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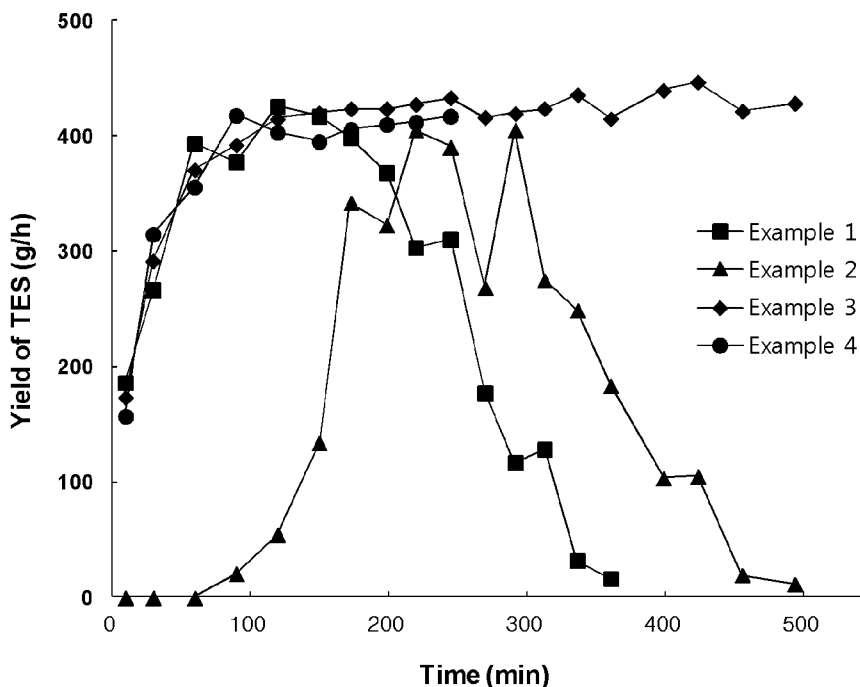
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[Continued on next page]

(54) Title: METHOD FOR PREPARING MONOSILANE BY USING TRIALKOXYLSILANE



(57) Abstract: Provided is a method for preparing monosilane, more particularly a method for economically preparing monosilane, which is useful for the composition of a thin semiconductor structure and multipurpose high-purity polycrystalline silicon, by preparing monosilane with high purity and high yield using trialkoxysilane.

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## Description

### Title of Invention: METHOD FOR PREPARING MONOSILANE BY USING TRIALKOXY-SILANE

#### Technical Field

[0001] The present invention relates to a method for preparing monosilane, and more particularly, to a method for economically preparing monosilane, which is useful for forming a thin film of a semiconductor and for multipurpose high-purity polycrystalline silicon, by preparing monosilane with high purity and high yield using trialkoxysilane.

[0002]

#### Background Art

[0003] Monosilane is present in a gas state with a boiling point of 112°C under general conditions. Monosilane is actively decomposed at a temperature of 700°C or more into silicon, which is a basis for obtaining high-purity silicon, and hydrogen.

[0004] A series of methods of synthesizing monosilane have been widely known. For example, as a catalytic disproportionation method of trichlorosilane, a two-step technology is known (German Patent No. 3311650 (October 13, 1983)). In the technology, the first step corresponds to performing catalytic hydrogenation for metal silicon, and at this time, the hydrogenation is conducted along with production of trichlorosilane at a temperature from 400°C to 600°C and a pressure from 0.7 bar to 41.4 bar. In the second step, a catalytic disproportionation reaction of trichlorosilane is performed. At this time, an anion exchange resin is used as a catalyst along with tertiary amine, and the disproportionation is performed at a maximum temperature of 150°C. Thereafter, impurities of monosilane are removed. However, when a corrosive chlorine compound is present, the invention makes it difficult to purify monosilane into high-purity monosilane due to transfer of impurities from the wall of equipment toward monosilane and causes an increase in the price of a final product, and thus it is difficult to widely use the method as one of the methods of preparing monosilane.

[0005] Further, as a method of preparing silane by using a reaction of silicon tetrachloride with lithium hydride, a method according to Russian Patent No. 2173297 (2001) is also widely known. In the method, lithium hydride is pulverized beforehand, and then the process is conducted at a temperature of 300°C. Lithium chloride produced during the reaction is used for regeneration of LiH. At this time, hydrogen chloride is produced. A major disadvantage of the method is that it is necessary to remove a starting reagent from silane, particularly, hydrogen chloride residue. In relation to this, there is a problem in that it is required to additionally perform a difficult process of removing

HCl from a final product.

[0006] As another method of preparing silane, there is a method of preparing silane by treating lithium silicide with a diluted solution of hydrochloric acid, nitric acid or sulfuric acid according to Russian Patent No. 2194009 (2002). As a major disadvantage of the method, there is a problem in that it is required to additionally perform a difficult process of removing a starting reagent, that is, hydrogen chloride or the corresponding acetic acid or sulfuric acid residue from silane. Examples of other limitations include high exothermicity, and when a violation occurs in the replenishment mode of a starting reagent in a reactor, the reactor is likely to explode.

[0007] A method of preparing monosilane by using the catalytic disproportionation of alkoxysilane is one of the promising methods. The method was proposed in US Patent No. 2530367 in 1947, and the disproportionation in the invention is performed by the following Reaction Equation A.

[0008]

[0009] [Reaction Equation A]

[0010]  $4\text{SiH}(\text{C}_2\text{H}_5\text{O})_3 \rightarrow \text{SiH}_4 + 3\text{Si}(\text{C}_2\text{H}_5\text{O})_4$

[0011] The foundation for the catalytic disproportionation of alkoxysilane was established in the former Soviet Union in the year 1957 to 1959, and the reason for this appears that triethoxysilane was usually developed at that time [Soviet Journal of Technical Physics, 1957, v. 27, No. 8, pp. 1645-1648 and Soviet Journal of Solid State Physics, 1959, v. 1, pp. 999-1001].

[0012] US Patent No. 3829555 (August 13, 1974) proposed a continuous synthesis process of monosilane. In the invention, sodium ethoxide in tetraethoxysilane acted as a catalyst in a disproportionation reaction of triethoxysilane, the reaction was conducted in a liquid phase, and the conversion ratio of triethoxysilane ranged from 70% to 90%.

[0013] Meanwhile, the numeral in the parenthesis [] represented in the following explanation means each number of the prior art literature cited by reference in the present invention.

[0014] Currently, two important routes have been proposed for the synthesis method of alkoxysilane. The core of the first route is that synthesis is conducted in a floating bed or fluidized bed of a vapor-gas medium. The core of the second route is that synthesis reaction is conducted in a liquid solvent environment in a reactor equipped with a stirring apparatus.

[0015] Here, the method of preparing alkoxysilane in the vapor-gas medium allows alcohol vapor to pass through a silicon powder layer mixed with a catalyst, in which it is possible for the mixture to be either in a floating state or in a fluidized state.

[0016] In addition, the method of preparing alkoxysilane by using a floating bed apparatus has difficulty in maintaining the same temperature through the entire volume of the

reactor, and thus failed to be broadly used. However, when a synthesis reaction of alkoxy silane is directly performed in a fluidized bed, it is possible to eliminate the disadvantage.

[0017] It is appropriate to separately conduct an activation process of a contact material composed of metal silicon and a catalyst before the reaction, and the process is conducted under nitrogen ventilation (see [1] and [4]) or under another inert gas at a temperature from 300°C to 350°C (see [2] and [5]) or a temperature of approximately 450°C (see [1]) for 5 hours to 8 hours.

[0018] Furthermore, the use of hydrogen was proposed for activation of silicon and the catalyst (see [6] to [9]). The activation using hydrogen is performed in a floating bed or fluidized bed at a temperature of approximately 400°C. Copper is contained in an amount of 1.5% or more in a mixture of silicon and the catalyst. However, data on the selectivity, reactivity and reaction stability for the work are not explicitly described.

[0019] When alcohol vapor is diluted with a buoyant gas, the non-uniform temperature may be prevented from being diffused or minimally decreased in a fluidized bed. As a carrier gas, argon, nitrogen, helium, neon, hydrogen and the like may be used (see [1]). On the contrary, when an additional work is introduced, the process price is increased and the vapor of an inert gas is transferred together, thereby significantly increasing the loss of alkoxy silane and alcohol.

[0020] The inventors of [2] have proposed that hydrogen together with alcohol vapor passes through the contact material. When hydrogen is used in the technology of obtaining alkoxy silane, it is necessary to divide the reaction system into a unit for obtaining hydrogen and a unit for removing hydrogen, and thus the costs of a final product obtained is increased. When pressure is decreased at a point where selectivity is 84.2% and the silicon conversion ratio is 90% and the synthesis process is conducted (see [1]), the selectivity and the silicon conversion ratio are only 48.8% and 65%, respectively, at normal pressure and thus the yield of a final product such as, for example, trimethoxy silane is increased. On the contrary, the reaction rate is slowed at low pressure, and accordingly, the productivity of the process is also decreased.

[0021] When triethoxy silane is prepared, the contact material may be activated even with nitrogen (see [2]). Further, zinc as an accelerator is additionally added to the contact material at a reaction temperature of 280°C in order to improve the yield of triethoxy silane. The content of triethoxy silane in the reaction product was 87%, but the silicon conversion ratio thereof was 23% or less, which was very low.

[0022] The inventors of [1] succeeded in improving the yield of the product and the silicon conversion ratio thereof by using ethyl alcohol. Here, the contact material was put into the reactor, the reactor was heated under nitrogen flow up to 350°C for 5 hours, and then vapors of ethyl alcohol and chloroethyl were injected thereinto. The synthesis

reaction was conducted at 250°C for 23 hours. In the above-described conditions, the yield of triethoxysilane was 74.3% (silicon conversion ratio: 62%), and the yield and silicon conversion ratio thereof were improved up to 82.4% and maximally 80%, respectively, under a pressure decreased to 660 mmHg.

