

This invention relates to the production of silicon hydrides by acid hydrolysis of ternary alloys of silicon.

Silane (or monosilane, or silicon tetrahydride; SiH_4) is mainly used as a silicon vector in the technique of vapour phase depositions. For the production of semiconductors, particularly in the V.L.S.I. (Very Large Scale Integration) technique, deposits of polycrystalline silicon, silica, silicon nitride are made by using silane as the silicon vector.

Thin-layer deposits of polycrystalline silicon, obtained from silane, enable solar cells to be manufactured having an energy efficiency greater than 6%.

On metals, coatings which are resistant to corrosion by acids may be obtained by cracking of silane.

Lastly, silane is capable of being added onto the multiple bonds of unsaturated hydrocarbons to yield organosilanes.

Many methods for synthesising silane have been proposed, but only three seem to have been industrially developed.

The method termed molten salts method consists of reducing a chlorosilane by lithium hydride, at a temperature of the order of 450°C in a molten bath of lithium chloride - potassium chloride. This technique has the advantage of directly producing silane of good purity; however, it has the disadvantage of entailing a high cost price, and of necessitating the handling of molten salts, generally not easy. A variant of this technique was envisaged by Sundermeyer, Glemser *Angew. Chem.* 70, p.625 (1958). It consists in electrolyzing lithium chloride in situ to produce lithium which is converted into hydride by introduction of hydrogen into the reactor. This process has not been worked industrially, mainly because of technological difficulties.

According to the method of reduction of silicon chloride using lithium aluminium hydride, the reaction is performed in the vicinity of ambient temperature in a heavy solvent such as diglyme or tetraglyme. This production process is no longer used because of its much too high cost and because of the deterioration of the solvent which strongly contaminates the silane with hydrocarbons, this

necessitating thorough purification.

The method using hydrolysis of silicon alloys is also known; various binary alloys have been considered such as CaSi , CaSi_2 , MgSi and Mg_2Si . According to E. Wilberg, *Hydrides*, Elsevier N.Y. 1971 p.473, only magnesium silicide of these alloys leads to a possibly advantageous yield. However, acting on this compound gives rates of conversion into silane which vary depending on the operating conditions. It appears that the yield is strongly linked to the size of the magnesium silicide grains, to the rate of introduction of the powder of the compound, to the reaction temperature and to the manner of putting the reagents into contact.

According to a variant of the process, a silane yield of the order of 80% with respect to the silicon is obtained by using ammonium chloride to act upon magnesium silicide in a liquid ammonia medium.

From the publication by F. Fehrer, in *Zeitschrift für anorganische und allgemeine Chemie*, page 208, volume 385, November 1971, the reaction conditions are known adapted to the decomposition of a binary composition: magnesium silicide, to obtain silane. According to these conditions, the use is recommended of a magnesium silicide powder having a granulometry of between 0.3 and 1 mm, introduced as quickly as possible into 20-22% phosphoric acid, the performance of the said reaction being fixed at a decomposition temperature of 50 to 60°C.

The principle of acting upon magnesium silicide has the advantage of relying on simple chemistry and of producing silane the main impurity of which consists of easily removable water.

However, the transposition of magnesium silicide hydrolysis to the industrial scale has two major economic and technical disadvantages. This initial product, of which the preparation requires special equipment and the sole current application is the production of silane, is an expensive product. Furthermore, since the obtaining of good yields depends on the performance of the reaction in the presence of liquid ammonia, it is necessary to work under a pressure of the order of 6 atmospheres, and then to perform a very effective silane/ammonia separation.

In 1956, Chrétien, Freundlich and Deschanvres, during their work on ternary alloys $\text{Ca}_3\text{Al}_6\text{Si}_2$ and $\text{Ca}_2\text{Al}_4\text{Si}_3$ had noted that these acid-sensitive compounds were producing, when attacked by dilute hydrochloric acid, a release of gas spontaneously inflammable in air (silane) (CR Acad. Sciences 6 February 1956 p. 784-5).

This laboratory work, not providing the conditions necessary to implement a profitable process, was not industrially developed.

A simple process has been found, using inexpensive raw materials and producing silicon hydrides with an industrial yield.

