass ratio of each of tert-butyl alcohol or ethyl alcohol and isopropyl alcohol in the crude isopropyl alcohol aqueous solution is 10 ppb or more, more preferably 100 ppb or more, and even more preferably 200 ppb or more.

[0040]

According to an embodiment, it is also possible to reduce the amount of six-carbon alcohols as by-products. Thus, the mass ratio of six-carbon alcohols relative to isopropyl alcohol in the crude isopropyl alcohol aqueous solution can be set to 200 ppb or more and 10,000 ppb or less, and can also be set to 2,000 ppb or more and 5,000 ppb or less. In particular, a reduction in the amount of 4-methyl-2-pentanol as a by-product resulting from hydration of 4-methyl-1-pentene will lead to a reduction in the amounts of tert-butyl alcohol and ethyl alcohol as by-products. Thus, the mass ratio of 4-methyl-2-pentanol relative to isopropyl alcohol in the crude isopropyl alcohol aqueous solution is preferably 1,000 ppb or more and 5,000 ppb or less, and more preferably 1,000 ppb or more and 3,000 ppb or less. In an embodiment, the

semiconductor process chemical liquid with further reduced contents of six-carbon alcohols can be produced through distillation of the crude isopropyl alcohol aqueous solution using a high-boiling distillation column in the purification step described below.

[0041]

Purification Step

The crude isopropyl alcohol aqueous solution recovered in the product recovery column is discharged from the product recovery column and purified. For example, the crude isopropyl alcohol aqueous solution is purified by distillation in a low-boiling distillation column, distillation in an azeotropic distillation column, dehydration, and distillation in a high-boiling distillation column.

[0042]

The low-boiling distillation column can remove compounds with boiling points lower than that of isopropyl alcohol. Examples of compounds with boiling points lower than that of isopropyl alcohol include ethylene, propylene, acetone, diisopropyl ether, acetaldehyde, and propionaldehyde. The azeotropic distillation column can remove water and compounds with boiling points higher than that of water, and form an azeotropic mixture of isopropyl alcohol and water. In the case of the dehydration being conducted in a dehydration distillation column, a third component capable of forming an azeotropic mixture with water may be added into the dehydration distillation column for the removal of water

through the production of an azeotropic mixture of water and the third component. The separated water may be collected in a tank and reused as the raw material water. The high-boiling distillation column can remove compounds with boiling points higher than that of isopropyl alcohol. It is thereby possible to reduce the content of six-carbon alcohols in the semiconductor process chemical liquid to 1 ppb by mass or less, and to reduce to 0.1 ppb by mass or less. The distillation residue taken out from the high-boiling distillation column can be passed through a filter to remove particles.

[0043]

The number of tower trays in each distillation column or the equivalent number of tower trays in each distillation column expressed in terms of tower trays therein is preferably, but not limited to, 5 or more and 320 or less, and more preferably 10 or more and 300 or less. Specifically, the number of tower trays in the high-boiling distillation column or equivalent number of tower trays expressed in terms of tower trays therein is preferably 5 or more and 20 or less. In an embodiment, such conditions can reduce the content of six-carbon alcohols in the semiconductor process chemical liquid. The reflux ratio in atmospheric distillation is preferably, but not limited to, 0.5 or more and 50 or less, and more preferably 1 or more and 10 or less. As used herein, the term "atmospheric" refers to a pressure (absolute pressure) in the range of 90 kPa or more and 120 kPa or less.

[0044]

Semiconductor Process Chemical Liquid

The semiconductor process chemical liquid of the present embodiment consists essentially of isopropyl alcohol. The semiconductor process chemical liquid according to an embodiment preferably has an isopropyl alcohol content of 99.99% by mass or more, and more preferably 99.999% by mass or more.

[0045]

The semiconductor process chemical liquid according to an embodiment has a tert-butyl alcohol content of at most 1,000 ppb by mass, and more preferably at most 500 ppb by mass. Since the semiconductor process chemical liquid according to the present embodiment has a tert-butyl alcohol content of at most 1,000 ppb by mass, even when the semiconductor process chemical liquid of the present embodiment is used to wash substrates, there will be less impact of tert-butyl alcohol residue on semiconductor devices. In view of cost and yield of the reaction step and the purification step, the semiconductor process chemical liquid according to an embodiment preferably has a tert-butyl alcohol content of 10 ppb by mass or more, more preferably 100 ppb by mass or more, and even more preferably 200 ppb by mass or more.

