

New method of solar grade silicon production

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1. Introduction

One of the main advantages of photovoltaic solar cells (PVC) is their ecological clarity of direct conversion of solar energy to electricity. For wide spreading of PV technologies it is necessary to ensure that there is no environment pollution at the stage of PVC-s manufacturing, beginning from producing of polysilicon feedstock [1].

The objective of this project is creation of ecologically clean method for production of solar grade polysilicon feedstock (SGPF) as raw material for PVCs, and also raw material for producing monocrystalline silicon, which is used in electronic industry.

Semiconducting silicon made from polycrystalline silicon is base material for electronic and electrotechnical industry, which produce millions discrete and integral devices, microprocessors. More than 80% of computing, radio-, video- , robotics, telecommunication, controlling automatization and PV and other equipment are manufactured with use of monocrystalline silicon.

World production of PVC-s reached 300 MW in 2001. From this amount about 80% is produced from polycrystalline silicon. To produce 1 MW of PVCs using modern technologies it is required 13 tons of SGPF [2]. According to more optimistic prognoses, this amount will decrease to 10 tons per 1 MW produced. For PVCs polycrystalline silicon with less purity, than for electronic industry, so named scrap. Usually, scrap is not more that 10% of electronic grade polycrystalline silicon. During last years, growth of world production of PVCs was bigger than production of scrap, therefore world reserves of scrap is almost depleted and it is necessary to create new way for production of solar grade SGPF.

Forecast for demand and delivery of polycrystalline silicon on world market is presented at fig.1 [3]. You can see that delivery of SGPF will be less than demand within next 10 years. Annual world demand in SGPF in 2010 can be 16-32 thousand tons; at the same time the delivery will be only 8 thousand tons.

To produce such amount of solar grade SGPF with cost less than 20 USD per kg new approaches are required, which ensure less energy consumption and higher ecological cleanness comparing to conventional methods.

Main obstacle for mass production of PVCs is high cost of SGPF. If the cost will decrease in several times, the cost of PVCs could decrease twice as less up to 1 USD per watt peak. In this case cost from PV stations will be competitive with cost of energy produced by conventional methods.

In [4] it is noted that silicon can be "oil of 21 century", because 1 kg of polycrystalline silicon used in filmed α -Si PVCs can produce during its lifetime the same amount of energy that can be produced from 100 tons of oil. However, this example is not typical for polycrystalline PVCs, because in α -Si PV cells the silicon film with thickness 1 μm is insignificant part from total thickness of the cell, which consists mainly from stainless steel and glass. Modern PVCs from crystalline silicon have thickness $\sim 350 \mu\text{m}$. At this thickness and efficiency 15%, to produce 1 MW of solar cells it is required 13 tons of polycrystalline silicon (or 1 kg for 100 W module). If

accept average number of peak-hours during a day equal 5, then during a year it will produce ~182 kWh, and during 30 years – 5475 kWh of energy. At electricity price 0.1 USD per kWh, the cost of energy produced will be 547.5 USD; for these money ~1.5 tons of petroleum can be bought. Let's assume that 1 kg of oil produces 9 kWh of heat and efficiency of conversion it to electricity is 30%. Then, to produce 5475 kWh of electricity about 2 tons of oil will be required; the same amount of energy can be produced by 1 kg of SGPF used for manufacturing of PVCs. Market price of solar modules is now ~3.5 USD/W, thus 100 W module price is 350 USD and pay-back period is about 19 years. Thus, already today the increase of solar cells production is economically expedient. Forecasted decrease of PV cells and modules price will decrease payback period to 10 years.

2. Known methods of pure silicon producing.

There are 2 SGPF producing methods dominated:

- with use of hydrogenous reduction of trichlorsilane SiHCl_3 , named "Siemens-process [5], and
- disproportionation for producing of monosilane SiH_4 , developed by Union Carbide Co.[6]

In the world about 80% of polycrystalline silicon is produced using first method and 20% using second method. Block-schemes of these processes are presented at fig. 2 and 3.