Instead of using binary alloys, according to the invention, an industrial ternary alloy represented by the formula Al30-38%, Ca15-25%; Si 35-45% containing at least 20% of alloyed silicon is made to react with an acid selected from hydric acids and orthophosphoric acid at a concentration of between 2N and 6N, by feeding the ternary alloy into the acid in the form of fine powder, of granulometry equal at most to 0.4 mm, the reaction being conducted at a temperature at least equal to 50°C, the metallic powder being fed into the acid at such a rate that the reaction temperature does not exceed 90°C.

The Al/Si/Ca alloys selected are currently available inexpensive foundry alloys. Of the alloys available, the alloys Al 30-38%, Si 35-45%, Ca 15-25% which perform especially well and give very good results, were selected. This type of designed industrial alloy can give one kilo of silane per 10 kg of alloy. In the same conditions another industrial alloy Al 11%, Si 58%, Ca 28%, forming part of the invention, gives 1 kg of silane per 18 kg of alloy.

The manner of addition of the powder and acid has a determining effect on the yield of the alloy. Experiments performed on the Al 33%, Ca 18%; Si 40% alloy in the same conditions showed that 18 kg of alloy are necessary to produce 1 kg of silane when the acid is made to react on the powder; whereas by feeding the powder into the acid 1 kg of silane is produced from only 10 kg of alloy. In the experimental conditions, the alloy powder can be fed onto the stirred acid solution at a rate of 4 to 8 kilogrammes per hour, knowing that a greater delivery increases the reactivity of the system.

Among hydracids, dilute hydrofluoric, hydrochloric and orthophosphoric acids may be selected, at a concentration of between 2N and 6N, preferably about 3N.

The effects of the nature and concentration of the acid on the silane yield of the alloy were studied on the alloy Al 33%, Ca 18%, Si 40%, by making the powder react on the acid, all of the other conditions being otherwise similar. With 3N orthophosphoric acid 1 kg of silane was obtained from 14 kg of alloy, and by the action of 3N hydrochloric acid, only 10 kg of alloy are necessary to produce 1 kg of silane. N hydrochloric acid enables only 1 kg of silane to be obtained by making 125 kg of alloy react, whereas only 16 kg and 10 kg of alloy are used to liberate 1 kg of silane using 6N and 3N HCl. In relation to the alloy, hydrochloric acid is used in relative proportions of 10 to 25 litres of acid per kilogramme of powder, and in the experimental conditions, the choice of 15 to 16 litres represents a good compromise.

The alloy powder on acid reaction may be performed at ambient temperature, but it has been noted that the kinetics increase with temperature, and that hydrochloric acid requires the reaction to be performed at a temperature at least equal to 50°C. To accelerate the kinetics, heating should be up to about 70°C. The maximum working temperature is limited by the boiling temperature of the solution, and is in practice about 90°C; the metal powder being fed in at such a rate that the reaction temperature does not exceed 90°C.

It has also been discovered that the granulometry of the powder has an effect on the kinetics and consequently on the yield. The kinetics increase as the size of the particles diminishes. Foam formation is the factor limiting the size of the particles. The granulometry of the industrial ternary alloy powder must be equal at most to 0.40 mm. A granulometry less than 0.2 mm is well suited to the type of reaction. All conditions being otherwise equal, when the particle size is divided by 10, the quantity of silane produced in the same time is multiplied by about 15.

The use of any silicon, calcium and aluminium based industrial alloy having in its composition the defined elements $\text{Si}_3\text{Ca}_2\text{Al}_4$ or magnesium silicon, Mg_2Si as an additive introduced in a quantity representing at least 10% by weight of all the alloys undergoing hydrolysis and less than 50%, substantially increases the yield of the process.

The importance of the amount of alloyed silicon $\text{Si}_3\text{Al}_4\text{Ca}_2$ has been established. The higher the amount of alloyed silicon in the alloy - all operating conditions being otherwise equivalent - the higher the yield, i.e. the mass of the total products formed increases. An alloy containing alloyed silicon will preferably be selected; starting from an amount of alloyed silicon of the order of 20%, an appreciable rise in the yield of silicon hydrides formed is observed. A variation from 20 to 30% of the amount of alloyed silicon may correspond to an increase of more than 30% in the total silicon hydrides formed. The effect of the amount of alloyed silicon is a factor determining the disilane content; the latter may be increased by about 80%. A rise in the alloyed silicon content in the alloys, and even 40%, can only favour the formation of silicon hydrides, and it is highly advantageous to use alloy having a high alloyed silicon content, the latter being limited only by the technological possibilities of production of the alloys.