[0046]

The semiconductor process chemical liquid according to the present embodiment has an ethyl alcohol content of at most 1,000 ppb by mass, and more preferably at most 500 ppb by

mass. In view of cost and yield of the reaction step and the purification step, the semiconductor process chemical liquid according to the present embodiment preferably has an ethyl alcohol content of 10 ppb by mass or more, more preferably 100 ppb by mass or more, and even more preferably 200 ppb by mass or more.

[0047]

The isopropyl alcohol of the semiconductor process chemical liquid according to the present embodiment can be produced by the method for producing the semiconductor process chemical liquid according to the embodiment.

[0048]

The semiconductor process chemical liquid according to the present embodiment preferably has a six-carbon alcohol content of at most 1 ppb by mass, and more preferably at most 0.1 ppb by mass.

[0049]

Examples of the six-carbon alcohol (alcohol having six carbon atoms) include 1-hexyl alcohol, 2-hexyl alcohol, 3-hexyl alcohol, 2-methyl-1-pentyl alcohol, 2-methyl-2-pentyl alcohol, 2-methyl-3-pentyl alcohol, 4-methyl-1-pentyl alcohol, 4-methyl-2-pentyl alcohol, 3-methyl-1-pentyl alcohol, 3-methyl-3-pentyl alcohol, 2,3-dimethyl-1-butyl alcohol, 2-ethyl-1-butyl alcohol, and other saturated aliphatic alcohols.

[0050]

When using a raw material gas with a high propylene purity in the conventional isopropyl alcohol production method,

for the separation of six-carbon alcohols from isopropyl alcohol, the isopropyl alcohol product must be dehydrated until the water content of the product reaches 100 ppm by mass or less, for example, and then distilled at a high reflux ratio using a distillation column with a large number of trays. In contrast, the semiconductor process chemical liquid production method according to an embodiment, which successfully reduces the production of six-carbon alcohols as by-products, can produce, at low cost, the semiconductor process chemical liquid with reduced content of six-carbon alcohols according to an embodiment.

[0051]

The semiconductor process chemical liquid according to an embodiment preferably has a water content of 0.1 ppm by mass or more and 100 ppm by mass or less, and more preferably 1 ppm by mass or more and 20 ppm by mass or less.

[0052]

Although embodiments of the present invention have been described above, the embodiments are not intended to limit the present invention and the above embodiments may be altered or modified as appropriate within a scope of the gist of the present invention.

EXAMPLES

[0053]

Hereinafter, examples of the present invention will be described, which are not intended to limit the present

invention.

[0054]

Measurement Methods

Water Content

The water content of samples was measured using a trace moisture analyzer CA-200 (manufactured by Mitsubishi Chemical Analytech). If necessary, samples were diluted with isopropyl alcohol before the measurement of their water content. The isopropyl alcohol reagent used for the dilution has a water content of at most 100 ppm by mass. In addition, samples with a water content of at most 100 ppm by mass were taken in an amount of 5 g or more with a Terumo syringe in a glove box with a dew point of -60°C or less, and the water content of the samples was measured. The lower limit for the quantification of the sample water content is 1 ppm by mass.

[0055]

Alcohol Content of Samples with Water Content of 10% by Mass or More

The alcohol content of samples was measured under the measurement conditions below using a GC-MS with headspace sampling. The lower limits for the quantification of the tert-butyl alcohol and ethyl alcohol contents of a standard sample consisting of water (95% by mass) and isopropyl alcohol (5% by mass) were each 5 ppb by mass. The lower limit for the quantification of the six-carbon alcohol content of the standard sample was 100 ppb by mass.

[0056]

Conditions for Measurement of Crude Isopropyl Alcohol Aqueous Solution

Instrument: 7890A/5975C (manufactured by Agilent Technologies)

Analytical column: J&W DB-1 (60 m × 0.32 mm, 5 µm)

Column temperature: 35°C (2 min hold) → 10°C/min ramp → 250°C (6 min hold)

Carrier gas: Helium

Injection pressure: 20 psi

Linear velocity: 31 cm/sec

Inlet temperature: 200°C

Sample injection method: Split method

Split ratio: 1:5

Injection volume: 1 mL

Headspace heating temperature: 60°C

Headspace heating time: 20 min

Transfer line temperature: 240°C

Ion source and quadrupole temperatures: 230°C and 150°C

Scanned ions: m/z = 25 to 250

SIM monitor ions: 31, 59

[0057]

Alcohol Content of Samples with Water Content of 10% by Mass or Less

The alcohol content of samples was measured under the conditions below using a GC-MS. The lower limits for the quantification of the tert-butyl alcohol and ethyl alcohol contents of a standard sample consisting of isopropyl alcohol

were each 10 ppb by mass. The lower limit for the quantification of the six-carbon alcohol content of the standard sample was 10 ppb by mass.