[0023] In the results of literatures [1] to [9] related to preparation of alkoxysilane in a fluidized bed under atmospheric pressure, the yield of triethoxysilane and silicon conversion ratio thereof were not so high, and major variables of synthesis during the reaction at low pressure were improved, but the invention is not preferred due to a problem in that the preparation process is complicated even though there is an advantage.

[0024] Process indices were increased by several times by additionally introducing a solubilizer together with alcohol, but the alkoxysilane synthesis process becomes complicated in a fluidized bed and small amounts of silicon and the catalyst are together transferred, thereby causing a problem in that the final product is subjected to additional filtration.

[0025] When a solvent is used in synthesizing alkoxysilane, the temperature region in the reaction mixture become uniform, overheating is significantly decreased, a side reaction is suppressed, and as a result, selectivity is improved and a silicon conversion ratio is also improved.

[0026] During the synthesis of alkoxysilane, the temperature is maintained up to 300°C, which is a relatively high temperature, and thus as a solvent to be used, it is required that a solvent that is not decomposed in a reaction region at such a temperature is selected. The solvent also needs to be effective such that the uniform temperature and dispersibility of silicon powder may be secured in a reaction system, and the solvent should not be oxidized at a reaction temperature from 100°C to 300°C. In a series of inventions, it has been proposed that as the solvent, alkylated benzene (see [2], [10] and [11]) and alkylated naphthalene - "THERMINOL" oil (see [12]) are used. Detailed information on a solvent suitable at a high temperature, such as THERMINOL 59, THERMINOL 60, THERMINOL 66, DOWTHERM HT, MARLOTHERM S, and MARLOTHERM, is provided in the literature, and examples thereof include literatures [13] and [25]. For the amount of the solvent used for the synthesis, the ratio of the solvent : silicon is in a range from 1:2 to 4:1, but a range from 1:1 to 2:1 is recommendable (see [13], [14] and [15]).

[0027] Literatures [16], [17], [18], [19] and [20] explicitly describe that an induction period is required for reaction of alcohol and silicon, and the length of the induction period is 1 hour to 12 hours. As a major reason for appearance of the induction period, it is suggested that an oxide film influences the surface of silicon. In order to decrease the induction period, it is proposed that an additional activation step is provided in the

synthesis process of alkoxy silane.

[0028] Literature [13] treats the activation process sufficiently in detail. According to the inventor's opinion, activation may be induced in another separate apparatus or in the reactor in which the reaction takes place, and when the separate apparatus is used, it is recommended to transfer activated silicon to a reactor in a dry and neutral environment. It is proposed that activation is implemented at a temperature from 20°C to 400°C (recommended temperature from 150°C to 300°C) and hydrogen and nitrogen are used together as activators. The inventors allowed a reaction suspension containing 1 kg of silicon, 14.1 g of copper hydroxide and 2.1 kg of the solvent MARLOTHERM S to be activated with hydrogen and nitrogen at a temperature from 150°C to 250°C for 65 minutes. Methyl alcohol was introduced thereinto at a rate of 4.3 g/min at 250°C for 5 hours. Thereafter, the temperature was decreased up to 230°C, the supply of methyl alcohol was stopped, and ethyl alcohol began to be supplied at the same rate. At this time, the supply of hydrogen was also stopped, but the supply of nitrogen was maintained. The total amount of the activator was stoichiometrically calculated, and needs to be sufficient for dissociating the copper catalyst in a divalent or monovalent state into free copper (see [13]). The inventors explicitly describe that it actually takes considerably long time for the activation process to be conducted, and according to the inventors' opinion, it is considered that the reason is that a silicon-copper material having a particle diameter from 50 μm to 300 μm has a very large surface area.

[0029] The inventors of literatures [21] and [22] have proposed that when the induction period is desired to be decreased, an oxide film is removed from the surface of powder prepared by treating silicon, previously pulverized before the synthesis process is conducted, with hydrofluoric acid (HF). However, this is only a temporary measure because it is necessary to remove and dry residue after treatment of silicon powder with hydrofluoric acid and it is inevitable that oxide appears again on the surface of silicon particle during this process.

[0030] In a series of literatures, it is proposed that a reaction material is activated by maintaining a high temperature in an inert environment such as nitrogen, argon and the like (see [10] and [22]), and that silicon is beforehand mixed with a catalyst in an inert environment over 8 hours (see [23]).

[0031] It is proposed that for activation of silicon, a halide such as alkyl chloride, hydrogen chloride, ammonium chloride (see [21]), and  $\text{NH}_4\text{HF}_2$  (see [24]), is introduced thereinto before the synthesis. When a process of preparing alkoxy silane is conducted based on the reaction of silicon with ethyl alcohol, it is proposed that the activation of silicon with methyl alcohol is conducted. The reason is that methyl alcohol has a better reaction activity for silicon than ethyl alcohol or higher alcohols (see [13]). For example, when 5% methyl alcohol is added to ethyl alcohol, the reaction rate is sig-

nificantly increased. It is necessary to pay attention to the fact that a process of removing impurities such as distillation is essentially performed from a target product prepared when a material such as halide, alkyl halide and methanol is introduced into a reactor before the synthesis. The reason is that impurities decrease productivity and make the process of preparing alkoxy silane complicated.

- [0032] Solutions widely known up until now fail to consistently explain the cause why the induction period occurs in the direct synthesis process of alkoxy silane and the characteristic thereof, and no technical solution by which the problems may be effectively handled is even present. A solution, in which additionally introducing a reagent during the synthesis process is a basic concept, makes it necessary to remove residue from the final product, and thus additional work is needed and the process of preparing alkoxy silane is made to be complicated, thereby making the price of the final product expensive.
- [0033] As another problem, it is also widely known that side reactions take place during the synthesis reaction of alkoxy silane in a reactor, and thus oligo-alkoxy silane, water, and other secondary side products are produced, and these side products are accumulated in a reaction environment, thereby decreasing the process rate (see [11], [13], [14], [17], and [21]). Most of the reactions use metal as a catalyst (see [14]), and the metal is usually present in the form of an impurity in silicon which is initially used. Metal copper is usually produced in a solvent component as a result of decomposition of a copper-containing material that is used as a catalyst in the main synthesis reaction.
- [0034] When residual silicon, impurities and alkoxy silane, which are contained in the processed silicon material, are accumulated, the accumulation also decreases the reaction rate. When the solvent is intended to be used later in the synthesis of alkoxy silane, the process essentially needs to regenerate the solvent.
- [0035] In order to improve the efficiency of the index of directly synthesizing alkoxy silane, it is proposed that aluminum (0.01% to 10%, 0.1% to 2% as a preferred concentration)(see [16]), zinc (see [2]), or an organic material having at least one binding phosphate, a non-organic material compound (see [25]) and the like are used as an accelerator for the alkoxylation reaction of silicon, but there is no unified opinion on the effect thereof.
- [0036] Literature [13] suggests special requirements for the particle size analysis element of the catalyst. The size of particles needs to be in a range from 1  $\mu\text{m}$  to 100  $\mu\text{m}$  (preferred size from 0.1  $\mu\text{m}$  to 50  $\mu\text{m}$ ). However, when the specific surface area of the catalyst in the initial product is in a range from 0.1  $\text{m}^2/\text{g}$  to 2  $\text{m}^2/\text{g}$  (preferred specific surface area from 10  $\text{m}^2/\text{g}$  to 50  $\text{m}^2/\text{g}$ ), the preferred size is from 0.1  $\mu\text{m}$  to 30  $\mu\text{m}$ .
- [0037] It is possible to conduct the direct synthesis reaction of silicon and alcohol in both the batch mode and the continuous mode. In the batch mode, the total amount of



silicon is introduced into a reactor at the start of the process, and alcohol is continuously supplied until the silicon is completely reacted. It is also allowed to use a method of supplying a predetermined amount of silicon in a dosage amount and continuously supplying alcohol.

[0038] In the continuous mode, only silicon or a catalyst-containing silicon is added after the operation thereof. Further, a regulation is needed in order to minimize the content of the catalyst and prevent a side reaction of decomposing alcohol from taking place.

[0039] The reaction is conducted at a temperature of 150°C or more. It is recommended that the process is conducted at a temperature from 200°C to 260°C, if possible. The reaction with methyl alcohol is conducted while maintaining the temperature from 220°C to 250°C, and the temperature 200°C to 240°C in the case of ethyl alcohol (see [13]).

[0040] The direct synthesis reaction of alkoxysilane is possible in both the cases of increasing and decreasing pressure, but it is recommended that the reaction is conducted under atmospheric pressure.

[0041] To sum up, what has been described above comes to a conclusion that the generalized form for main characteristics of widely known methods (see [1] to [25]) is reflected in literature [26].

[0042] Literature [26], which is a method of preparing trialkoxysilane, is selected as an analogue of the proposed method, and includes a reaction process of silicon and alcohol under the premise of pulverization work of silicon, heating of a solvent, the presence of a catalyst, and activation of a reagent. In the method of [26], the pulverization work of silicon having a particle size of up to 500  $\mu\text{m}$  is performed at the atmosphere. Ethanol or methanol is used as an alcohol reagent, and triethoxysilane or trimethoxysilane is prepared as a final product. As a catalyst, compounds containing copper are usually used, and among them., copper (I) chloride ( $\text{CuCl}$ ) is frequently used and a major technical process of reacting pulverized silicon with alcohol is conducted under an environment in which the above-described polyaromatic oils and other oils as a solvent are heated up to 200°C. In the known method of [26], a reagent is used as a technical activation method. The reagent is used under the following conditions, and when trialkoxysilane is prepared in the reaction material according to the described scheme, impurities present in the starting reagent are accumulated, and first, when copper is present in the final product, the quality of the semiconductor-level silicon, that is, the efficiency of the solar cell is usually degraded. The reaction material is disproportionately consumed, and a portion of the solvent is sometimes consumed in a side reaction that produces impurities from the starting reagent, and therefore, unreacted silicon is present in the reaction material.