The raw gas coming from the reaction zone is constituted of hydrogen and silicon hydrides; silane SiH_4 , disilane Si_2H_6 , trisilane Si_3H_8 and polysilanes or higher silanes $\text{Si}_n\text{H}_{2n+2}$ where $n > 3$.

The silicon hydrides are condensed in solid form, optionally by trapping in cooling mixtures such as ice and water, or cryogenic coolants such as liquid nitrogen. Separation by fractional evaporation under a partial vacuum enables three fractions to be obtained, each being then subjected to purification, for example, using the technique of preparative chromatography in the gaseous phase.

The first fraction corresponding to silane, SiH_4 is isolated by evaporation at a temperature of -78°C under a vacuum of 300 mbar, 3.10^4 Pa .

The second fraction corresponding to disilane, i.e. constituted substantially by disilane 80%, and trisilane in a proportion of at least 15% and the remainder of silane, is separated at 0°C, under a vacuum of 500 mbar, $5 \cdot 10^4$ Pa.

The third fraction, corresponding to the heavy higher silanes or polysilanes, $\text{Si}_n\text{H}_{2n+2}$ where $n \geq 3$, in particular to trisilane, in a proportion of at least 75%, with a remainder of approximately 22% disilane, and approximately 1% silane, is separated by heating to + 80°C, under 100 mbar, $1 \cdot 10^4$ Pa.

The reaction zone is shielded from the air and at the end of the reaction the alloy which has not reacted is neutralised; the reaction zone together with all the associated parts of this zone and the fractionating zone is purged with nitrogen.

The hydrogen and the gaseous products formed in the reaction after separation of the silicon hydrides are collected, and after filtration, recovered or burned.

The process of producing silicon hydrides is carried out in a sealed reactor (1) fitted with heating means such as a double circulation of water (2) blanked off at the top by the plate (3) into which are inserted in a sealed manner the stirrer (4), the pipe (5) supplied with acid, the flow of which is controlled by the valve (6), the temperature probe (7), the alloy powder feed system. The powder (8) is routed towards the reactor via the sealed distribution hopper (9) then the pipe (10), the feed rate of the powder being monitored and controlled by the system (11); the powder is fed into the bath of acid (12) of dilute concentration, while stirring. Water vapour and the gaseous products escape through the evacuation pipe (13) towards the water condenser (14). In case of excess pressure in the reactor, a system (15) is available associated with a water nozzle.

The gaseous products: hydrogen and silicon hydrides escape at the upper part of the condenser (14); after circulation in the pipe (16) they are filtered in the filter (17), with a view to elimination of metallic traces and dust; afterwards they are directed by the circuit (18) towards the series of air-tight

cryogenic traps (19) (20) and (21) where the silicon hydrides are condensed at the temperature of the liquid nitrogen. The major part of the silicon hydrides is condensed in the first trap, the last two performing above all a safety function. The traps are fitted with pressure monitoring systems.

After condensation of the silicon hydrides in the trap (19), the hydrogen is evacuated at the upper part of the trap via the pipe (22A) towards the circuit (23) for evacuation of the hydrogen towards the flare for burning of combustible gases. After having passed through the other traps, the uncondensable materials are filtered out, recovered by (22B) introduced into the evacuation circuit (23).

The circuit (18), of the filter (17) at the outlet from the last trap, is provided in each section with means for opening and closing, such as valves, enabling each trap to be isolated and the inward and outward movement of the gaseous products entering it or escaping from it to be controlled.

After condensation of the silicon hydrides and evacuation of the uncondensables, the cryogenic traps are then heated by external application of heat and subjected to a vacuum, the temperature and the vacuum being regulated to precise values corresponding to each of the fractions, which after fractional evaporation is stored in a bottle, before purification.

