



Low-temperature catalytic hydrogenation of silicon and germanium tetrachlorides on the modified nickel chloride



Andrey V. Vorotyntsev^{a,*}, Anton N. Petukhov^a, Ilya V. Vorotyntsev^a,
Tatyana S. Sazanova^a, Maxim M. Trubyanov^a, Irina Yu. Kopersak^a, Evgeny N. Razov^b,
Vladimir M. Vorotyntsev^a

^a Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nanotechnology and Biotechnology Department, Nizhny Novgorod, 603950, Russian Federation

^b Institute for Problems in Mechanical Engineering, Russian Academy of Sciences, Nizhny Novgorod 603024, Russian Federation

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ABSTRACT

The catalytic reduction of SiCl_4 and GeCl_4 by hydrogen to silicon and germanium nanopowder was carried out over a modified nickel chloride catalyst. The effects of nickel chloride surface on the reaction were intensively investigated. The results show that modified nickel chloride surface play an important role in reduction the value of the activation energy and reaction temperature of the catalytic hydrogenation SiCl_4 and GeCl_4 . Elemental analysis of the catalyst and reaction results demonstrate that the catalyst operates in a temperature range from 423 to 573 K. Further temperature increase above 623 K was impractical as it led to a change in catalyst composition and silicide/germanide is formed in reactor. The resulting knowledge has helped to assume the reaction mechanism which is based on the formation of SiCl_2 and GeCl_2 in the reaction zone. This study will be useful in understanding the reduction of SiCl_4 and GeCl_4 with hydrogen and provides information regarding the development of a SiCl_4 converter for a Siemens reactor to produce poly-Si in the solar cell industry and produce Ge nanopowders with minimum energy consumption.

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1. Introduction

Nowadays nanotechnology is the recent progress in the manufacture and characterization of low-dimensional nanostructures such as nanowires, nanodots, nanotubes, nanoparticles, etc. made from materials and alloys with unique properties. Nanostructures have been studied and tested in detail nanoelectronic systems and Nanooptics, Nanomechanics and Nanobiology. Formation of Ge nanodots (CT) and nanoparticles crystallographic pristine silicon surfaces have been studied for many years [1,2]. Further studies have focused on the deposition multistructures with built nanoparticles [3]. Dislocations stress and dangling bonds at the interface of the Ge and Si to the different lattice constants can affect the quality of these structures and their changes expected physical behavior [4–6].

* Corresponding author. Nizhny Novgorod State Technical University n.a. R.E. Alekseev, Nanotechnology and Biotechnology Department, Minina st 24, Nizhny Novgorod, 603950.

E-mail address: an.vorotyntsev@gmail.com (A.V. Vorotyntsev).

Silicon tetrachloride is a major byproduct of polycrystalline silicon (poly-Si) production through the chemical vapor deposition (CVD) process of SiHCl_3 [5]. Because a drastic increase in the production capacity of poly-Si in the solar cell industry is expected in the near future, finding an efficient process of converting SiCl_4 to useful products is becoming more and more important environmental and economically, and the reaction of hydrogenation of SiCl_4 has become the focus of recent basic scientific and technological research.

There are several approaches to reducing silicon tetrachloride. The main commercially successful process is silicon tetrachloride processing and reuse through high-temperature reduction in the form of chlorosilanes [7]. There are a number of other, less widespread methods: hydrogenation with the application of highly reactive reductants (for example, metal hydrides) [8], plasma hydrogenation [9] and catalytic reduction [10–18].

All these methods have their own advantages and drawbacks. Their disadvantages include high energy consumption; high production cost; contamination of reaction products with electroactive impurities which is unacceptable in modern microelectronic appli-