[0043] For this reason, the activation of the reagent is conducted, and according to the

method of [26], the activation process is summarized as discharging a suspension containing unreacted silicon from the reaction mixture to be kept, replenishing the solvent and the catalyst as much as necessary, and again circulating the reagent, in which the component is replenished, by the technical process. While the process is conducted, a series of complicated bleeding works are conducted regularly several times until unreacted silicon forms a precipitate in a reactor.

[0044] The method of [26] is similar to a series of analogues performed beforehand in terms of a decrease in side reaction intensity, an increase in yield of the product, a decrease in loss and an increase in productivity of the equipment, but the technical solution applied to the method activates the process by regularly discharging the reaction mixture and regularly replenishing the loss of the solvent and the catalyst to unreacted silicon, thereby making the process extremely complicated. In addition to that, the above method is usually related to the synthesis of alkoxysilane among the major problems.

[0045] The present invention developed a method of preparing monosilane based on the catalytic disproportionation of alkoxysilane described in US Patent No. 6103942 (August 15, 2000), and applied the method to the prototype of the present invention.

[0046] In the prototype, the preparation of monosilane may be implemented as follows.

[0047] For preparation of high-purity monosilane, metal silicon is first reacted with an organic alcohol, preferably ethyl alcohol at a high temperature by using a catalyst. At a high temperature, it is possible to produce alkoxysilane of which the target product is trialkoxysilane. When the method is implemented, it is preferred to obey one of the two known schemes. That is, the preparation of monosilane is conducted in a gas state (see [1]), or in an environment of a solvent having a high boiling point (see [16]).

[0048] According to the first scheme in which fluid metal silicon is reacted with an organic alcohol, reaction is conducted in the gas phase by using halide, preferably chloromethyl or chloroethyl as a catalyst. When pressure drops to atmospheric pressure or less, it is not necessary to condense a compound having a high boiling point at silicon particles and the site of equipment wall, and thus the process temperature is decreased and the yield of the target product is increased. Besides, the conversion ratio of metal silicon is increased, and selectivity in production of trialkoxysilane is increased.

[0049] According to the second scheme in which metal silicon is reacted with an organic alcohol, the reaction is conducted by using a copper compound as a catalyst in an environment of a solvent having a high boiling point (acetate, oxalate or chloride), and aluminum or an Al-Si alloy is added thereto. In this case, the conversion ratio of metal silicon is high (maximally 99.8%), and thus a solvent having a high boiling point is easily separated from a metal precipitate and it is possible to use the separated solvent

again in the process.

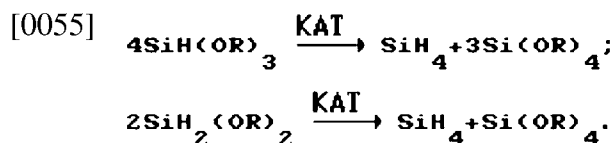
[0050] When a final product produced by reacting metal silicon with an organic alcohol according to the above two schemes is then condensed, trialkoxysilane (about 50% by weight), tetraalkoxysilane (about 10% by weight), unreacted alcohol (about 25% by weight), diethoxysilane impurities (maximally about 3% by weight), a chlorine compound (maximally about 1% by weight) and the like are included therein. In order to decrease the possibility of substituting the hydrogen bond with ethoxy group, which results in decreasing the content of triethoxysilane in the reaction product, the organic alcohol is first separated in the first-step purification of the condensate. When rectification is performed at a low pressure (about 100 mmHg) in the process, the organic alcohol is separated at a temperature close to room temperature, and the bonding of silicon to hydrogen may be almost perfectly broken. The separated organic alcohol contains no moisture and contains small amounts of alkoxy silane and a volatile chlorine compound, but there is no particular problem in reaction with silicon for preparation of alkoxy silane. The subsequent purification of alkoxy silane is conducted according to the known technology.

[0051] For the purpose of separating and purifying an alkoxy silane mixture from a condensate produced after metal silicon is reacted with the organic alcohol, the technology applied to the prototype has the following advantages. A volatile component, that is, the organic alcohol is separated well from the condensate, the process in the prototype is performed in a state in which the lowest electric power is consumed, the temperature is lowered, and the bonding of di- and tri-alkoxy silane is not almost broken, thereby increasing the yield of monosilane under the disproportionation.

[0052] The purified alkoxy silane mixture composed of di-, tri- and tetra-alkoxy silane is transferred to the catalytic disproportionation. At this time, the reaction equation is represented by the following Reaction Equation B.

[0053]

[0054] [Reaction Equation B]



[0056]

[0057] A solution of alkoxide, an alkaline earth metal and aluminum in tetraalkoxy silane is used as a catalyst. Alkoxy silane and the catalyst with a ratio of 20:1 to 10:1 are regularly or continuously, and preferably continuously supplied to a disproportionation reactor.

[0058] The monosilane produced is saturated with alkoxy silane vapor, and when the disproportionation reaction temperature is increased, the vapor concentration of alkoxy silane in monosilane is also increased. Accordingly, disproportionation is supposed to be performed at a temperature as low as possible, and preferably in a range from -20°C to +40°C. The most important characteristic of the disproportionation process is the conversion ratio of alkoxy silane in which the bonding of silicon and hydrogen is contained into monosilane. In order to obtain the maximum conversion ratio, the reaction proceeding time serves a very important role in addition to other conditions. When the disproportionation process is conducted in a continuous process, the contact time is essentially from 1 hour to 50 hours, but preferably from 10 hours to 25 hours. In consideration of fire caused by monosilane and explosiveness of monosilane, and contamination of ambient environments caused by impurities, disproportionation is performed in a sealed equipment, and the equipment does not need a stirring apparatus and allows an engine disposed outside the reactor to perform stirring in the stirring apparatus. When the proposed disproportionation mode is performed, the conversion ratio of alkoxy silane may reach 98%.

[0059] This kind of prototype is disadvantageous in that the activity of a catalyst used during the disproportionation is insufficient and thus the process time is prolonged up to 50 hours, and the process time is a maximum of 25 hours under preferred conditions.

[0060] When tetraethoxy silane and tetramethoxy silane are used as an adsorbent, restrictions occur in the purification of monosilane at a limiting temperature, thereby degrading the efficiency of process. At this time, the limiting temperature is about -80°C (in the case of tetraethoxy silane) or about 0°C (in the case of tetramethoxy silane). As described above, the prototype closest to the proposed method is significantly disadvantageous in that it takes a long time for the disproportionation reaction process and monosilane is insufficiently purified. Further, the prototype has problems in that a solution appropriate for decreasing or removing the induction period of the trialkoxy silane production reaction has not been proposed, and reactivity may be rapidly decreased or the reaction itself may be stopped when a new batch of a reagent is added.

[0061]

[0062] [Citation List]

[0063] [Patent Literature]

[0064] (Patent Literature 1) [1] US Patent No. 5,260,471: Process for producing trialkoxy silane / Yashinori Yamada 1993

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## Summary of Invention

### Technical Problem

- [0091] In order to solve the problem of the induction period during the initial period of the reaction when alkoxysilane is prepared, the decrease in selectivity and conversion ratio of a final product, the problem of continuous reaction, the decrease in productivity and the like in the related art, an object of the present invention is to provide a new method for preparing monosilane, which simplifies and improves the preparation process while ensuring continuity, operability, productivity, and stability.
- [0092] Further, in order to remove the above-described disadvantages in the related art, an object of the present invention is to provide a method for preparing monosilane, which ensures a rapid decrease or removal of the initial induction period of the synthesis reaction of alkoxysilane, simplification of the technology, improvement in reaction selectivity, and possibility of the synthesis process of monosilane in a continuous process.

[0093]

### Solution to Problem

- [0094] In order to solve the above-described problems, the present invention provides a method for preparing monosilane, which includes a pulverization work in a solvent environment for preventing an oxide film from being produced when a raw material silicon is prepared, a reaction of anhydrous ethyl alcohol with silicon pulverized by using a copper-based catalyst in a solvent environment heated up to 160°C to 300°C, an activation of a reagent caused by removing impurities, a replenishment of an amount of silicon consumed, a separation of a reaction product, a purification of triethoxysilane and a catalytic disproportionation reaction of triethoxysilane, which

produces monosilane gas, and a purification of monosilane, the method including: the following synthesis process steps of:

- [0095] (a) conducting a wet pulverization work in a liquid environment until silicon particles have a size from 30  $\mu\text{m}$  to 100  $\mu\text{m}$  and directly using the liquid as a solvent in a subsequent synthesis process of alkoxysilane;
- [0096] (b) continuously supplying a reactor with a suspension, which is obtained while the synthesis process is conducted, to a reactor, wherein an amount of a suspension of silicon supplied is allowed to be the same as an amount of silicon reacted in order to ensure that a continuous and stable reaction is conducted and the amount of silicon reacted is calculated from an amount of alkoxysilane synthesized according to the following Equation 1,
- [0097] [Equation 1]
- [0098]  $m_{\text{Si}} = k_1 \cdot m_{\text{TES}} + k_2 \cdot m_{\text{TEOS}}$
- [0099] Here,  $m_{\text{TES}}$  is a mass of triethoxysilane,  $m_{\text{TEOS}}$  is a mass of tetraethoxysilane prepared as a result of direct reaction for a unit time, and coefficients  $k_1$  and  $k_2$  are a molar ratio of silicon consumed during a synthesis process of tri-ethoxysilane and tetra-ethoxysilane, respectively;
- [0100] (c) removing the accumulated impurities from the reactor in a state of liquid suspension by continuously discharging the solvent in the same amount as that of the solvent supplied to the reactor, from the reactor;
- [0101] (d) directly removing an azeotropic mixture of unreacted ethyl alcohol and tri-ethoxysilane during a condensation of a target product under the atmospheric pressure;
- [0102] (e) purifying triethoxysilane produced;
- [0103] (f) performing a disproportionation process of triethoxysilane by using, as a catalyst, sodium ethoxide synthesized and prepared beforehand immediately before the disproportionation process step at a temperature from 0°C to 50°C; and
- [0104] (g) purifying monosilane by adsorbing impurities in monosilane by using tri-ethoxysilane at a temperature of - 140°C or less.