In the Siemens process the SiHCl_3 is produced in boiling bed reactor as results of exothermal interaction of powdered metallurgical silicon with HCl. The vapor-gas mixture obtained is separated through filtration and condensation, and HCl and H_2 are recycled. The condensate is separated and SiHCl_3 is purified through multilevel rectification. Purified SiHCl_3 mixed with H_2 is directed to rod reactor for producing SGPF, where only 30% of SiHCl_3 is converted to SGPF. Main amount of SiHCl_3 remains in balanced mixture and along with other matters is removed from the reactor. Further this mixture is separated cryogenically and products of separation are directed to recycle. This process is complex, energy consuming and ecologically dangerous.

SGPF production process developed by "Union Carbide Co" started from hydrochlorination of metallurgical silicon in boiled bed reactor. Only silicon is spent, and SiCl_4 from all stages of the process is returned to hydrochlorination, ensuring maximal return of Si and Cl into the process. After separation of H_2 , SiHCl_3 is multi-rectified and directed to disproportionation, where SiH_4 is obtained. The SGPF is obtained through pyrolysis of SiH_4 at temperature 800°C in rod reactor with special design.

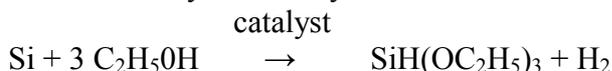
Disadvantages of this method are conducting the process in chemically aggressive media at high pressure and temperature, which require costly equipment made from heat-resistant and chemically inert materials. The presence of chemically aggressive Cl compounds leads to transfer of admixtures from the equipment walls (sides) to monosilane and create ecological danger.

In former USSR, beginning from 1983, the main method of producing of high purity SiH_4 , and then SGPF, was catalytical disproportionation of triethoxysilane $\text{SiH}(\text{OC}_2\text{H}_5)_3$ [7]. Block-scheme of used technological process presented at fig. 4. Raw material for producing of $\text{SiH}(\text{OC}_2\text{H}_5)_3$ were SiHCl_3 and dehydrated ethanol. The process of synthesis of $\text{SiH}(\text{OC}_2\text{H}_5)_3$ and desorption of HCl is implemented in film type apparatus. This method was realized in "Kremni polimer" plant in Zaporozhie city (Ukraine) and production volume of SiH_4 was 12,6 t per year. From the monosilane was produced SGPF through pyrolysis, and then high-resistant monocrystals for nuclear particles detectors and IR-receivers were produced by float zone technique.

Disadvantage of this method are: high consumption of ethanol, big amount of wastes, use of energy consuming method of monosilane rectification at liquid nitrogen temperature and use of ecologically dangerous Cl-containing materials.

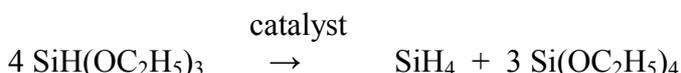
3. Main features of the new method.

In the new alcoxysilane method of SGSF production the technology existed in the plant “Krasny polimer” was partially used. The block-scheme of the method of producing of SGPF through monosilane is presented on fig.5.. At the first stage as raw material powdered metallurgical silicon and dehydrated ethyl alcohol is used instead of trichlorsilane.



It is noted, that purity degree of powdered metallurgical silicon has no such importance as in case of synthesis of trichlorsilane, thus less expensive silicon with purity 98% can be used. The reaction is conducted in high-boiled siloxane liquid at presence of Cu-based catalyst at atmospheric pressure and temperature not less than 180°C. At low pressure not reacted alcohol is removed, which prevents conversion of triethoxysilane to tetraethoxysilane. At optimal conditions 85-90% of SiH(OC₂H₅)₃ is obtained, and the rest is diethoxysilane.