[0058]

Conditions for Measurement of Semiconductor Process Chemical Liquid

Instrument: 7890A/5975C (manufactured by Agilent Technologies)

Analytical column: J&W DB-1 (60 m × 0.32 mm, 5 μm)

Column temperature: 35°C (2 min hold) → 10°C/min ramp → 250°C (6 min hold)

Carrier gas: Helium

Injection pressure: 20 psi

Linear velocity: 31 cm/sec

Inlet temperature: 200°C

Sample injection method: Split-less method

Injection volume: 2 μL

Headspace heating temperature: 60°C

Headspace heating time: 20 min

Transfer line temperature: 240°C

Ion source and quadrupole temperatures: 230°C and 150°C

Scanned ions: m/z = 25~250

SIM monitor ions: 31, 59

[0059]

Conditions for Measurement of Raw Material Gas and Gas Components

Instrument: 7890A/5975C (manufactured by Agilent

Technologies)

Analytical column: TC-BOND Alumina/Na₂SO₄ (30 m × 0.25 mm, 4 μm)

Column temperature: 35°C (2 min hold) → 10°C/min ramp → 200°C (6 min hold)

Carrier gas: Helium

Injection pressure: 18 psi

Linear velocity: 52 cm/sec

Inlet temperature: 150°C

Sample injection method: Split method

Split ratio: 1:5

Injection volume: 1 mL

Headspace heating temperature: 60°C

Headspace heating time: 20 min

Transfer line temperature: 240°C

Ion source and quadrupole temperatures: 230°C and 150°C

Scanned ions: m/z = 25~150

[0060]

Concentration Method

The samples of the present examples as measurement targets, which had reduced content of impurities, were concentrated as needed before analysis so that compounds with boiling points higher than that of isopropyl alcohol could be analyzed with improved accuracy. Although the concentration method is as shown below, if necessary, the operations described below were repeated to change the concentration rates. The sample was distilled for 10 hours using a precision

distillation apparatus with a distillation column top temperature of about 82°C. The number of theoretical trays in the super fractionation apparatus was in the range of 3 to 30, which enabled the concentration of the sample. In order to prevent sample oxidation, nitrogen was provided into the precision distillation apparatus in advance to establish an inert gas atmosphere. Further, during the distillation, nitrogen was also provided into the distillate receiver to perform distillation under an inert gas atmosphere. In the examples, when the standard sample consisting of isopropyl alcohol was concentrated 1,000 times, the lower limit for the quantification of the six-carbon alcohol content of the standard sample was 0.01 ppb by mass.

[0061]

Example 1

Raw Material Gas

The composition of the raw material gas was analyzed. For the analysis, a standard gas with a known concentration was prepared and subjected to quantification. Propylene content: 99% by volume or more

Propane content: 1,000 ppm by volume

Methane content: Less than 0.1 ppm by volume

Ethane content: Less than 0.1 ppm by volume

Ethylene content: Less than 0.1 ppm by volume

Cyclopropane content: 1 ppm by volume

1-Butene content: Less than 0.1 ppm by volume

Isobutene content: Less than 0.1 ppm by volume

Five-carbon alkene (pentene) content: Less than 0.1 ppm by volume

Six-carbon alkene (hexene) content: Less than 0.1 ppm by volume

The raw material gas had a density of 1.87×10^{-3} kg/L under the standard conditions (101.3 kPa, 0°C).

[0062]

Raw Material Water

The raw material water was obtained by adding phosphotungstic acid to water so that the pH thereof at 25°C reached 3.0.