[0105]

### **Advantageous Effects of Invention**

- [0106] When monosilane is prepared as according to the above-described technical solution according to the present invention, the work performance is excellent, and feasibility is sufficient under laboratory conditions as well as in industrial application. In addition, there is an effect that the preparation process may be simplified and improved while ensuring the continuity, operability, productivity, and stability of the preparation process.
- [0107] Furthermore, as a specific effect, there are the improved effects as follows.

- [0108] - It is possible to decrease the initial induction period of the synthesis of alkoxysilane by approximately 15 times.
- [0109] - The process selectivity of triethoxysilane which is a main product is ensured at the 96% level.
- [0110] - A synthesis reaction of triethoxysilane and monosilane may be performed in a continuous process which maintains a high and stable synthesis rate.
- [0111] - The productivity of the preparation process is increased by decreasing the contact time of a reagent by 5 times or more.
- [0112] - The conversion ratio of triethoxysilane into monosilane is excellent.

[0113]

### **Brief Description of Drawings**

- [0114] FIG. 1 is a graph illustrating the comparison of a change in yield of triethoxysilane per unit time and an induction time of the initial reaction vs the synthesis process time of triethoxysilane each prepared in Examples 1 to 4 according to the present invention.

[0115]

### **Best Mode for Carrying out the Invention**

- [0116] [Best Mode]
- [0117] Hereinafter, the present invention will be described in detail as one embodiment.
- [0118] In the present invention, the "analogue" means a preparation method of alkoxysilanes by Gorshkov A.S., Markacheva A.A., and Starogenko P.A. (Russian Patent No. 2235726, C 1 Wikipedia data: C07 F 7/18, C07 F 07/04., Registration Date: May 28, 2003).
- [0119] Further, the "prototype" means a type of method proposed in Y. S. Tsuo et al., Method of high purity silane preparation (US 6,103,942, published on Aug. 15, 2000).
- [0120] In the present invention, in a method for preparing monosilane through a pulverization work of silicon, a process of reacting anhydrous alcohol with silicon pulverized by using a catalyst in a heated solvent environment, an activation of a reagent by removing impurities, a replenishment of an amount of silicon consumed, and a catalytic disproportionation process of triethoxysilane including a synthesis process of alkoxysilane, the problems of the invention are solved by sequentially performing the following steps.
- [0121] When the method is specifically described, a silicon pulverization work is first conducted in a wet type manner without contacting the surface of silicon with air in a liquid environment until the size of particles becomes from 30  $\mu\text{m}$  to 100  $\mu\text{m}$ , and then a liquid suspension to be produced is directly used as a solvent in a synthesis process of alkoxysilane. The prepared liquid suspension is continuously supplied to a reactor while the synthesis process is conducted.



- [0122] In order to ensure that a continuous and stable reaction is conducted, the amount of liquid suspension of silicon supplied to the reactor is allowed to be the same as the amount of silicon reacted while the reaction is conducted, and determined by calculating the amount of alkoxysilane synthesized, and a numerical formula for the calculation is the same as the following Equation 1.
- [0123]
- [0124] [Equation 1]
- [0125]  $m_{Si} = k_1 \cdot m_{TES} + k_2 \cdot m_{TEOS}$
- [0126]
- [0127] Here,  $m_{TES}$  is a mass of triethoxysilane,  $m_{TEOS}$  is a mass of tetraethoxysilane prepared as a result of direct reaction for a unit time, and coefficients  $k_1$  and  $k_2$  are a molar ratio (coefficient) of silicon consumed during a synthesis process of triethoxysilane and tetra-ethoxysilane, respectively.
- [0128] In order to prevent the decrease in reactivity caused by accumulation of impurities in a reaction environment, impurities accumulated from the reactor are removed by continuously discharging the liquid suspension from the reactor to conduct an additional bleeding work, and at this time, a shortage is allowed to be replenished by continuously supplying the reactor with the solvent in a liquid suspension state in the same amount as the discharged amount.
- [0129] Even when the length of silicon piece is 20 mm or more before the pulverization, the established object may be achieved.
- [0130] Even when the mass ratio of silicon to the solvent mass is from 1:2 to 2:1, the established object may be achieved.
- [0131] While silicon is pulverized in a solvent environment, the established object is achieved even when a necessary amount of a catalyst is directly introduced into the silicon material.
- [0132] In order to stably maintain the ratio of the silicon, the solvent, and the catalyst before supplying the reactor with the liquid suspension in a measured and predetermined amount, the established object may be achieved even when the reactor is continuously stirred.
- [0133] When the solvent is discharged along with the impurity components produced during the reaction process through a ceramic membrane filter mounted in the main body of the reactor, the established object may also be achieved.
- [0134] When the size of pores in the ceramic membrane is set in a range from 1  $\mu\text{m}$  to 10  $\mu\text{m}$ , the established object may be achieved.
- [0135] Even when the amounts of silicon, solvent and catalyst in the reaction environment throughout the overall process of the synthesis of alkoxysilane are maintained at a predetermined level, the established object may be achieved.

- [0136] When unreacted ethyl alcohol and an azeotropic mixture of triethoxysilane and ethyl alcohol are continuously removed under the atmospheric pressure from a reaction product in the condensation process of a target product, the established object may be achieved.
- [0137] When a disproportionation reaction of triethoxysilane is conducted at a temperature from 0°C to 50°C by using sodium ethoxide directly prepared immediately before the process as a catalyst, the established object may be achieved.
- [0138] Monosilane is purified by a method of adsorbing impurities in monosilane by using triethoxysilane at a temperature of -140°C or less, and at this time, when monosilane is supplied to an adsorbent in a liquid phase and the purification process is performed in the direct flow mode, the established object may be achieved.
- [0139] In addition, when ethyl alcohol and an azeotropic mixture of ethyl alcohol and triethoxysilane formed from the reaction product are allowed to be continuously recycled to the reactor for synthesis of triethoxysilane, the object may be preferably achieved.
- [0140] When the azeotropic mixture of ethyl alcohol and triethoxysilane is allowed to be supplied from the bottom side of the reactor, the object may be preferably achieved. Thereafter, triethoxysilane produced from the reaction product is purified by a method such as the multi-stage distillation well known in the related art, and then through a catalytic disproportionation reaction of the synthesis process of monosilane, the object may be preferably achieved.
- [0141] When sodium ethoxide is directly prepared through a reaction of metallic sodium with anhydrous ethyl alcohol in an environment of an inert gas immediately before the catalytic disproportionation reaction in the synthesis process of monosilane, and then used as a catalyst, the object may be preferably achieved. At this time, the reaction is performed as the following Reaction Equation 1.
- [0142]
- [0143] [Reaction Equation 1]
- [0144]  $C_2H_5OH + Na = C_2H_5ONa + 1/2H_2$
- [0145]
- [0146] When the anhydrous ethyl alcohol is reacted in an amount excess of the stoichiometric amount by 2 to 5 times, the object may be preferably achieved.
- [0147] When tetraethoxysilane is added to a solution of sodium ethoxide produced in the anhydrous ethyl alcohol, the object may be preferably achieved.
- [0148] When ethyl alcohol is distilled from the solution, the object may be preferably achieved.
- [0149] When sodium ethoxide is supplied to a synthesis reactor of monosilane in which a mass ratio of sodium ethoxide dissolved in tetraethoxysilane is 1:100 to 1:2, the object may be preferably achieved.

