FINAL REPORT

Single Molecule Source Reagents for Chemical Vapor Deposition of ß-Silicon Carbide

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Phase I conclusively showed the feasibility of rational design of single molecule source reagents that could lead to improvements in the chemical vapor deposition of stoichiometric ß-silicon carbide. Four single molecule sources were synthesized, their decomposition pathways studied, and their utility in ß-silicon carbide CVD investigated. Dramatic differences in the CVD process resulted from small changes in the reagent structure. A strained cyclic molecule, 1,3-disilacyclobutane, allowed growth of a ß-silicon carbide film at a temperature >300°C lower than was possible with a similar straight chain reagent. Furthermore, the highest quality film was grown from the analogous chlorinated cyclic source reagent: 1,1,3,3-tetrachloro-1,3-disilacyclobutane. We propose that decomposition of the cyclic precursors directly produces intermediates that can lead to deposition of stoichiometric silicon carbide. The Phase I results clearly showed that ß-silicon carbide CVD can be improved by molecular engineering of the source reagents. Cyclic precursors are promising for both the deposition of single crystal films at high temperature and for polycrystalline and single crystal films at low temperature. In Phase II we will optimize the precursor for low temperature deposition and the integration of silicon and silicon carbide HBT device structures.

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Summary

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Four single molecule sources were synthesized, their decomposition pathways studied, and their utility in the chemical vapor deposition of ß-silicon carbide investigated. Dramatic differences in the CVD process resulted from (seemingly) small changes in the molecular structure of the source reagent. For example, a strained cyclic molecule, 1,3-disilacyclobutane, allowed growth of a ß-silicon carbide film at a temperature >300°C lower than was possible with a similar straight chain source reagent. Furthermore, the highest quality film was grown from the analogous chlorinated cyclic source reagent: 1,1,3,3-tetrachloro-1,3-disilacyclobutane. We propose that decomposition of the cyclic precursors directly produces intermediates that can lead to deposition of stoichiometric silicon carbide films.

The Phase I results clearly showed that improvements in chemical vapor deposition of ß-silicon carbide can be made via molecular engineering of the source reagents. Cyclic precursors are promising for both the deposition of single crystal films at high temperature and for polycrystalline and single crystal films at low temperature. In Phase II we will optimize the precursor for low temperature deposition and the integration of silicon and silicon carbide HBT device structures.

Introduction

High power, high frequency electronic devices are critical for both strategic defense and commercial applications. These devices may require electronic materials with dramatically improved properties relative to standard silicon- or gallium arsenide-based semiconductors. Silicon carbide, particularly in its cubic beta phase, possesses both the electrical and thermal properties to meet the challenge of next generation power devices.

Beta silicon carbide has a high breakdown voltage (2.5×10^6 V/cm), relatively large band gap (2.35 eV), low dielectric constant, and a thermal conductivity (3.9 W/cm-deg) of more than three times that of silicon at ambient temperature.[1] ß-silicon carbide also has a high melting point, good strength, good resistance to radiation damage, and good corrosion resistance in many environments. In addition, beta silicon carbide is resistant to the diffusion of impurity species. ß-silicon carbide may be processed by several techniques similar to those used in silicon device technology, and in many instances silicon carbide devices may be substituted at moderate and low temperatures for silicon devices. ß-silicon carbide semiconductor device technology therefore offers the opportunity to meet the stringent requirements of electronic devices for strategic defense applications.

ß-silicon carbide may be formed or deposited by many techniques, one of which is chemical vapor deposition (CVD). Chemical vapor deposition is a particularly desirable fabrication approach, as it permits the controlled growth of undoped and doped layers and structures of a variety of forms. The traditional approach for CVD of ß-silicon carbide has been to use silane (SiH_4) as the source of silicon, and low molecular weight hydrocarbons such as methane, propane, or ethylene as the carbon source. A mixture of these two gases in a hydrogen carrier gas is passed over a substrate maintained at a temperature of about 1400°C. ß-silicon carbide is deposited upon the substrate as the silicon-containing species and the carbon-containing species pyrolyze at the substrate.