[0063]

Reaction Step

A continuous reactor with an internal volume of 22.0 L was controlled to maintain a liquid phase with a volume of 20.0 L at the lower part of the continuous reactor and a gas phase with a volume of 2.0 L at the upper part of the continuous reactor. The raw material water heated at 110°C was fed at a feed rate of 45 kg/h to the continuous reactor, and the raw material gas was fed at a feed rate of 3 kg/h, which corresponded to 1.87×10^3 L/h (expressed in terms of standard conditions), to the continuous reactor, while the gas components were discharged at a discharge rate of 200 L/h (expressed in terms of standard conditions) from the gas phase of the continuous reactor. During this operation, the temperature and the pressure inside the continuous reactor were set to 280°C and 250 atm, respectively, to react the

propylene and water and form isopropyl alcohol. During this operation, since the density of the raw material water was 0.75 kg/L at 280°C and 250 atm, the residence time of the raw material water inside the continuous reactor was 20 minutes. During this operation, since the discharge rate of the gas components at 280°C and 250 atm was 1.6 L/h, the residence time of the gas components inside the continuous reactor was 74 minutes.

[0064]

Table 1 shows the reaction conditions in the reaction step. Table 2 shows the composition of the gas components (volume basis). In the table, the term "hexenes" refers to hexenes other than 4-methyl-1-pentene.

[0065]

[Table 1]

	Example1	Example2	Example3	Example4	Example5	Example6	Comparative Example1	Comparative Example2	Comparative Example3
Feed rate A of raw material water (kg/h)	45	60	45	75	75	80	30	45	30
Feed rate B of raw material gas (kg/h)	3	3	3	3	3	3	3	3	3
B/A(-)	0.067	0.050	0.067	0.040	0.040	0.038	0.10	0.067	0.100
Feed rate B of raw material gas (L/h)	1.87×10^4	1.87×10^4	1.87×10^3	1.87×10^3	1.87×10^3	1.87×10^3	1.87×10^3	1.87×10^3	1.87×10^3
Discharge rate C of gas components (L/h)	200	200	250	120	250	500	80	30	200
C/B(-)	0.11	0.11	0.13	0.06	0.13	0.27	0.04	0.02	0.11
Residence time of raw material water (min)	20	15	20	12	12	11	30	20	30
Residence time of gas components (min)	74	74	59	123	59	30	185	494	74

[0066]

[Table 2]

	Example1	Example2	Example3	Example4	Example5	Example6	Comparative Example1	Comparative Example2	Comparative Example3
Hexenes (%)	2	2	1	3	1	0.3	5	12	2
4-Methyl-1-pentene (%)	0.4	0.4	0.3	0.7	0.3	0.1	1	2	0.4
Isobutene (ppm)	10	10	7	13	7	3	30	50	10
Ethylene (ppm)	5	5	3	7	3	1	10	30	5

[0067]

Product Recovery Step

The liquid components were discharged from the liquid phase of the continuous reactor and transported to a product recovery column. At this time, by setting the temperature and pressure inside the recovery column to 140°C and 18 atm, respectively, the propylene dissolved in the water included in the liquid components was separated, thereby obtaining a crude isopropyl alcohol aqueous solution. During the process, the propylene conversion rate was 95%, and the isopropyl alcohol selectivity was 99.5%. After being separated, the propylene was collected in a drum to be reused as the raw material gas.

[0068]

Table 3 shows the composition (mass basis) of the crude isopropyl alcohol aqueous solution. In the table, the term "hexanols" refers to hexanols other than 4-methyl-2-pentanol, 2-methyl-2-pentanol, 2-methyl-3-pentanol, 3-methyl-3-pentanol, 3-methyl-1-pentanol, 2,3-dimethyl-2-butanol, and 4-methyl-1-pentanol.

[0069]

[Table 3]

	Example1	Example2	Example3	Example4	Example5	Example6	Comparative Example1	Comparative Example2	Comparative Example3
Water (%)	95	95	95	95	95	95	95	95	95
Isopropyl alcohol (%)	5	5	5	5	5	5	5	5	5
Tert-butyl alcohol (ppb)	50	30	40	40	20	10	200	400	100
Ethyl alcohol (ppb)	50	30	40	40	20	10	200	500	100
4-Methyl-2-pentanol (ppb)	4000	2000	3000	4000	2000	1000	23000	50000	10000
2-Methyl-2-pentanol (ppb)	2000	1000	1000	1000	1000	500	7800	15000	3000
2-Methyl-3-pentanol (ppb)	1000	600	800	500	500	200	4000	7000	2000
3-Methyl-3-pentanol (ppb)	300	300	300	300	200	<100	2000	3000	700
3-Methyl-1-pentanol (ppb)	200	<100	100	100	<100	<100	1000	2000	300
2,3-Dimethyl-2-butanol (ppb)	200	100	100	100	<100	<100	1000	2000	300
4-Methyl-1-pentanol (ppb)	<100	<100	<100	<100	<100	<100	500	1000	200
Hexanols (ppb)	<100	<100	<100	<100	<100	<100	<100	<100	<100