- [0150] When triethoxysilane is supplied to the synthesis reactor of monosilane, in which triethoxysilane is continuously supplied at a rate which ensures that the concentration of triethoxysilane in the reactant may be constantly maintained, the object may be preferably achieved.
- [0151] When monosilane gas is continuously discharged from the upper portion of the reactor and condensed in a collection vessel, the object may be preferably achieved.
- [0152] When monosilane is transferred to a chilled adsorbent in a liquid phase, the object may be preferably achieved.
- [0153] When a portion of tetraethoxysilane, in which the sodium ethoxide catalyst is dissolved, is discharged from the bottom of the reactor, the object may be preferably achieved.
- [0154] When tetraethoxysilane is separated from the solution and distillation is performed until the sodium ethoxide reaches the concentration of the solution supplied, the object may be preferably achieved.
- [0155] When a portion of the sodium ethoxide solution in the tetraethoxysilane is allowed to be recycled to the reactor, the object may be preferably achieved.
- [0156] When 5% to 50% of the amount of the catalyst solution is replaced as much as an amount of the catalyst solution of sodium ethoxide, the object may be preferably achieved.
- [0157] Collecting tetraethoxysilane obtained in each process of the present invention, removing impurities, then first using tetraethoxysilane for drying ethyl alcohol, and then using tetraethoxysilane in a complete hydrolysis for preparation of high-purity silicon dioxide (silica) and ethyl alcohol may also be additionally included in the preferred method of the present invention.
- [0158] In the preparation method of the present invention, the physical basis of the proposed technical solution to the activation work of the reagent is that the initial pulverization of silicon is performed in a solvent environment, not in atmosphere, as in [26] on the analogue and the methods close thereto (see [1] to [25]), and the method of the prototype known in the art and the methods close thereto, and in this case, the oxidation layer ( $\text{SiO}_2$ ) may be naturally prevented from being produced on the surface of metal silicon when silicon particle is pulverized and then in contact with oxygen in atmosphere. The oxidation reaction may take place at any temperature including room temperature, and is regardless of the chemical purity of silicon. That is, when the pulverization work of silicon is performed in atmosphere by using the methods [1] to [26] on the analogue and the prototype method, or a pulverized silicon raw material is generally allowed to be in contact with a specified environment at any step, the oxidation reaction takes place, and thus the initial reaction induction time is essentially generated during the synthesis reaction of triethoxysilane, thereby prolonging the

process time and decreasing productivity. Further, thin silicon particle has a strong moisture adsorbing capacity and thus tends to adsorb moisture from the ambient environment. When moisture is introduced into the reaction environment, the feasibility of a side reaction is sharply increased and a main reaction is suppressed.

[0159] On the contrary, when a natural oxide and moisture are present on the surface of pulverized silicon particle, there are many difficulties in conducting a technical process using silicon and alcohol. Examples thereof include one referred to as "induction period" of the reaction; a need to heat a mixture of pulverized silicon and the catalyst according to [1]; a incomplete reaction in which the production of unreacted silicon takes place; a need to additionally supply a catalyst in the form of a halide according to [1], or a need to feedback a mixture, in which components are supplemented, to a reaction volume according to [26], and as a result, complication of technology and apparatus equipment, and the like.

[0160] Since the pulverization of silicon is conducted in a solvent environment in the method proposed in the present invention, silicon particle prepared as a result is not in contact with air and oxide is not generated, and subsequently, an activated surface which may be used in a main chemical reaction appropriate for the use thereof is formed, and thus it is possible to eliminate major disadvantages of the prototype and the aforementioned known methods. According to the technical solution in the present invention as described, an activated surface, which is not covered with oxide, is produced and a preparation to participate in the chemical reaction is completed, and the surface of the initial silicon particle is activated through a major reagent of the technical process.

[0161] Further, the size of particles specified in the method proposed in the present invention is smaller than those of the analogue [26] and the prototype by maximally 10 times, and thus is helpful in significantly decreasing the induction period, thereby increasing the contact area between major reagents. However, when silicon is pulverized as in the method proposed in the analogue [26] or the prototype, that is, silicon is pulverized in atmosphere, the induction period is increased and other negative characteristics of the known methods are increased. On the surface of silicon thus minutely pulverized, a natural oxide is produced, and when the particle size of silicon even in the same amount is decreased, the total surface area is sharply increased. The other major disadvantages of [26] are that it is necessary to replenish a reaction mixture several times by adding a new reagent to unreacted silicon, and thus it is not only necessary to periodically remove a precipitate produced as components in the liquid suspension are settled down but also necessary for the component to be left to stand for a long time. Nevertheless, the method of the present invention rules out the problems against which these measures need to be taken due to the continuous process. In

addition, in the method proposed in the present invention, it is preferred that a liquid suspension containing a precipitate is filtered by using a ceramic membrane filter not to remove reactive silicon particle from the reactor, and it is necessary to maintain the amount of the liquid suspension of silicon supplied to the reactor to be the same as the amount of already reacted silicon, which may be calculated by using the amount of synthesized alkoxy silane. Furthermore, it is necessary to remove impurities which are discharged from the reactor and cause decrease in reactivity by continuously discharging the solvent at the exit of the reactor in the same amount as that of the solvent in a state of liquid suspension, which is supplied to the reactor.

[0162] Further, according to the present invention, when particles having a size of 20  $\mu\text{m}$  or more are selected before the pulverization thereof, it is possible to prevent a considerable amount of silicon particle with an oxide present on the surface thereof from being introduced into a reaction mixture.

[0163] When a catalyst is added to the silicon material immediately before the pulverization thereof, the following characteristics are shown: First, it is possible to simultaneously pulverize these two materials (silicon and catalyst) into the same size. Second, the two materials are uniformly mixed in a liquid suspension containing a solvent and pulverized in the above-described environment. The size of pores in the ceramic membrane is 1  $\mu\text{m}$  to 10  $\mu\text{m}$ . Pores having a size less than 1  $\mu\text{m}$  make it difficult to perform the filtering process and pores having a size more than 10  $\mu\text{m}$  allow a silicon particle having reactivity to pass through the membrane, thereby increasing the loss of silicon. If the size of silicon particle is 30  $\mu\text{m}$  to 100  $\mu\text{m}$ , a preferred pore size of the ceramic membrane is 5  $\mu\text{m}$ , and the total loss of silicon is 0.5% or less.

[0164] The method suggested as an embodiment according to the present invention is implemented as follows.

[0165] For example, the initial silicon such as metal silicon having a purity from 98% to 99% is pulverized by using a hammer crusher (maximum particle size 1 mm). Thereafter, the metal silicon is crushed by using a general planetary mill according to the proposed method until the particle size is 30  $\mu\text{m}$  to 100  $\mu\text{m}$ . To the operating volume of the crusher, a solvent such as, for example, THERMINOL 66 or other polyaromatic oils is added beforehand, and then silicon is pulverized in a solvent environment as described above. Thereafter, for reaction of silicon with alcohol, a liquid suspension prepared by using a metering pump is continuously supplied to the reactor. At this time, the solvent is not separated from silicon powder. Simultaneously, a contact material is produced in predetermined amount and components in the reactor. In the main process reaction, known anhydrous ethyl alcohol or methyl alcohol is used. For example, a known copper-containing catalyst such as copper (I) chloride is also used. The technical process is performed in an environment of a solvent having a high

boiling point as previously mentioned, and as a solvent used at this time, THERMINOL59, THERMINOL60, THERMINOL 66, DOWTHERM HT, MARLOTHERM S, MARLOTHERM, other polyaromatic oils and the like may be used, and the temperature range is 180°C to 260°C as in the methods of [1] and [26]. In other words, the core of the technical process is that a liquid suspension (for example, silicon to which a pulverized copper (I) chloride catalyst is added in a solvent environment such as THERMINOL 66) is supplied to the reaction volume (according to a desired method among the known methods) and heated to 180°C to 260°C while being vigorously stirred, and then alcohol such as, for example, ethanol is added thereto. It is preferred that silicon in a state of a liquid suspension containing a solvent is supplied to the reactor and the ratio thereof is 1:2 by mass ratio, and silicon is continuously supplied in consideration of the consumed amount as a result of reaction with ethanol according to the proposed method. That is, silicon is supplied at a rate of the amount consumed as a result of reaction. At this time, the amount of silicon consumed per unit time is calculated according to Equation 1 which is a mass balance equation of the reaction.

[0166] [Equation 1]

[0167]  $m_{Si} = k_1 \cdot m_{TES} + k_2 \cdot m_{TEOS}$

[0168] Here,  $m_{TES}$  is a mass of triethoxysilane,  $m_{TEOS}$  is a mass of tetraethoxysilane prepared as a result of direct reaction for a unit time, and coefficients  $k_1$  and  $k_2$  are an amount (molar ratio) of silicon consumed during a synthesis of tri-ethoxysilane and tetra-ethoxysilane, respectively.

[0169] According to the method thus proposed in the present invention, in order to remove impurities accumulated in the reaction liquid suspension, the solvent is continuously discharged from the reactor through a ceramic membrane filter, an additional solvent and raw material silicon are continuously supplied in order to replenish the amount discharged at this time, and the amount is allowed to be the same as the amount of a pure solvent in the form of liquid suspension, which is supplied to the reactor. By doing this, a reaction product is continuously produced from the reactor.

[0170] In the condensation process of a target reaction product in the atmospheric state, unreacted ethyl alcohol and an azeotropic mixture of ethyl alcohol and triethoxysilane are removed from the reaction product. Thereafter, triethoxysilane obtained through the distillation process from the reaction product is purified by one of the known methods, and then transferred to a catalytic disproportionation process for preparation of monosilane gas. At this time, sodium ethoxide directly prepared immediately before the disproportionation reaction process is used as a catalyst. The catalyst, which is directly prepared in a state of inert gas immediately before the process in the disproportionation reaction, not only serves a positive role in the synthesis rate and se-

lectivity of monosilane during the disproportionation reaction but also minimizes the influence of oxygen and moisture in an ambient environment on the surface of sodium ethoxide particle. When tetraethoxysilane is added beforehand to the catalyst solution, the influence of moisture in atmosphere may be blocked by hydrophobicity of tetraethoxysilane.

[0171] In order to prepare the catalyst, sodium metal having a purity of 99.9% or more is slowly dissolved in anhydrous ethyl alcohol in an amount larger than the stoichiometric amount by 2 to 5 times. Sodium is completely dissolved and then tetraethoxysilane is added to the solution, the amount is set such that the mass ratio of sodium ethoxide dissolved in tetraethoxysilane is 1:100 to 1:2, and thereafter, ethyl alcohol is separated from the solution, and a solution of sodium ethoxide in tetraethoxysilane is directly supplied to a disproportionation reactor for synthesis of monosilane.

