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Single Molecule Source Reagents for CVD of Beta Silicon Carbide

Monthly Report

Sponsored by

Strategic Defense Initiative Organization
Small Business Innovation Research Program

Issued by Office of Naval Research Under

Contract #N00014-91-C-0096

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Effective Date of Contract: 6/1/91
Contract Expiration Date: 11/30/91
Reporting Period: 6/1/91-6/30/91

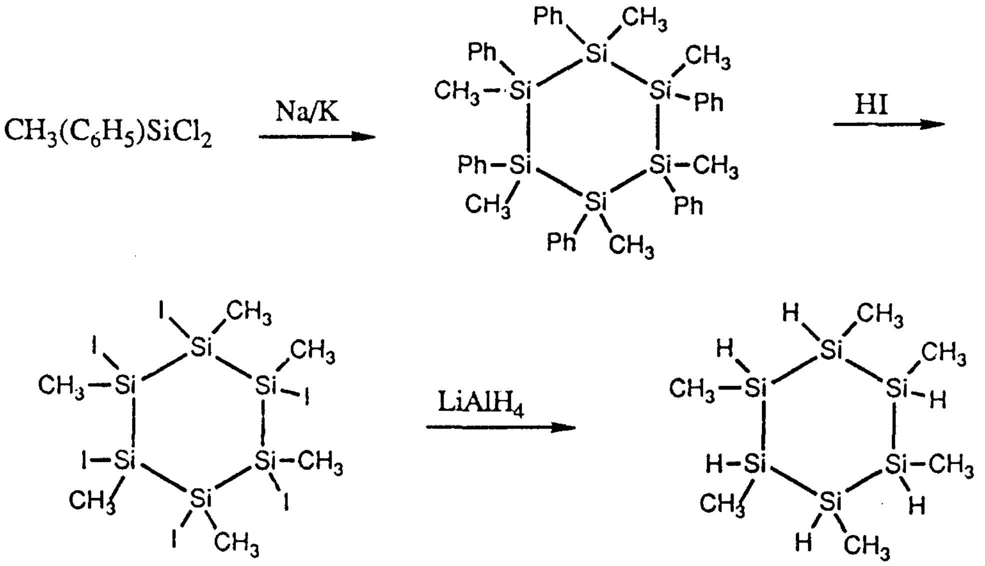
Beta silicon carbide is an excellent candidate semiconductor material for demanding applications in high power and high temperature electronic devices due to its high breakdown voltage, relatively large band gap, high thermal conductivity and high melting point. Use of silicon carbide thin films is hampered, however, by the inability to reproducibly grow stoichiometric films free from excess silicon or carbon. The principal difficulty is that absolutely reproducible flows of the source gases cannot be provided with existing gas flow control equipment. The very finest gas flow control equipment has been used in the CVD systems, but small disparities remain between successive deposited films. The production of practical beta silicon carbide devices has been hindered by the lack of a reproducible process for deposition of stoichiometric beta silicon carbide films.

The goal of the Phase I effort is to synthesize single molecule source reagents, study their decomposition pathways, and investigate their use for the CVD of beta silicon carbide investigated. The ultimate objective is to produce a high purity, unimolecular source reagent which will introduce equivalent amounts of *reactive* silicon and carbon to the growth surface and lead to growth of intrinsic, stoichiometric ß-SiC for device applications.

The Phase I effort consists of the following tasks:

- Task 1: Synthesis and characterization of 1,3-disilacyclobutane, hexamethylcyclohexasilane, and 1,4-disilabutane.
- Task 2: Investigation of thermal decomposition of 1,3-disilacyclobutane, hexamethylcyclohexasilane, and 1,4-disilabutane
- Task 3: Growth of ß-SiC films from 1,3-disilacyclobutane, hexamethylcyclohexasilane, and 1,4-disilabutane
- Task 4: Characterization of physical properties of ß-SiC films and correlation with thermal decomposition behavior of source reagents
- Task 5: Preparation of final report

During the first month a large scale synthesis of 1,4-disilabutane and a small scale synthesis of 1,1,3,3-tetrachloro-1,3-disilacyclobutane have been carried out. Both syntheses followed the literature prcedures as described in the Phase I proposal and shown below. Considerable experimentation was necessary to determine the corrrect conditions for the pyrolysis reaction leading from 1,1-dichlorosilacyclobutane to 1,1,3,3-tetrachloro-1,3-disilacyclobutane.



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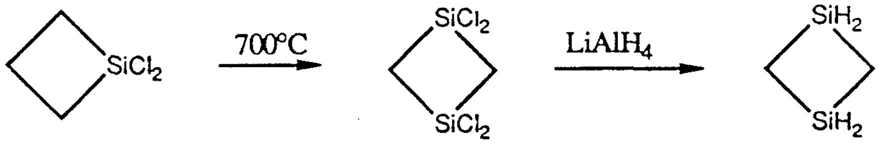

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$$Cl_3SiCH_2CH_2SiCl_3 \xrightarrow{LiAlH_4} H_3SiCH_2CH_2SiH_3$$

The experimental details are given below:

1,4-disilabutane

A 3-liter, oven dried, 3-necked flask was equipped with an overhead stirrer and thermocouple and connected via a Claisen head and transfer tube to a 3-necked, 200 ml receiver flask topped with a dry ice condenser which was vented to a nitrogen bubbler. The entire apparatus was flushed with nitrogen and one liter of tetraglyme (Aldrich, dried by passage through activated alumina) was added via cannula. The receiving flask was cooled in a dry ice/isopropanol bath and dry ice was also added to the condensor. Lithium aluminum hydride (LAH) (90g, 2.37 moles, Aldrich) was weighed out in a helium filled glovebox and added to the tetraglyme solution over two hours via a flexible Teflon solids transfer tube. 1,2-bis(trichlorosilyl)ethane (400g, 1.35 moles, Petrarch) was dissolved in 400 ml of tetraglyme and added to the LAH slurry via cannula over 3 hours. The reaction mixture warmed to a maximum of 70° and the product distilled out of the mixture and collected in the receiving flask. A total of 102 grams (1.13 moles, 84% yield) of 1,4-disilabutane was collected.

1,1,3,3-tetrachloro-1,3-disilacyclobutane
A 3/4" i.d. quartz pyrolysis tube with ground glass joints at each end was packed with quartz chips and placed in a Lindberg tube furnace. At one end of the tube a vacuum ampoule containing 1,1-dichlorosilacyclobutane (16.1g, 0.114 moles, Petrarch) was attached and at the other end a -78°C trap was attached which then was connected to a -196°C trap and a vacuum pump. Between the two traps a needle valve and a manometer were inserted. After flushing the system with nitrogen the ampoule valve was opened and the needle valve adjusted to give a pressure in the system of 12-16 torr. Under these conditions the starting material evaporated in ~240 minutes. While still under vacuum the -78° trap was taken into the drybox and white crystals of product (5.3g, 0.0235 moles, 41 % yield) were scraped from the sides. In addition a clear liquid (3.7g) was collected from the bottom of the trap which GC revealed to be primarily unreacted starting material. The procedure was repeated and the crude products from the two runs were combined and sublimed at 25°/0.1 torr to give 7.0g of 1,1,3,3-tetrachloro-1,3-disilabutane. NMR (C_6D_6, δ, ppm): 1.30,s; m.p. 57-63°, lit. m.p. 60°.