This process can be used to deposit ß-silicon carbide, but it has not been understood and controlled well enough to reproducibly grow semiconductor grade ß-silicon carbide. In addition, the temperatures required for deposition (>1300°C)

do not permit the integration of silicon carbide with silicon-based device structures.

Sources in which the silicon and carbon are provided in a single molecule have been used, but the deposited film has been either silicon rich or carbon rich – it has proved impossible to obtain reproducibly precise stoichiometric compositions. We believe that this results from failure to understand the reaction chemistry of potential source reagents which leads to failure to deposit pure thin films. For example, methylsilane (CH_3SiH_3) has been used as a source reagent for CVD of ß-silicon carbide. The dominant pathway for decomposition of methylsilane is formation of dihydrogen and methylsilylene (CH_3SiH:). However, about 5-8% of the methylsilane decomposes along an alkane elimination path to yield a mixture of silylene, $:SiH_2$, and methane, CH_2.[2] In this latter pathway, the silicon-containing fragment is substantially more reactive than the carbon-containing fragment. The result is deposition of a silicon-rich product that is not pure stoichiometric ß-silicon carbide. Another candidate material, dimethyldisilane, $(CH_3SiH_2)_2$, suffers from the same problem. Neither of these materials is acceptable as a source for unimolecular deposition of beta silicon carbide.

Solutions to problems in CVD of electronic thin films require an understanding of the reaction mechanisms and reaction kinetics of new and existing source reagents. Rational design of source reagents through the coordination of studies in mechanistic organometallic chemistry with research in chemical engineering and electronic film growth is most likely to yield an optimum process.

Results

Synthesis of Single Molecule Source Reagents

Four source reagents were synthesized in Phase I: 1,4-disilabutane; 2-methyl-1,3-disilapropane; 1,1,3,3-tetrachloro-1,3-disilacyclobutane; and 1,3-disilacyclobutane (Figure 1). In addition, considerable effort was made to synthesize hexamethylcyclohexasilane, but we were unable to isolate this compound in pure form.

$H_3SiCH_2CH_2SiH_3$ $(H_3Si)_2CHCH_3$

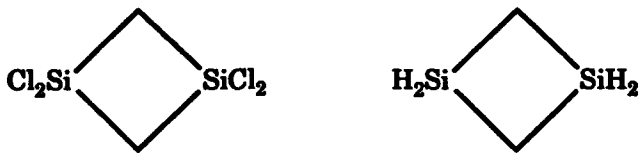

Figure 1. Single molecule source reagents

The synthetic routes to the single molecule source reagents followed literature procedures as shown in Figure 2.[1] 1,4-Disilabutane and 1,1,3,3-tetrachloro-1,3-disilacyclobutane were obtained in very high purity as shown by gas chromatography and nuclear magnetic resonance spectroscopy. The small quantities of 2-methyl-1,3-disilapropane and 1,3-disilacyclobutane which were isolated prevented rigorous purification procedures from being carried out. These materials were used as isolated, containing small amounts (1-5%) of other organosilane impurities.