[0172] As a result of the disproportionation reaction of triethoxysilane, additional tetraethoxysilane produced and a portion of the catalyst are continuously separated from the bottom portion of the reactor, and separated by a method of distilling tetraethoxysilane from the solution. The concentration of tetraethoxysilane is regulated to a value set to return tetraethoxysilane to the reactor through distillation. 5% to 50% of the amount of the sodium ethoxide solution is replaced with a catalyst solution directly prepared immediately before the disproportionation process. Monosilane produced from the reactor is continuously collected, and then purified in a liquid environment. When trialkoxysilane is used as an adsorbent, the content of impurities may be further decreased by purifying monosilane at a lower temperature, thereby increasing adsorbing capacity.

[0173] Hereinafter, the present invention will be described in detail with reference to Examples.

[0174] The following Examples are composed of the contents that verify the advantages of the corresponding examples through comparison with known analogous methods performed according to the same experimental conditions explicitly described in Examples of various methods (Examples 2 to 4) proposed for preparation of triethoxysilane and Example 1.

[0175] All the experiments were conducted in the equipment specially manufactured for synthesis of alkoxy silane. The synthesis of triethoxysilane was conducted in a reactor equipped with a quad blade stirrer, which could electrically heat the reaction volume with an operating volume of 9 L and could regulate the stirring rate within a range from 300 rpm to 1500 rpm. The procedure of the synthesis process was controlled by directly taking a sample from a product produced from the reactor, analyzing the sample using the gas chromatography Agilent GC7890A, and then using the apparatus.

- [0176] Examples 5 and 6 show the selection of the optimum range of silicon particle size during the synthesis of triethoxysilane.
- [0177] Examples 7 to 10 show the selection of optimum conditions for preparation of monosilane.
- [0178] In Example 11, the continuous mode that enables a continuous preparation during the synthesis of monosilane was implemented.
- [0179]
- [0180] Example 1
- [0181] Silicon metal was pulverized in atmosphere with a planetary mill until the particle size thereof became 30  $\mu\text{m}$  to 100  $\mu\text{m}$ . 3.3 kg of pulverized silicon, 6.6 kg of a solvent with a trademark of THERMINOL 66 and 0.2 kg of the catalyst CuCl were put into a reactor. The contact material was heated up to 242+2°C while a stirrer is continuously operated at a rate of 850 rpm, and dried alcohol - ethanol began to be supplied to the reactor at a maximum rate of 600 mL/h by using a metering pump (digital dosing pump) GRUNDFOS DME 60-10 AR. From the instant when a liquid product was produced from the reactor, the sample was collected every 30 minutes. When observing a sample analysis using gas chromatography Agilent GC7890A, the synthesis reaction of triethoxysilane taking place as a result of reaction of silicon metal with ethyl alcohol began to take place after 150 minutes as a reaction initial induction period after alcohol is supplied thereto, and the intensity of the reaction was gradually increased (see the curve of Example 1 in FIG. 1). Thereafter, the reaction was terminated 500 minutes after supplying alcohol. 1435 g of triethoxysilane and 614 g of tetraethoxysilane were obtained for 500 minutes. The selectivity of triethoxysilane was 70%.
- [0182]
- [0183] Example 2
- [0184] An experiment was conducted the same as in Examples 1, but the preparation environment of the reaction reagent was completely different. According to the proposed method, silicon metal was continuously pulverized in an environment of 6.6 kg of the solvent THERMINOL 66, and the amount was 3.3 kg. In the pulverization process, 0.2 kg of copper (I) chloride was introduced into a liquid suspension. Alcohol was supplied to the reactor, and then the synthesis reaction began after 10 minutes of the initial reaction induction period and the reaction rate was increased for initial 60 minutes (see the curve of Example 2 in FIG. 1). After 180 minutes, the synthesis reaction rate of triethoxysilane began to be decreased, and the reaction was completely terminated 260 minutes after supplying alcohol. 1635 g of triethoxysilane and 105 g of tetraethoxysilane were obtained. The selectivity of triethoxysilane reached 94%.
- [0185]



[0186] Example 3

[0187] An experiment was conducted the same as in Example 2, but there is a significant difference in that a continuous process was performed by continuously supplying a reactor with silicon in a state of liquid suspension mixed with a solvent according to the proposed method, and the ratio of mass consumed during the reaction with ethyl alcohol was 1:2. That is, during the synthesis process of alkoxysilane, silicon in a state of liquid suspension was supplied thereto at a rate suitable for the consumption rate of silicon according to the reaction. The amount of silicon consumed to unit time was calculated according to the mass balance equation of the reaction of the following Equation 1.

[0188]

[0189] [Equation 1]

[0190]  $m_{Si} = k_1 \cdot m_{TES} + k_2 \cdot m_{TEOS}$

[0191]

[0192] Here,  $m_{TES}$  is a mass of triethoxysilane,  $m_{TEOS}$  is a mass of tetraethoxysilane obtained as a result of direct reaction for a unit time, and coefficients  $k_1$  and  $k_2$  are an amount (molar ratio) of silicon consumed during a synthesis of tri-ethoxysilane and tetra-ethoxysilane, respectively. Here,  $k_1 = 0.171$  and  $k_2 = 0.135$ , and these were experimentally verified.

[0193] Alcohol was supplied to the reactor, and then the synthesis reaction began after 10 minutes of the initial reaction induction period and the reaction rate was increased for initial 90 minutes, and then stabilized when the triethoxysilane level reached 400 g/h (see the curve of Example 3 in FIG. 1). The reaction was forcefully stopped because a large amount of bubbles began to be generated on the reaction product 250 minutes after supplying alcohol. A mixture of 290 g of silicon and 580 g of the solvent THERMINOL 66 in a state of liquid suspension was continuously supplied to the reactor. The solvent was additionally supplied thereto, and then the amount of the contact material in the reactor was increased, which was responsible for the generation of bubbles. For 250 minutes of the reaction process, 1600 g of triethoxysilane and 120 g of tetraethoxysilane were obtained. The selectivity of triethoxysilane was 93%.

[0194]

[0195] Example 4

[0196] An experiment was conducted the same as in Example 3, but there is fundamental difference in that impurities accumulated in a reaction environment were continuously purified by continuously discharging the solvent from the reaction volume through a ceramic membrane filter amounted in the main body of the reactor according to the proposed method. The solvent in which impurities were dissolved was collected in a collection vessel, regenerated, and then reused. A vacuum of 10 mbar was formed on

the back of the membrane to conduct filtration through a ceramic membrane filter. The solvent was continuously discharged through the ceramic membrane from the reactor, and the amount was 2 mSi and determined according the Mathematic Equation 1, and corresponds to the amount of the solvent supplied to the reactor in a state of liquid suspension. By doing this, the components of the contact material and the level of the contact material in the reactor volume may be constantly maintained. The components of the contact material were regulated with the amount of the sample collected, and the level of the contact material in the reactor volume was visually regulated through a test window. The synthesis reaction began 10 minutes of the initial reaction induction period after alcohol was supplied to the reactor, and the reaction rate was rapidly increased for initial 60 minutes and slowly increased until 120 minutes, and then the rate was stabilized at a triethoxysilane level from 420 g/h to 450 g/h (see the curve of Example 4 in FIG. 1). 3380 g of triethoxysilane and 141 g of tetraethoxysilane were obtained while a liquid suspension composed of 600 g of silicon and 1200 g of the solvent THERMINOL 66 was continuously supplied to the reactor for 500 minutes. The selectivity of triethoxysilane reached 96%.

[0197] The results according to Examples 1 to 4 are shown in the following Table 1.

[0198]

[0199]

[Table 1]

Examp le	Silicon Pul- verization method	Reaction starts after supplying alcohol (induction period), (min)	Work			Result		
			Supply		Obtain	Amoun t of tri- ethoxys ilane, (g)	Amou nt of tetraet hoxysi lane, (g)	Selectivit y of tri- ethoxysila ne, (%)
			Silicon, (g)	Solvent , (g)	Solvent , (g)			
1	Dry type	150	-	-	-	1435	614	70
2	Wet type in a solvent en- vironment	10	-	-	-	1635	105	93
3	Wet type in a solvent en- vironment	9	290	580	-	1600	120	94
4	Wet type in a solvent en- vironment	10	600	1200	1200	3380	141	96

[0200]

[0201] Example 5

[0202] An experiment was conducted the same as in Example 4, but there is a fundamental difference in that silicon metal has a particle size of 100  $\mu\text{m}$  or more.

[0203]

[0204] Example 6

[0205] An experiment was conducted the same as in Example 4, but there is a fundamental difference in that silicon metal has a particle size of 30  $\mu\text{m}$  or less

[0206] The productivity and selectivity of the technical process are indicated and shown in the following Table 2 by comparing the indices obtained in Example 4 were compared with those in Examples 5 and 6.

[0207]

[Table 2]

	Example 5	Example 4	Example 6
Process parameter	Particle size of 100 $\mu\text{m}$ or more	Particle size from 30 $\mu\text{m}$ to 100 $\mu\text{m}$	Particle size of 30 $\mu\text{m}$ or less
Process production capacity	47%	100%	105%
Selectivity of triethoxysilane	92%	97%	93%
Loss of silicon during filtration	1% or less	1% or less	30% or more

[0208] Example 7

[0209] Preparation was performed according to Example 4, and then 875 g of triethoxysilane purified until the purity thereof became 99.999% was put into a reactor having a volume of 5 L. In the reactor, a solution of sodium ethoxide in tetraethoxysilane was put beforehand. The catalyst solution contained 68 g of commercially available sodium ethoxide manufactured by Sigma-Aldrich and 680 g of tetraethoxysilane. The temperature of the reaction material was 50°C. As a result of a catalytic disproportionation of triethoxysilane, monosilane gas prepared was discharged from the upper portion of the reactor and condensed with liquid nitrogen in a collection vessel. The sample was collected from the reactor every 10 minutes, and then the components of the reaction material were analyzed by performing gas chromatography. The conversion ratio of triethoxysilane into monosilane after 150 minutes was 95%.