At the second stage the triethoxysilane is converted into silane and tetraethoxysilane according reaction:



Small amount of produced diethoxysilane is converted into silane according to reaction:



Unlike to existing in “Kremni polimer” plant technology, at disproportionation of SiH(OC₂H₅)₃ stage better catalyst was used and also the process of purifying of monosilane was modified. This allowed to implement disproportionation at ambient temperature, increased equipment efficiency and reduced energy consumption. New method has stage of tetraethoxysilane hydrolysis; this allows to receive valuable by-products, and to return waterless alcohol to the stage of SiH(OC₂H₅)₃ synthesis. The waterless ethyl alcohol is obtained without additional reagents due to absorption of water by tetraethoxysilane. At this stage more than 95 % of ethyl alcohol is recycled and it is required to add only 5% of ethyl alcohol into the process.

The main advantage is absence of Cl in the process, eliminating the possibility of ingress of Cl-contained contamination to environment. Moreover, all stages of the silane purifying and pyrolysis are conducted at ambient temperature or at lower temperatures, down to temperature of the silane liquefaction; these reduce the risk when work with monosilane.

Every admixtures of elements of III-V group, which present in metallurgical silicon, are converted to saturated metalorganic compounds without link element-hydrogen and, thus, are not disproportionated with creation of volatile hydrides like diborane, phosphine and arsine. In this case main polluting admixtures in monosilane are high-boiled ethoxysilanes. Ethoxysilanes and other metalorganic compounds are removed at the next stage by adsorption of admixtures by liquid tetraethoxysilane cooled to -60°C. Final purity of monosilane 99,999% is reached by adsorption of tracking admixtures by activated charcoal and final purifying on chucks with chemisorbent. Such purifying guarantees content of carbon and oxygen at level less than 1.10¹⁵ at/sm³ and characterized by minimal energy consumption and material capacity. Big temperature difference between main substance and carbon-containing admixtures simplifies the purifying process at stages of ethoxysilane and monosilane purifying. In table boiling temperatures if these substances are presented.

Table.

№	Name of substance	Boiling temperature at pressure 1 atm
1	Carbon oxide	- 192
2	Carbon dioxide	- 78,6
3	Methan	- 161,5
4	Ethan	- 88,6
5	Ethylene	- 103,7
6	Ethyl alcohol	+ 78,5
7	Triethoxysilane	+ 131,5
8	Tetraethoxysilane	+ 168,5
9	Monosilane	- 112

For producing SGPF the monosilane is pyrolysed at 800-850⁰C; the process can be implemented in rod reactor or in reactor with “boiling” layer of seed silicon particles. In second case the pyrolysis process requires minimal energy at level 10 kWh/kg.

4. Characteristics of main and by- products

Main production for the new method of SGSF production are:

- Monosilane and monosilane mixtures with other gases,
- Electronic grade polycrystalline silicon,
- SGPF for PV industry.

The technological process allows to change assortment and shares of the products in total amount depending on market situation.

High quality of monosilane and SGPF are confirmed by measurements. The admixtures presence is at the level of sensitivity of modern instruments. Specific resistance of monocrystalline silicon samples produced by float zone technique is more than 10 000 Ω.sm, and life time of minority carriers is up to 1000 μs.

At the same time there is 24 kg of tetraethoxysilane per 1 kg of monosilane in the yield. To transform it to other useful materials several technologies were elaborated:

- As result of hydrolysis of tetraethoxysilane, silica sols are produced; they can be used as coupling agent at manufacturing transfer-molds, for textile and construction materials strengthening, for creation of composite and other new materials. After thermal treating of silica sols Si dioxide is obtained; it can be used for manufacturing of fibre-optic and quartz wares
- Through organomagnesium synthesis of tetraethoxysilane wide used silicone polymers are obtained
- By thermal-oxidation of tetraethoxysilane superfine silicon dioxide (white soot) is obtained; it is used as a filler material

5. Possibilities of perfection of the new method

At annual yield of silicon 10000 tons about 240000 tons of tetraethoxysilane will be produced; this is close to current world tetraethoxysilane annual production. Currently accepted tetraethoxysilane production scheme [9], presented on fig. 6, in many respects coincides with alcoxysilane technology of monosilane production. For creation of joint manufacture it is expedient to combine 2 schemes to one, which should be close to scheme presented on fig.5. To do this it is necessary to create conditions for maximal yield of di-and triethoxysilane during the first stage of alcoxysilation of silicon; in this case the main product will be silicon and materials produced from tetraethoxysilane.