The installation further comprises a nitrogen circuit (24) intended for the purging and flushing of all of the equipment: reactor, hopper, filters and the various traps, after the end of the reaction. The various sections 24A, 24B, 24C, 24D and 24E are fitted with valves.

The apparatus also comprises the vacuum pump (25) protected by the cryogenic trap (26) against any possible silicon hydrides driven along. The gaseous products not condensed in the trap are carried by the pipe (22C) towards the hydrogen recovery circuit (23) leading to the flare.

Furthermore, the lower part of the reactor (1) is connected to the neutralisation tank (27) via the pipe (28). In this tank the reaction medium is drained and neutralised.

Examples which illustrate but do not limit the invention are given below.

EXAMPLE 1

Reagent:

Alloy powder. Al 35%, Ca 18%, Si 40%.

Granulometry < 0.2 mm.

3.4 N hydrochloric acid (12% W).

Relative proportions: 15 litres of acid per kilogramme of alloy.

Operating conditions:

Feeding of the powder onto the stirred acid solution;

Initial temperature of the reaction medium: 50°C;

Equilibrium temperature of the reaction: 75°C;

Feed rate of the alloy 8 kg/hour.

The raw gas leaving the reactor has the composition by volume:

hydrogen	65%
mineral hydrides	35%

Fractional evaporation under partial vacuum enables three fractions to be obtained having the following compositions by mass:

1st fraction:

(-78°C, $3 \cdot 10^{-4}$ Pa)	SiH ₄	97%
	Si ₂ H ₆	2.5%
	other impurities	0.5%

2nd fraction:

(0°C, $5 \cdot 10^{-4}$ Pa)	SiH ₄	4.5%
	Si ₂ H ₆	79%
	Si ₃ H ₈	16%
	other impurities	0.5%

3rd fraction:

(80°C, $1 \cdot 10^{-4}$ Pa)	SiH ₄	1.5%
	Si ₂ H ₆	22%
	Si _n H _{2n+2}	76.5% $n \geq 3$

Products obtained after separation and purification.

70 kg of alloy and 1100 litres of hydrochloric acid producing:

3.3 kg of silane SiH_4
 1 kg of disilane
 and 1.3 kg of polysilanes or higher silanes.

The first two fractions are treated in order to obtain silane and disilane of electronic quality.

The third fraction enables in particular the silane to be replaced in the process of opalising bulbs using the dry method.

The silicon hydrides are also usable in other sectors such as photovoltaic cells and photocopier drums.

EXAMPLE 2

Reagents:

Alloy powder. Al 31.9%, Ca 23.5%, Si 38.2%, Fe 2.9%

Proportion of alloyed silicon 32.9%;

Granulometry ≤ 0.4 millimetres;

3.4N hydrochloric acid (12% W);

Relative proportions : 16 litres of acid per kilogramme of alloy;

Operating conditions

Feeding of the powder onto the stirred acid;

Initial temperature of the reaction medium: 50°C ;

Equilibrium temperature of the reaction : $80 - 90^\circ\text{C}$;

Feed rate of the alloy 8 kg/hour.

The raw gas leaving the reactor has the following composition by volume:

hydrogen about 35%,

mineral hydrides 65%.

Fractional evaporation under partial vacuum in the same conditions as in the preceding example produces from an initial 4 kg of the alloy, three fractions:

1st fraction:

$(-78^\circ\text{C}, 3.10^4 \text{ Pa})$	352 g
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2nd fraction:

$(0^\circ\text{C}, 5.10^4 \text{ Pa})$	154 g
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3rd fraction:

$(80^\circ\text{C}, 1.10^4 \text{ Pa})$	165 g
	671 g

EXAMPLE 3Reagents:

Alloy powder. Al 30.9%, Ca 21%, Si 42%, Fe 3.1%.

Proportion of alloyed silicon 23.1%.

Granulometry $\leq$ 0.2 millimetre.

3.4N hydrochloric acid (12% W).

Relative proportions: 16 litres of acid per kilogramme of alloy.