[0210]

[0211] Example 8

[0212] An experiment was conducted the same as in Example 7, but there is a fundamental difference in that sodium ethoxide directly prepared in an inert gas environment was used as a catalyst immediately before the synthesis process. When sodium metal having a purity of 99.9% or less was used during the preparation of the catalyst, sodium metal was slowly dissolved in anhydrous ethyl alcohol and collected in an amount than the stoichiometric amount by 5 times. Sodium was completely dissolved in the solution and then 680 g of tetraethoxysilane was added thereto, and thereafter, ethyl alcohol was separated from the solution and the solution of sodium ethoxide in tetraethoxysilane directly prepared immediately after the separation was introduced into the reactor for synthesis of monosilane. The peak of triethoxysilane disappeared 30 minutes after performing chromatography spectra, and thus it was verified that the conversion ratio of triethoxysilane into monosilane was 100%.

[0213]

[0214] Example 9

[0215] An experiment was conducted the same as in Example 8, but there is fundamental difference in that the synthesis process of monosilane was conducted at a temperature of 30°C. After 30 minutes, the conversion ratio of triethoxysilane into monosilane reached 99% or more.

[0216]

[0217] Example 10

[0218] An experiment was conducted the same as in Example 8, but there is a fundamental difference in that the synthesis process was conducted at a temperature of 0°C, which ensures liquid nitrogen on the ventilation wall of the reactor. After 30 minutes, the conversion ratio of triethoxysilane into monosilane was reached 95% or more.

[0219]

[0220] The results of Examples 7 to 10 are shown in the following Table 3.

[0221]

[0222] [Table 3]

Example	Catalyst	Temperature (° C)	Reaction duration (min)	Conversion ratio of triethoxysilane
7	Sodium ethoxide from Sigma-Aldrich	50	150	95%
8	Sodium ethoxide as prepared	50	30	100%
9	Sodium ethoxide as prepared	30	30	> 99%
10	Sodium ethoxide as prepared	0	90	> 95%

[0223] Example 11

[0224] An experiment was performed the same as in Example 8, but triethoxysilane was supplied into the reactor at a constant rate of 2,000 mL/h by using a metering pump (digital dosing pump) GRUNDFOS DME 60-10 AR. A reactor sample was tested by using gas chromatography, and as a result, the content of triethoxysilane in the reaction material was maintained constantly in a range within  $\pm 5\%$ . Monosilane gas was continuously collected in a collection vessel, and condensed on the wall of the collection vessel cooled with liquid nitrogen. At the exit of the reactor, monosilane gas was allowed to pass through an adsorption trap, and thus ethoxysilane vapor is separated therefrom. Triethoxysilane cooled to -140°C or less was transferred to a place in which monosilane in a liquid phase, which had been in the collection vessel, was purified by using an adsorbent. The contact time with the adsorbent was 15 minutes. Thereafter,

monosilane was separated from triethoxysilane through the phase separation at a temperature of  $-80^{\circ}\text{C}$ .

[0225] As a result of the above-described experiments through the Examples, the following results were confirmed from FIG. 1 and Tables 1 to 3.

[0226] a) When silicon is pulverized in atmosphere (dry type, and see Example 1 and the curve of Example 1 in FIG. 1), as in [26] and [2 to 25], an induction period corresponding to maximally 150 minutes in Example 1 was inevitably generated, and besides, the selectivity of triethoxysilane failed to exceed 74% and the reaction was completely terminated over 260 minutes from the instant when anhydrous ethyl alcohol was supplied to the reactor, and thus there are restrictions on the duration of the reaction.

[0227] b) In the case of a proposed method (wet type, see Example 2 and the curve of Example 2 in FIG. 1) including preparing silicon in a wet type manner, in other words, when silicon is pulverized in a liquid environment without contact with the atmosphere and the liquid suspension is applied immediately as solvent for the synthesis of alkoxy silane, the induction period is decreased by minimally 15 times and the selectivity of triethoxysilane is ensured at the level of maximally 93%, unlike Example 1, that is, the analogues [2 to 25] and the prototype [26].

[0228] c) When the raw material is prepared in a wet type manner, that is, silicon is pulverized according to a method (wet type, see Example 3 and the curve of Example 3 in FIG. 1) proposing two characteristics that silicon is pulverized into powder in a solvent environment and the activation of the continuous process is ensured by continuously supplying the reactor with a mixture of silicon and the solvent according to the amount of Equation 1, the induction period is decreased by 15 times or more, and the process selectivity of triethoxysilane is increased to 94%. The preparation process of Example 3 was intentionally left to stand (see the curve of Example 3 in FIG. 1) because the rate at the instant when the reaction was intentionally left to stand, not when the reaction was terminated, was high enough to be at the level of maximally 400 g/h. The reason why the process was left to stand was described above, and was completely ruled out in Example 4.

[0229] d) When three characteristics of the invention explicitly described in the technical solution (claim 1) of the preparation method proposed according to the present invention are simultaneously applied, that is, when implementing a process of pulverizing silicon in a liquid environment, continuously supplying a reactor with a predetermined amount of the prepared liquid suspension which is explicitly described in the method of the present invention, and removing impurities accumulated from the reactor by continuously discharging the solvent, in an amount similar to the amount of the solvent additionally supplied to the reactor as the component of the initial liquid

suspension, from the reactor while maintaining the amount of the solvent supplied and performing purification, the results as shown in Example 4, Table 1 and the curve of Example 4 in FIG. 1 are obtained.

[0230] The results are summarized as follows.

[0231] - The induction period is decreased by minimally 15 times or more.

[0232] - The process selectivity of triethoxysilane which is a main product is ensured at the 96% level.

[0233] - A synthesis process may be performed by a continuous process that maintains a high and stable reaction rate.

[0234] e) As can be seen from the results explicitly described in Table 2, a particle size from 30  $\mu\text{m}$  to 100  $\mu\text{m}$  is optimal for the triethoxysilane synthesis process according to the method of the present invention.

[0235] f) When the experiment is performed with the catalyst as prepared under the conditions in Example 4, the following effects are ensured as can be seen in Examples 7 to 10.

[0236] - The productivity of the technical process is increased by decreasing the contact time with the reagent by 5 times or more.

[0237] - The conversion ratio of triethoxysilane into monosilane reaches the maximum value.

[0238] g) Finally, when all the characteristics of the invention according to the method proposed in the present invention are simultaneously implemented as in Example 11, it is possible to conduct the synthesis reaction of monosilane composed of a continuous process that maintains a high and stable synthesis rate.

[0239] As described above, the technical solutions and embodiments, which are proposed in the present invention, are essential and sufficient conditions in solving major technical problems of the invention. Conditions explicitly described as preferred technology in the embodiments implement the technical solution according to the proposed method more easily and preferably, and optimize performance conditions. The preparation method proposed according to the present invention has excellent work performance, the fact was already verified through the experiments, and when the known technical means are appropriately used, feasibility is sufficient under laboratory conditions as well as in industrial application.

[0240] Furthermore, there is an effect that may simplify and improve the process of preparing monosilane while ensuring sustainability, operability, productivity and stability.

## Claims

[Claim 1]

A method for preparing monosilane, which comprises a pulverization work in a solvent environment for preventing an oxide film from being produced when a raw material silicon is prepared, a reaction of anhydrous ethyl alcohol with silicon which is pulverized in a liquid environment, by using a copper-based catalyst in a solvent environment heated up to 160°C to 300°C, an activation of a reagent caused by removing impurities, a replenishment of an amount of silicon consumed, a separation of a reaction product, a purification of triethoxysilane and a catalytic disproportionation reaction of triethoxysilane, which produces monosilane gas, and a purification of monosilane, the method comprising: the following synthesis process steps of:

(a) conducting a wet pulverization work in a liquid environment until silicon particles have a size from 30 μm to 100 μm and directly using the liquid as a solvent in a subsequent synthesis process of alkoxy silane;

(b) continuously supplying a reactor with a liquid suspension obtained while the synthesis process is conducted, wherein an amount of a liquid suspension of silicon supplied to the reactor is allowed to be the same as an amount of silicon reacted in order to ensure that a continuous and stable reaction is conducted and the amount of silicon reacted is calculated from an amount of alkoxy silane synthesized according to the following Equation 1,

[Equation 1]

$$m_{\text{Si}} = k_1 \cdot m_{\text{TES}} + k_2 \cdot m_{\text{TEOS}}$$

here,  $m_{\text{TES}}$  is a mass of triethoxysilane,  $m_{\text{TEOS}}$  is a mass of tetraethoxysilane prepared as a result of direct reaction for a unit time, and coefficients  $k_1$  and  $k_2$  are a molar ratio of silicon consumed during a synthesis process of tri-ethoxysilane and tetra-ethoxysilane, respectively;

(c) removing impurities accumulated in a state of liquid suspension from the reactor by continuously discharging the solvent in an amount which is the same as that of the solvent supplied to the reactor;

(d) directly removing an azeotropic mixture of unreacted ethyl alcohol and triethoxysilane during a condensation of a target product under the atmospheric pressure;