At the initial stage of industrial scale use of this new technology at SGSF production volumes about 1000 tons annually, in the existing production of tetraethoxysilane only part of metallurgical silicon can be converted into triethoxysilane according to scheme presented on fig.7.

Another approach for the problem solving is selection of new catalysts and conditions of silicon and alcohol interaction ensuring increase of diethoxysilane yield and decrease of tetraethoxysilane amount in disproportionation reaction.

Part of tetraethoxysilane can be converted into triethoxysilane through hydration:



Realization of this method will allow to return the tetraethoxysilane into technological process for increasing of the monosilane yield.

Comparing to using of traditional catalysts, more effective can be implementation of plasma catalysis with use of nonequilibrium plasma generated by various types of electrical discharges.

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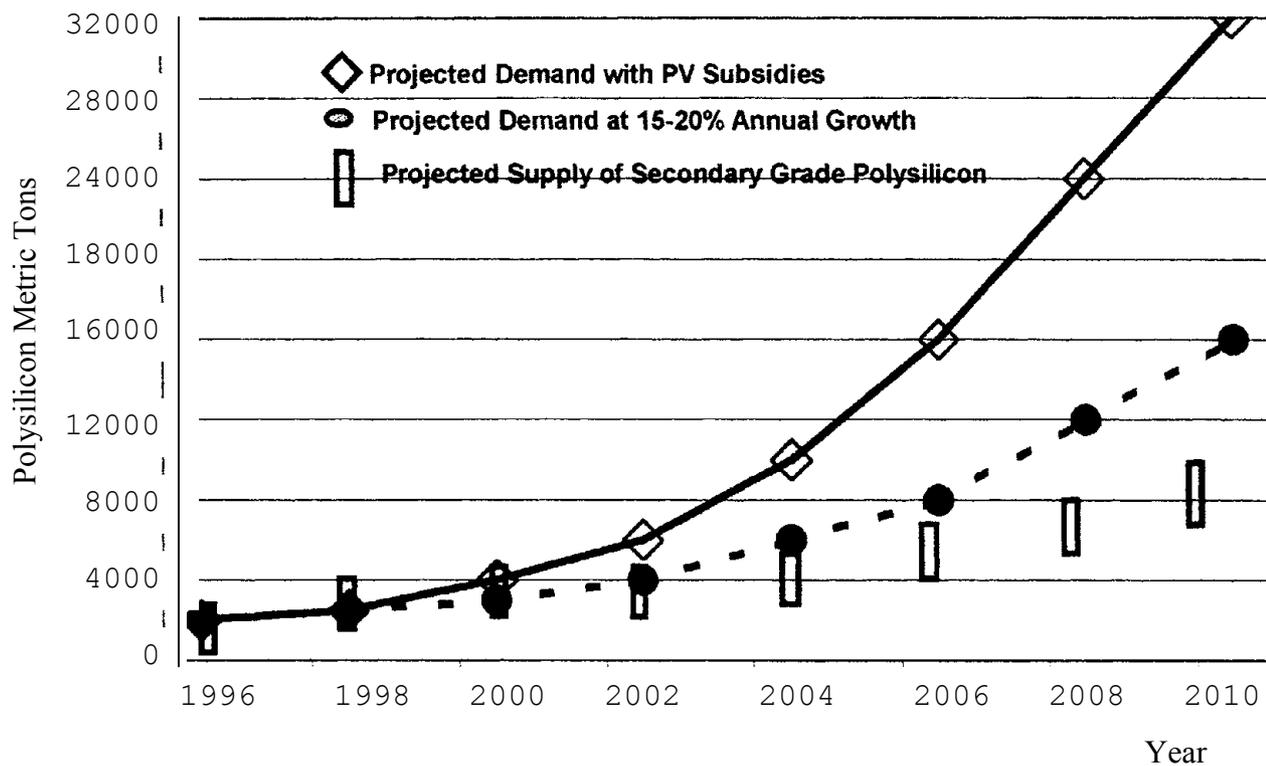


Figure 1. Forecasted PV Feedstock Demand and Secondary Polysilicon Supply in Metric Tons by Year.