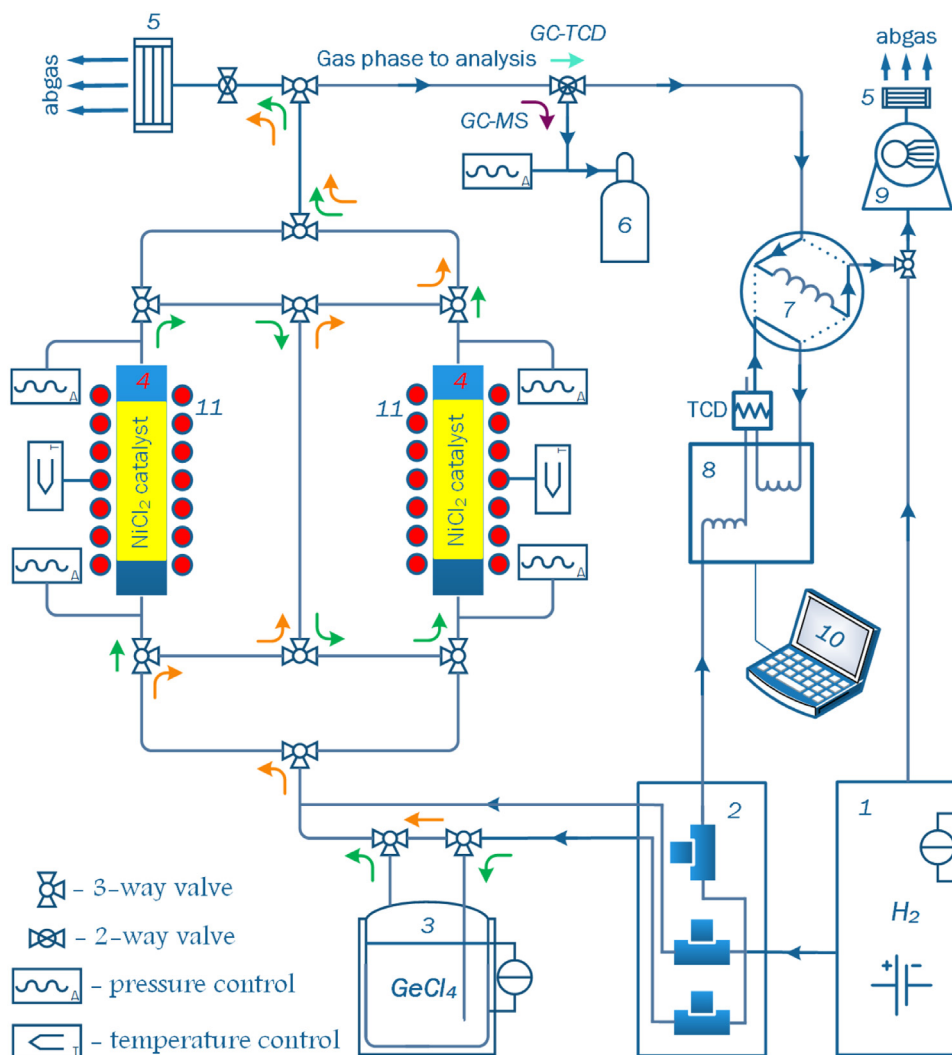


Fig. 1. Apparatus for investigation of the catalytic reduction of silicon/germanium tetrachloride: 1–hydrogen source, 2–mass flow controller, 3–bubbler (tank with $\text{SiCl}_4/\text{GeCl}_4$), 4–continuous-flow reactor, 5–cartridge filter, 6–GCMS sampler, 7–6-way Swagelok valve, 8–GC analysis (with TCD), 9–vacuum pump, 10–PC; \rightarrow – operating mode, \rightarrow – purge mode, \rightarrow – GCMS analytic line, \rightarrow – GC analytic line.

cations; necessity of toxic waste disposal; complicated apparatus and low product yield.

Recent years have seen great advances in catalytic reduction processes. The following catalysts are in common use: Ni and Si powders and their mixtures [10,11], copper (I) oxide, copper (I) chloride and iron (II) chloride [10,12,14]. Bulan and Weber [14] reduced silicon tetrachloride in the presence of aluminum, vanadium, and antimony chlorides, bromides and iodides. Koether [15] used copper silicide as a catalyst. Bohmhammel et al. [16] used a niobium, tantalum, or tungsten heating element as a catalyst. Good results were obtained when applying mixtures of Group 2A metals and their salts as catalysts [17]. Qiguo Chen and Wenlong Chen [12] used copper halides mixed with alkali metals as catalysts. Yank et al. [18] proposed applying activated charcoal with a specific surface area above $104 \text{ m}^2/\text{kg}$ as a hydrogenation catalyst support.

Transition metal silicides, formed by the reaction of the metal with $\text{SiCl}_4\text{-H}_2$ mixtures under hydrogenating reaction conditions, are known to allow a substantial lowering of the reaction temperature of the hydrogenation of SiCl_4 as compared to the uncatalyzed reaction [19–22]. Ingle and Peffley reported that copper hydride was an active catalyst which reacted with SiCl_4 , forming copper chloride and SiHCl_3 , and the process parameters affecting SiHCl_3 yields [23]. Meanwhile, Gusev et al. offered a plasma process, as

well as a catalytic hydrogenation process, coming to the conclusion that pressure in the reaction zone played a key role in determining the SiHCl_3 yield of SiCl_4 plasma hydrogenation [24,25].

When dealing with transition metals in a catalytic reaction containing chlorine, it is important to note whether the metals are removed from the solid phase in the form of volatile metal chlorides or the silicide catalysts are stable under the reaction conditions. Therefore, Acker and Bohmhammel reported the thermodynamics results of transition metal silicides and suggested that these can be formed in situ by reaction of metal with a SiCl_4/H_2 atmosphere [20].

Vorotyntsev et al. [26,27] performed quantum-chemical calculations of the hydrogen reduction of silicon chlorides and theoretically determined the relevant activation parameters. It is of interest to experimentally determine these parameters and compare them with calculation results.

Silicon tetrachloride finds wide application in microelectronic and chemical industries but a large amount of silicon tetrachloride forming in semiconductor silicon production is not used. The reason for this is the following: reduction of silicon tetrachloride requires much energy. In view of semi-conductor silicon production scale-up, the problem of silicon tetrachloride processing and reuse in semi-conductor silicon production is of great practical importance.

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