

# Reactive Distillation Assisted Electronic Grade Silane Gas Production: From Basic Research to Industrial Applications

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## Highlights

- RD is ideally suited to silane synthesis via chlorosilane redistribution.
- RD route is superior to fixed-bed reactor route in terms of both equipment and operating costs.
- DCS redistribution process promotes closer integration with the modified Siemens process.

## 1. Introduction

Silane gas is the most used silicon precursor in microelectronics and optoelectronics fabrication, such as integrated circuits (IC), display panels, and solar cells. Recently it is also recognized as the most ideal silicon precursor for manufacturing high capacity silicon/carbon anode for lithium-ion batteries. The increasingly growing market demand calls for efficient and low-cost solutions to high-purity silane.

There are four typical approaches to synthesis silane gas: a) magnesium silicide with mineral acids; b) lithium hydride with trichlorosilane ( $\text{SiHCl}_3$ , TCS) or silicon tetrachloride ( $\text{SiCl}_4$ , STC); c) silicon tetrafluoride with sodium aluminum tetrahydride; d) catalytic redistribution of chlorosilanes. Among these methods, the trichlorosilane redistribution method is the workhorse due to its convenient combination with the modified Siemens process for polysilicon production, however, the redistribution reaction is characterized by low to 0.2% equilibrium conversion in thermodynamics. The conventional solution is to execute the process with a two-step method that employs two fixed-bed reactors and three distillation columns, being faced with large amount of material circulation and huge energy consumption.

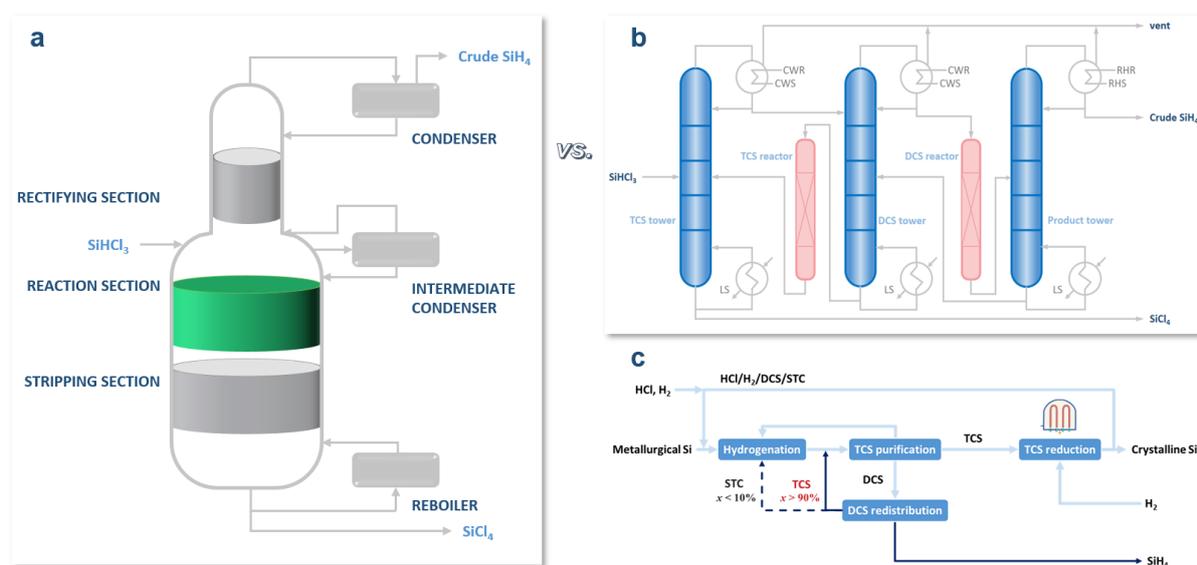
Our group has been studying the chlorosilane redistribution method for years. We developed a novel scheme facilitated by reactive distillation (RD) technology (Fig. 1a) to overcome the thermodynamic limit by continuous removal of products from the reaction zone, achieving nearly complete conversion of the feedstock. After systematic laboratory experiments and computer-assisted process simulations, we developed the process design package (PDP) and established a pilot plant with silane production capacity of 600 tons per year in Henan province of China. Successful startup was achieved in the first trial at the end of 2014, and the purity of final product reached 99.99999% with TCS conversion above 98%. This is also the first commercial production of electronic grade silane gas in China. After that, the phase II project with silane production capacity of 2500 tons per year went into operation in 2018. Recently, we proposed a new process that uses a by-product of the modified Siemens process for polysilicon production, dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ , TCS), to produce silane gas with TCS as a by-product. The latter can be directly used to produce polysilicon after purification, significantly enhancing the compatibility between the silane process and the polysilicon process. The industrial demonstration unit of this new technology will go into operation in the first half of this year in TONGWEI CO., LTD (Sichuan, China), which is the largest high-purity crystalline silicon producer in the world.

## 2. Methods

We successively carried out experimental studies of the hydrogenation reaction of STC in the presence of elemental silicon to TCS and the redistribution reaction of TCS to silane, involving reaction mechanism, kinetic modeling, catalyst screening, and reaction condition screening. Then computer simulations were conducted to establish and optimize the production process, and the result was used to develop the process design package.

### 3. Results and discussion

Compared to the fixed-bed reactor based process (Fig.1b), the RD based process (Fig.1a) uses a single set of column superseding two reactors and three columns of the former, thus saving lots of equipment investment. Meanwhile, benefiting from the continuous and in-situ removal of redistribution products, the equilibrium conversion limit in thermodynamics is broke, together with the favorable boiling points distribution of species involved that facilitates the concentration of reaction intermediates at the middle of the RD column, the chlorosilane feedstock can achieve nearly 100% conversion thus the amount of material circulation between the reaction section and the purification section reduces largely, so does the operating cost.



**Fig. 1** Chlorosilane redistribution method for silane synthesis, a) RD based route; b) conventional fixed-bed reactor based route; c) process flow chart with DCS as starting material.

In Siemens process for polysilicon production, DCS acts as a by-product in both the hydrogenation section and the reduction section. The new process we proposed with DCS as starting material is shown in Fig. 1c. By modulating the RD column configuration and operating conditions, it is possible to make TCS to be the dominant by-product while STC selectivity can be below 10%. The by-product TCS can be recycled to the TCS purification section and then reduced to elemental silicon, thus the new process promotes closer integration with the modified Siemens process.

### 4. Conclusions

The RD facilitated chlorosilane redistribution method for silane gas synthesis exhibits superiority in terms of both equipment investment and operating cost over the conventional fixed-bed reactor based route. In consideration of the fact that the photovoltaic field has been the largest segment of silane gas market, the newly developed process with DCS as the starting material is suitable for photovoltaic grade silicon players which are usually also key players of solar cells.

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### Keywords

Silane; Reactive distillation; Trichlorosilane; Dichlorosilane; Redistribution reaction