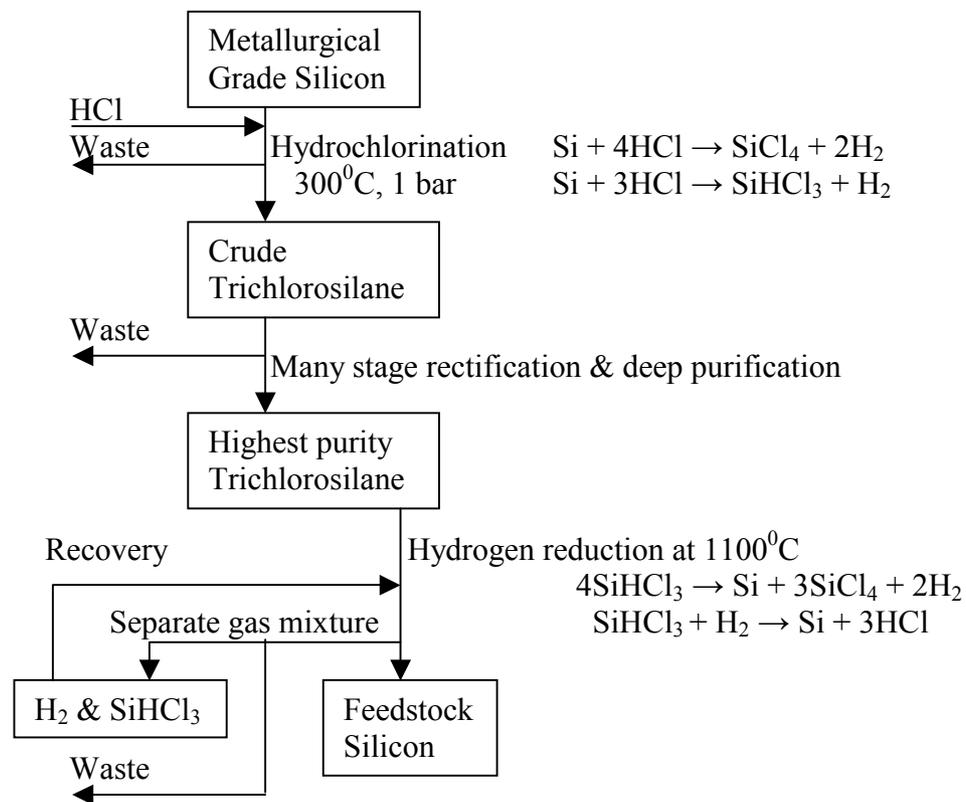


Figure 2. Schematic of semiconductor grade silicon produced (Siemens process).