Operating conditions

Feeding of the powder onto the stirred acid solution;

Initial temperature of the reaction medium : 50°C;

Equilibrium temperature of the reaction:: 80 - 90°C;

Feed rate of the alloy : 8 kg/hour;

The raw gas leaving the reactor has the following composition by volume :

hydrogen : about 50%

mineral hydrides : 50%

Fractional evaporation under partial vacuum, in the conditions of the example produces, from an initial 4 kg. of the alloy, three fractions:

1st fraction:

(-78°C, $3 \cdot 10^{-4}$ Pa) 273 g

2nd fraction:

(0°C, $5 \cdot 10^{-4}$ Pa) 109 g

3rd fraction:

(80°C, $1 \cdot 10^{-4}$ Pa) 126 g

508 g

Typical analysis of the three fractions at the production outlet, without purification, for the two preceding examples is as follows:

	Fraction 1	Fraction 2	Fraction 2	Fraction 3
	gas phase	gas phase	liquid phase	gas phase
light	0.5	0.15	1	0.09
SiH ₄	98.75	42.6	3.52	20.3
PH ₃	0.04	0.23	0.043	0.033
H ₂ S	0.06	1	0.18	0.179

	Fraction 1	Fraction 2	Fraction 2	Fraction 3
	gas phase	gas phase	liquid phase	gas phase
AsH_3			0.006	0.006
$\text{Si H}_3\text{OSi H}_3$	0.03	2.7	5.86	0.69
Si_2H_6	0.56	52.3	85.8	68.75
$\text{Si H}_3\text{OSi H}_2\text{OSi H}_3$		0.11	0.096	0.01
$\text{Si}_2\text{H}_5\text{OSi H}_3$		0.015	0.248	0.115
Si_3H_8	0.048	0.91	3.37	9.83
Si_4H_{10}		0.026	0.018	



CLAIMS

1. Process for producing silicon hydrides by hydrolysis, with a dilute acid, of ternary silicon alloys of the general formula $Al_x Si_z Ca_y$, characterised in that an industrial ternary alloy, represented by the formula Al 30-38%, Ca 15-25%, Si 35-45%, containing at least 20% alloyed silicon, is reacted with an acid selected from among hydric acids and orthophosphoric acid, in a concentration between 2N and 6N, by adding into the acid the ternary alloy in the form of fine powder of a granulometry at most equal to 0.4 mm, the reaction being conducted at a temperature of at least 50°C, the metal powder being introduced into the acid at a rate such that the reaction temperature does not exceed 90°C.

2. Process for producing silicon hydrides according to claim 1, characterised in that acid hydrolysis of the ternary alloy is conducted in the presence of an additive formed of magnesium silicide introduced in a quantity representing at least 10% by weight of all the alloys subjected to the hydrolysis and less than 50%.

3. Process for producing silicon hydrides according to claim 1, characterised in that the various prepared hydrides, silane, disilane, trisilane and polysilane, are condensed in solid form, then separated by fractional evaporation under partial vacuum, each fraction then being subjected to a purification.

4. Process for producing silicon hydrides according to claim 3, characterised in that the first fraction corresponding to silane is isolated by evaporation at -78°C under $3 \cdot 10^4$ pascal, the second fraction corresponding to disilane is isolated by evaporation at 0°C under $5 \cdot 10^4$ pascal and the third fraction corresponding to polysilanes $Si_n H_{2n+2}$ wherein $n \geq 3$ is separated at +80°C under $1 \cdot 10^4$ pascal.

5. Process for producing silicon hydrides according to claim 4, characterised in that the reaction zone is shielded from contact with air, at the end of reaction the alloy that has not reacted is neutralised, and the reaction zone, all its accessory parts and the fractionating zone are purged with nitrogen.



6. Use of the silicon hydrides prepared according to claim 4, obtained from the two first fractions, after purification, in the electronic component industry and related industries, and from the third fraction, for opalisation of bulbs by the dry method.

7. Equipment for implementing the process for producing silicon hydrides according to claim 3, comprising a fluid-and-air-tight reactor (1) equipped with heating means (2), means for introducing the alloy powder by the fluid-and-air-tight distributing hopper (9), and additionally a water condenser (14), a series of cryogenic traps (19) (20) and (21) for the silicon hydrides, a circuit (22), 23) for recovering and evacuating the hydrogen, a vacuum pump (25) protected by a cryogenic trap (26), a circuit for scavenging and purging with nitrogen (24) and a neutralisation tank (27).