[0070]

Purification Step

The crude isopropyl alcohol aqueous solution was fed to a low-boiling distillation column for removal of low-boiling impurities, and the distillation residue was obtained from the column bottom. Next, the distillation residue was fed to an azeotropic distillation column to remove the high-boiling impurities, and an azeotropic mixture of isopropyl alcohol and water (in a mass ratio of 87.5:12.5) was obtained from the column top. Next, the azeotropic mixture was dehydrated by feeding to a dehydration distillation column, and the distillation residue was obtained from the column bottom. The distillation residue was fed to a high-boiling distillation column to remove high-boiling impurities, and the distillate was obtained from the column top. The high-boiling distillation column had 15 trays. The distillate was then

passed through a fluoro-resin filter with a pore size of 10 nm to give a semiconductor process chemical liquid.

[0071]

Table 4 shows the composition (mass basis) of the semiconductor process chemical liquid. In the table, the term "hexanol" refers to a six-carbon alcohol.

[0072]

[Table 4]

	Example1	Example2	Example3	Example4	Example5	Example6	Comparative Example1	Comparative Example2	Comparative Example3
Isopropyl alcohol (%)	>99.99	>99.99	>99.99	>99.99	>99.99	>99.99	>99.99	>99.99	>99.99
Water (ppm)	5	5	5	5	5	5	5	5	5
Tert-butyl alcohol(ppb)	900	500	600	800	300	100	4100	8100	1900
Ethyl alcohol (ppb)	1000	500	700	800	300	100	4100	9500	2000
Hexanol (ppb)	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.02	0.05	0.01

[0073]

Example 2

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the feed rate of the raw material water in the reaction step was changed to 60 kg/h and that the residence time of the raw material water in the continuous reactor was changed to 15 minutes (see Table 1). During the process, the propylene conversion rate was 95%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the compositions of the gas components, the crude isopropyl alcohol aqueous solution, and the semiconductor process chemical liquid.

[0074]

Example 3

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the discharge rate of the gas components in the reaction step was changed to 250 L/h (expressed in terms of standard conditions) and that the residence time of the gas components in the continuous reactor was changed to 59 minutes (see Table 1). During the process, the propylene conversion rate was 94%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the compositions of the gas components, the crude isopropyl alcohol aqueous solution, and the semiconductor process chemical liquid.

[0075]

Example 4

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the feed rate of the raw material water in the reaction step was changed to 75 kg/h, the residence time of the raw material water in the continuous reactor was changed to 12 minutes, the discharge rate of the gas components in the reaction step was changed to 120 L/h (expressed in terms of standard conditions), and the residence time of the gas components in the continuous reactor was changed to 123 minutes (see Table 1). During the process, the propylene conversion rate was 97%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the proportions of the gas components, the composition of the crude isopropyl alcohol aqueous solution, and the composition of the

semiconductor process chemical liquid.

[0076]

Example 5

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the feed rate of the raw material water in the reaction step was changed to 75 kg/h, the residence time of the raw material in the continuous reactor was changed to 12 minutes, the discharge rate of the gas components in the reaction step was changed to 250 L/h (expressed in terms of standard conditions), and the residence time of the gas components in the continuous reactor was changed to 59 minutes (see Table 1). During the process, the propylene conversion rate was 94%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the compositions of the gas components, the crude isopropyl alcohol aqueous solution, and the semiconductor process chemical liquid.

[0077]

Example 6

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the feed rate of the raw material water in the reaction step was changed to 80 kg/h, the residence time of the raw material water w in the continuous reactor was changed to 11 minutes, the discharge rate of the gas components in the reaction step was changed to 500 L/h (expressed in terms of standard conditions), and the residence time of the gas components in the continuous reactor was changed to 30 minutes (see Table 1). During the process,

the propylene conversion rate was 88%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the compositions of the gas components, the crude isopropyl alcohol aqueous solution, and the semiconductor process chemical liquid.

[0078]

Comparative Example 1

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the feed rate of the raw material water and the discharge rate of the gas components in the reaction step were respectively changed to 30 kg/h and 80 L/h expressed in terms of standard conditions (0.65 L/h in terms of the internal volume of the reactor), and that the residence times of the raw material water and the gas components in the continuous reactor were respectively changed to 30 minutes and 185 minutes (see Table 1). During the process, the propylene conversion rate was 98%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the compositions of the gas components, the crude isopropyl alcohol aqueous solution, and the semiconductor process chemical liquid.