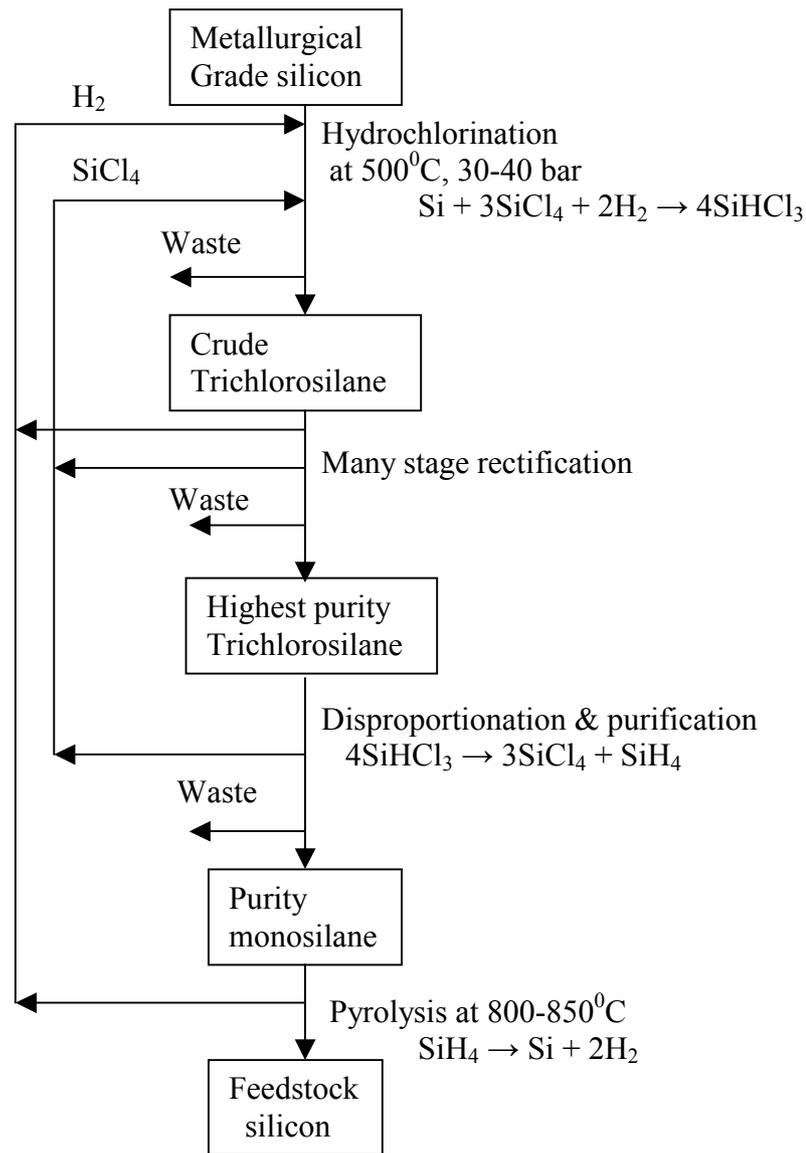


Figure 3. Schematic of semiconductor grade silicon produced (Union Carbide).