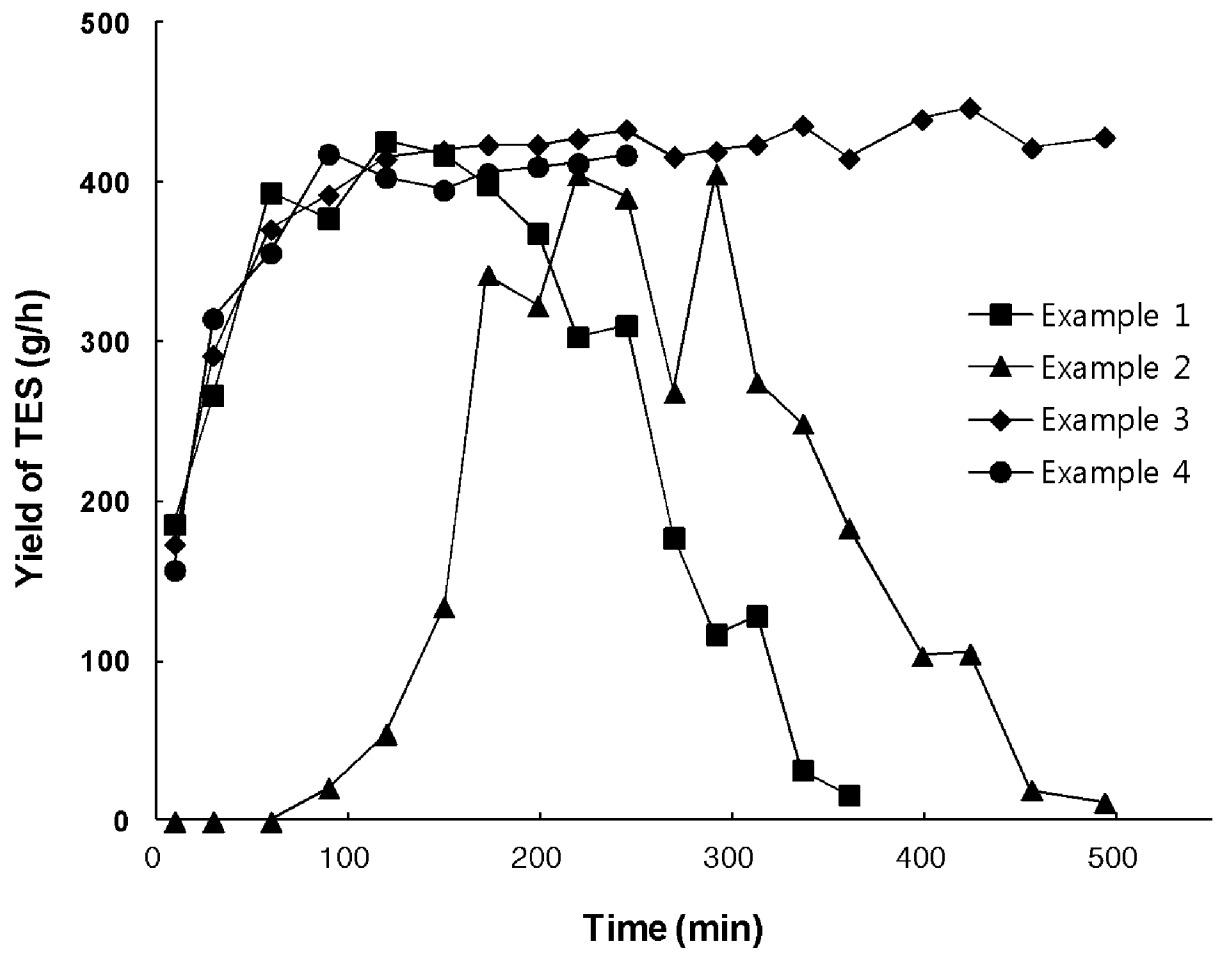


- (e) purifying triethoxysilane produced;
- (f) performing a disproportionation process of triethoxysilane at a temperature from 0°C to 50°C by using sodium ethoxide synthesized and prepared beforehand as a catalyst immediately before the disproportionation process step; and
- (g) purifying monosilane by adsorbing impurities in monosilane by using triethoxysilane at a temperature of 140°C or less.

- [Claim 2] The method of claim 1, wherein a size of silicon piece is 20 mm or less before the pulverization.
- [Claim 3] The method of claim 1, wherein a ratio of a weight of silicon to a weight of the solvent is from 1:2 to 2:1.
- [Claim 4] The method of claim 1, wherein a catalyst is directly introduced into silicon during the pulverization process in a solvent environment.
- [Claim 5] The method of claim 1, wherein in order to stably maintain a ratio of amount of the silicon, the solvent, and the catalyst before the liquid suspension is weighed and supplied to the reactor, the reactor is continuously stirred.
- [Claim 6] The method of claim 1, wherein when the solvent, in which impurities are dissolved during the reaction, is discharged from the reactor through a ceramic membrane filter mounted in a main body of the reactor is used.
- [Claim 7] The method of claim 6, wherein a size of pores in the ceramic membrane filter is selected in a range from 1 μm to 10 μm.
- [Claim 8] The method of claim 1, wherein the amounts of the silicon, the solvent and the catalyst in the reaction environment are maintained at a predetermined level throughout the overall process of the synthesis of alkoxy silane.
- [Claim 9] The method of claim 1, wherein ethyl alcohol and an azeotropic mixture of ethyl alcohol and triethoxysilane formed from the reaction product are continuously recycled and supplied to the reactor for synthesis of triethoxysilane.
- [Claim 10] The method of claim 9, wherein ethyl alcohol and the azeotropic mixture of ethyl alcohol and triethoxysilane are supplied from a bottom side of the reactor.
- [Claim 11] The method of claim 1, wherein sodium ethoxide is directly prepared through a reaction of sodium metal with anhydrous ethyl alcohol in an environment of an inert gas immediately before the synthesis process of monosilane, and then directly used as a catalyst.

- [Claim 12] The method of claim 11, wherein the anhydrous ethyl alcohol is reacted in an amount excess of the stoichiometric amount by 2 to 5 times.
- [Claim 13] The method of claim 11 or 12, wherein tetraethoxysilane is added to a solution of sodium ethoxide produced in the anhydrous ethyl alcohol.
- [Claim 14] The method of claim 13, wherein ethyl alcohol is distilled from the solution.
- [Claim 15] The method of claim 1, wherein sodium ethoxide is supplied to a synthesis reactor of monosilane in which a mass ratio of sodium ethoxide dissolved in tetraethoxysilane is 1:100 to .
- [Claim 16] The method of claim 1, wherein triethoxysilane is supplied to the synthesis reactor of monosilane, in which triethoxysilane is continuously supplied at a rate which ensures that a concentration of triethoxysilane in the reactant is capable of being constantly maintained.
- [Claim 17] The method of claim 1, wherein monosilane gas is continuously discharged from the upper portion of the reactor and condensed in a collection vessel.
- [Claim 18] The method of claim 1, wherein monosilane is transferred to a chilled adsorbent in a liquid phase.
- [Claim 19] The method of claim 1, wherein a portion of tetraethoxysilane, in which a sodium ethoxide catalyst is dissolved, is discharged from the bottom of the reactor.
- [Claim 20] The method of claim 19, wherein tetraethoxysilane is separated from the solution and distillation is performed until the sodium ethoxide of claim 15 reaches the concentration of the solution supplied.
- [Claim 21] The method of claim 20, wherein a portion of the sodium ethoxide solution in the tetraethoxysilane is recycled and supplied to the reactor.
- [Claim 22] The method of claim 1, wherein tetraethoxysilane obtained in each process is collected, impurities are removed, then tetraethoxysilane is first used for drying ethyl alcohol, and then tetraethoxysilane is used in a complete hydrolysis for preparation of high-purity silicon dioxide (silica) and ethyl alcohol.

[Fig. 1]



## INTERNATIONAL SEARCH REPORT

International application No.  
**PCT/KR2013/003743****A. CLASSIFICATION OF SUBJECT MATTER****C01B 33/021(2006.01)i, C01B 33/029(2006.01)i, B01J 23/72(2006.01)i**

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

C01B 33/021; C01B 33/04; C07F 7/02; C07F 7/04; B01J 23/72; C01B 33/029

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Korean utility models and applications for utility models

Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

eKOMPASS(KIPO internal) &amp; Keywords: monosilane, alkoxysilane, triethoxysilane, catalyst, alcohol, ethanol, disproportionation

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2615798 B2 (MITSUBISHI KASEI CORP.) 11 March 1997 See claim 1; column 3, lines 32-50; column 4, line 11; column 5, lines 10-12.	1-14, 16-22
A	JP 07-025534 B2 (MITSUBISHI CHEM. IND. LTD.) 22 March 1995 See claim 1; column 3, lines 25-31; column 4, lines 4-7.	1-14, 16-22
A	JP 10-168084 A (TOAGOSEI CO., LTD.) 23 June 1998 See abstract; paragraphs [0009],[0015],[0016],[0024],[0025].	1-14, 16-22
A	US 2012-0226064 A1 (OHNO, HIROMOTO et al.) 06 September 2012 See abstract; paragraphs [0016],[0031],[0032]; claim 1.	1-14, 16-22
A	US 2011-0200513 A1 (OHNO, HIROMOTO et al.) 18 August 2011 See abstract; paragraphs [0016],[0034]; claim 1.	1-14, 16-22

 Further documents are listed in the continuation of Box C. See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same patent family


Date of the actual completion of the international search

09 August 2013 (09.08.2013)

Date of mailing of the international search report

**12 August 2013 (12.08.2013)**

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## INTERNATIONAL SEARCH REPORT

International application No.

**PCT/KR2013/003743****Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.: 15  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:  
The range of the mass ratio of sodium ethoxide dissolved in tetraethoxysilane is not clearly defined in claim 15. Therefore, it is not possible to define the subject matter for which protection is sought for claim 15.
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

Information on patent family members

International application No.

**PCT/KR2013/003743**

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		TW 201034952 A	01/10/2010
		WO 2010-050579 A1	06/05/2010