[0079]

Comparative Example 2

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the discharge rate of the gas components in the reaction step was changed to 30 L/h (expressed in terms of standard conditions) and that the

residence time of the gas components in the continuous reactor was changed to 494 minutes (see Table 1). During the process, the propylene conversion rate was 99%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the compositions of the gas components, the crude isopropyl alcohol aqueous solution, and the semiconductor process chemical liquid.

[0080]

Comparative Example 3

A semiconductor process chemical liquid was obtained similarly to Example 1, except that the feed rate of the raw material water in the reaction step was changed to 30 kg/h, and that the residence time of the raw material water in the continuous reactor was changed to 30 minutes (see Table 1). During the process, the propylene conversion rate was 95%, and the isopropyl alcohol selectivity was 99.5%. Tables 2 to 4 show the compositions of the gas components, the crude isopropyl alcohol aqueous solution, and the semiconductor process chemical liquid.

[0081]

It is evident from Table 4 that the semiconductor process chemical liquid of each of Examples 1 to 6 has lower contents of tert-butyl alcohol, ethyl alcohol, and hexanol. In contrast, the semiconductor process chemical liquid of Comparative Example 1 had higher contents of tert-butyl alcohol, ethyl alcohol, and hexanol, due to the residence times of the raw material water and the gas components in the

continuous reactor being 30 minutes and 185 minutes, respectively. The semiconductor process chemical liquid of Comparative Example 2 had higher contents of tert-butyl alcohol, ethyl alcohol, and hexanol, due to the residence time of the gas components in the continuous reactor being 494 minutes and C/B being 0.02. The semiconductor process chemical liquid of Comparative Example 3 had higher contents of tert-butyl alcohol, ethyl alcohol, and hexanol, due to the residence time of the raw material water in the continuous reactor being 30 minutes.

EXPLANATION OF REFERENCE NUMERALS

[0082]

- 1: Continuous reactor
- 2: Control valve
- G: Gas phase
- L: Liquid phase

CLAIMS

[Claim 1]

A semiconductor process chemical liquid essentially comprising isopropyl alcohol,

wherein a content of a tert-butyl alcohol is at most 1,000 ppb by mass, and

wherein a content of ethyl alcohol is at most 1,000 ppb by mass.

[Claim 2]

The semiconductor process chemical liquid according to claim 1, wherein a content of a six-carbon alcohol is at most 1 ppb by mass.

[Claim 3]

A method for producing a semiconductor process chemical liquid consisting essentially of isopropyl alcohol, the method comprising:

reacting a raw material water and a raw material gas containing propylene and having an isobutene content of at most 1 ppm by volume and an ethylene content of at most 1 ppm by volume, by feeding to a continuous reactor,

wherein, a gas phase and a liquid phase exist upon the reacting, and the continuous reactor discharges gas components from the gas phase,

wherein a mass ratio of the raw material gas relative to

the raw material water fed to the continuous reactor is 0.01 or more and 0.20 or less,

wherein a residence time of the raw material water inside the continuous reactor, which is a ratio of volume (L) of the liquid phase relative to a feed rate (L/min) of the raw material water fed to the continuous reactor, is 10 minutes or more and 25 minutes or less,

wherein a residence time of the gas component inside the continuous reactor, which is a ratio of volume (L) of the gas phase relative to a discharge rate (L/min) of the gas component discharged from the continuous reactor, is 10 minutes or more and 150 minutes or less, and

wherein a volume ratio of a discharge amount of the gas component discharged from the continuous reactor relative to a feed amount of the raw material gas fed to the continuous reactor is 0.03 or more and 0.30 or less.

[Claim 4]

The method for producing a semiconductor process chemical liquid according to claim 3, further comprising:

recovering a crude isopropyl alcohol aqueous solution from the liquid phase; and

distilling the crude isopropyl alcohol aqueous solution in a high-boiling distillation column.

[Claim 5]

The method according to claim 3 or 4, wherein the raw

material gas has a propylene content of 99% by volume or more.

[Claim 6]

The method according to claim 3 or 4,

wherein the continuous reactor has an internal temperature of 200°C or more and 300°C or less and

wherein the continuous reactor has an internal pressure of 150 atm or more and 280 atm or less.