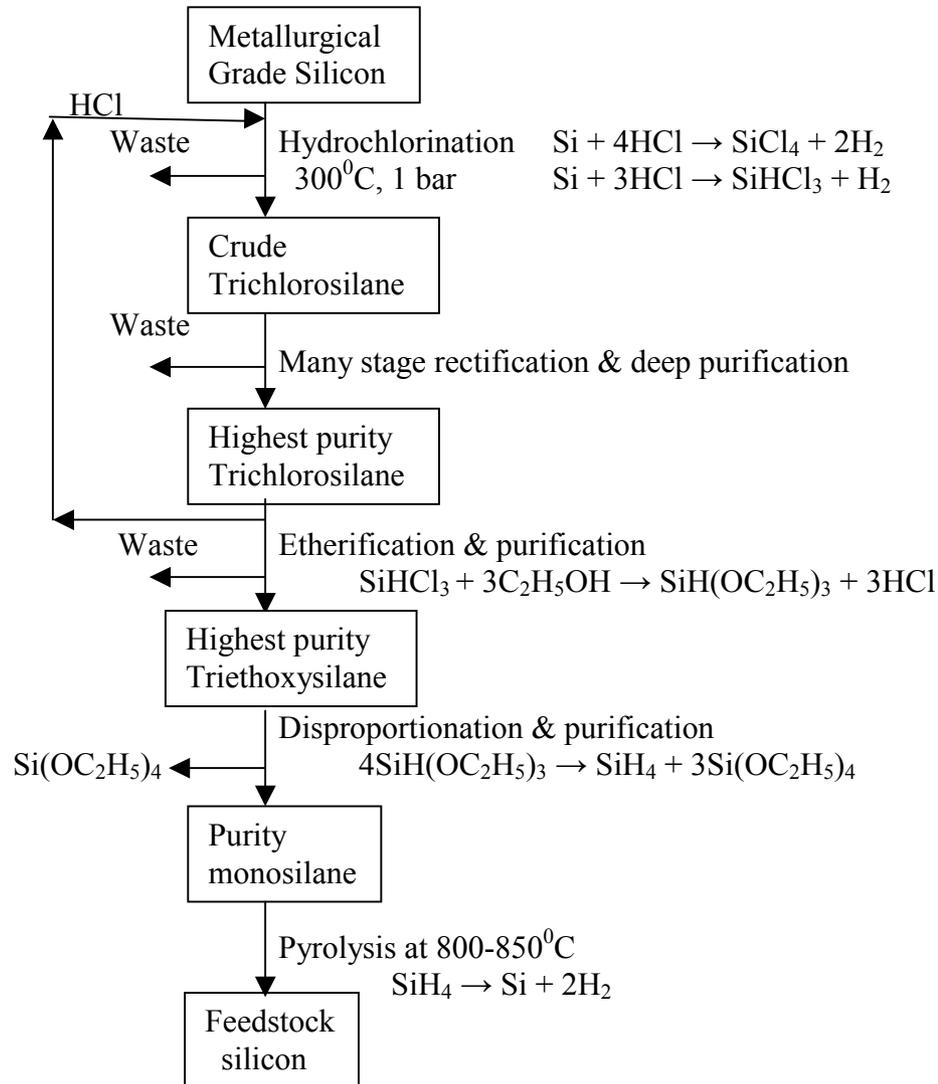


Figure 4. Schematic of semiconductor grade silicon produced through monosilane in former USSR.

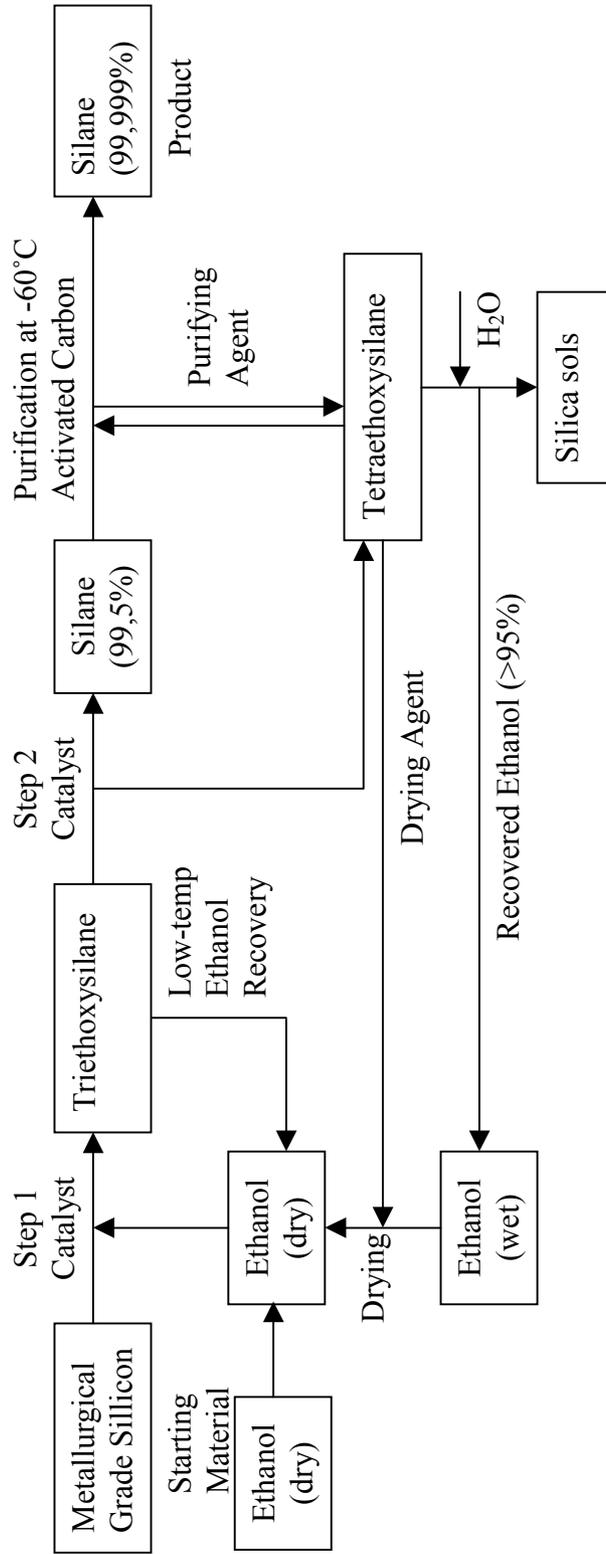


Figure 5. Scheme of new silane production process

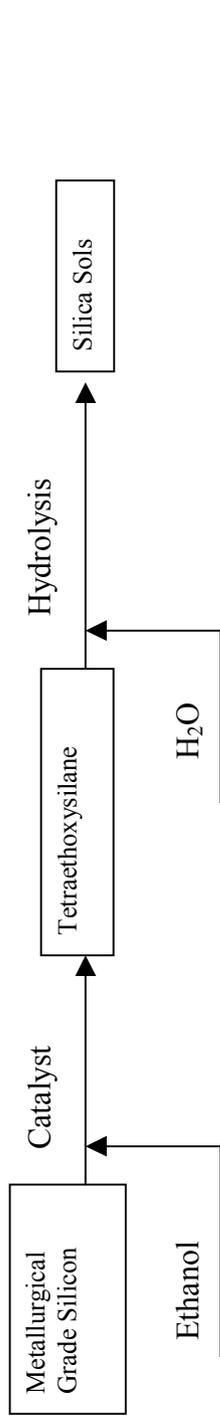


Figure 6. Existing Process for Production Silica Sols.

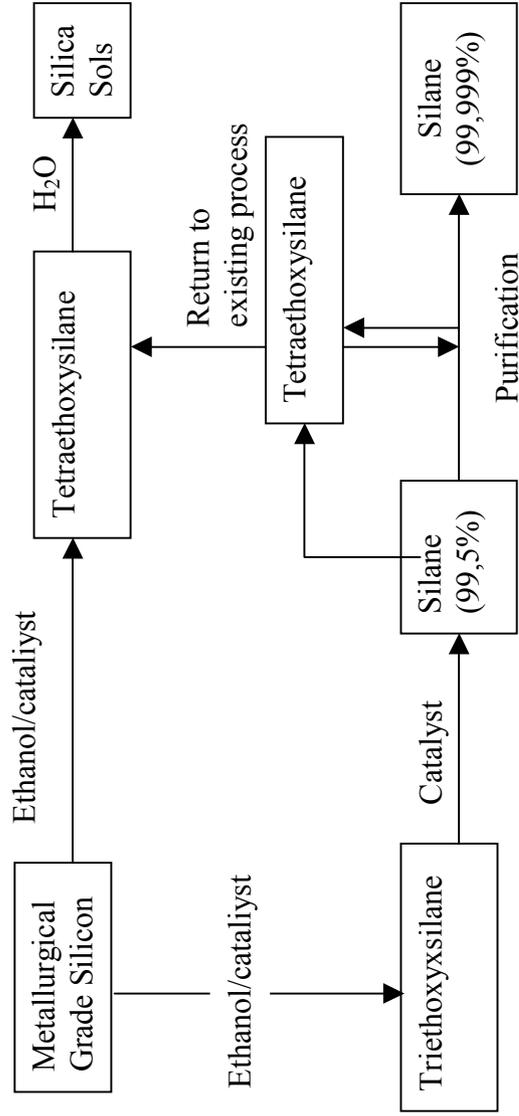


Figure 7. Schematic combined process for producing silane and silica sols.