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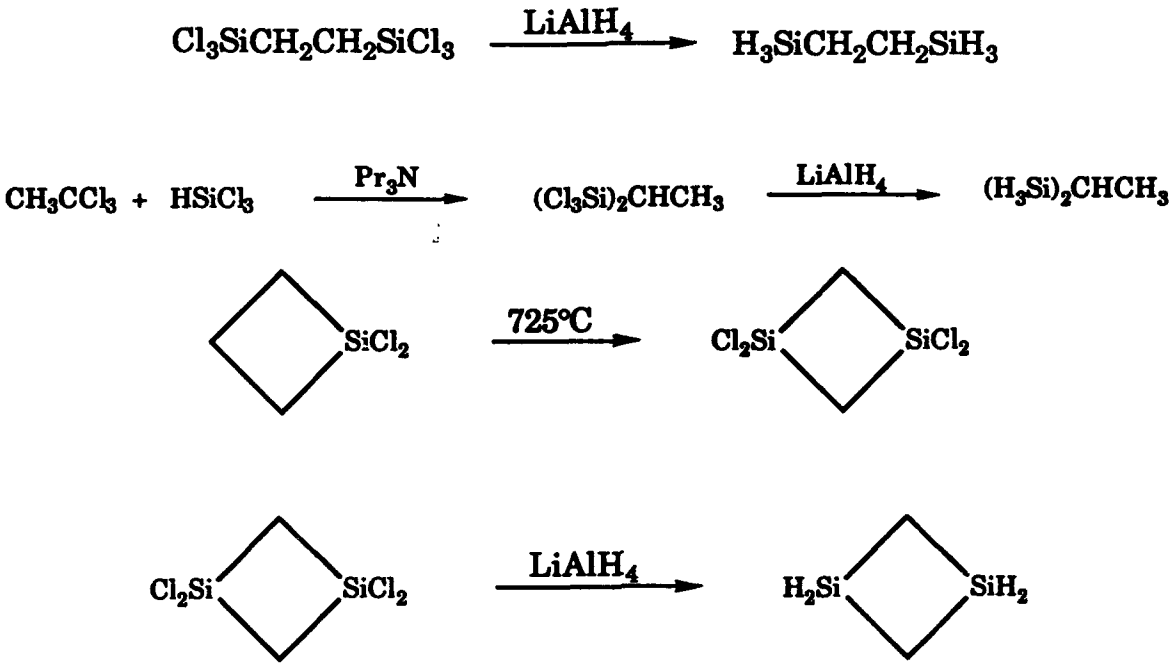


Figure 2. Synthetic routes to single molecule source reagents

Decomposition Studies

Decomposition studies of 1,4-disilabutane; 2-methyl-1,3-disilapropane; and 1,3-disilacyclobutane were carried out in the apparatus shown in Figure 3.

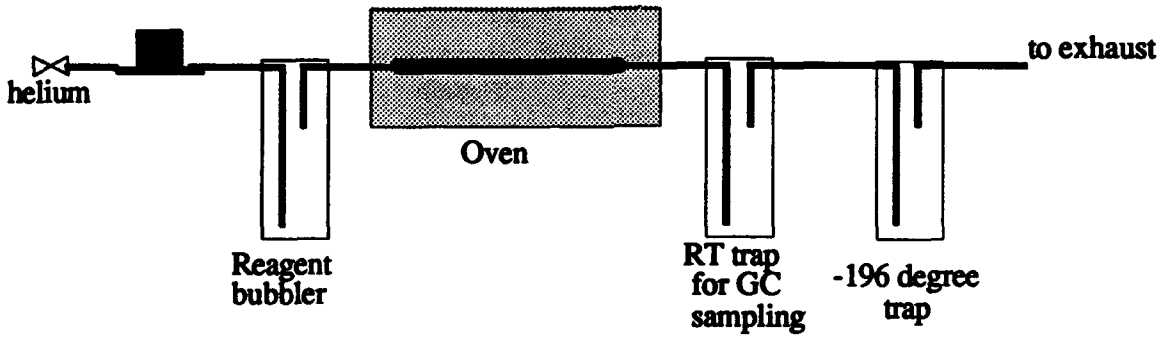


Figure 3. Schematic of the flow pyrolysis apparatus used in the study of the decomposition pathways of the organosilanes.

Decomposition of 1,4-disilabutane was carried out with the bubbler held at 20°, 0°, or -27°C, resulting in partial pressures of 280, 134, and 41 torr respectively. No significant differences were observed. For the other reagents only one concentration was used.

The room temperature trap was sampled with a gas-tight syringe and the products analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS). Two major decomposition products were observed, ethylene and ethylsilane. Graphs summarizing this data are shown below (Figure 4).

Small amounts of other products were also observed. These included ethane, silane, vinylsilane, 1,4-disila-2-butene and a product which has not been conclusively identified but appears to be the result of silylene (SiH_2) insertion into a molecule of starting disilabutane. These products can be explained by the sequence of reactions shown below (Scheme 1), all of which have precedent in the chemical literature. The silylene (SiH_2) species, in addition to undergoing insertion reactions, dimerize and eliminate hydrogen, eventually forming hydrogenated silicon which is deposited on the walls of the pyrolysis tube.

The graphs show that at higher temperatures the amount of ethylene produced decreases. This could have been due to ethylene decomposition or a change in reaction pathways resulting in the production of unstable intermediates that could not be detected by gas chromatography.

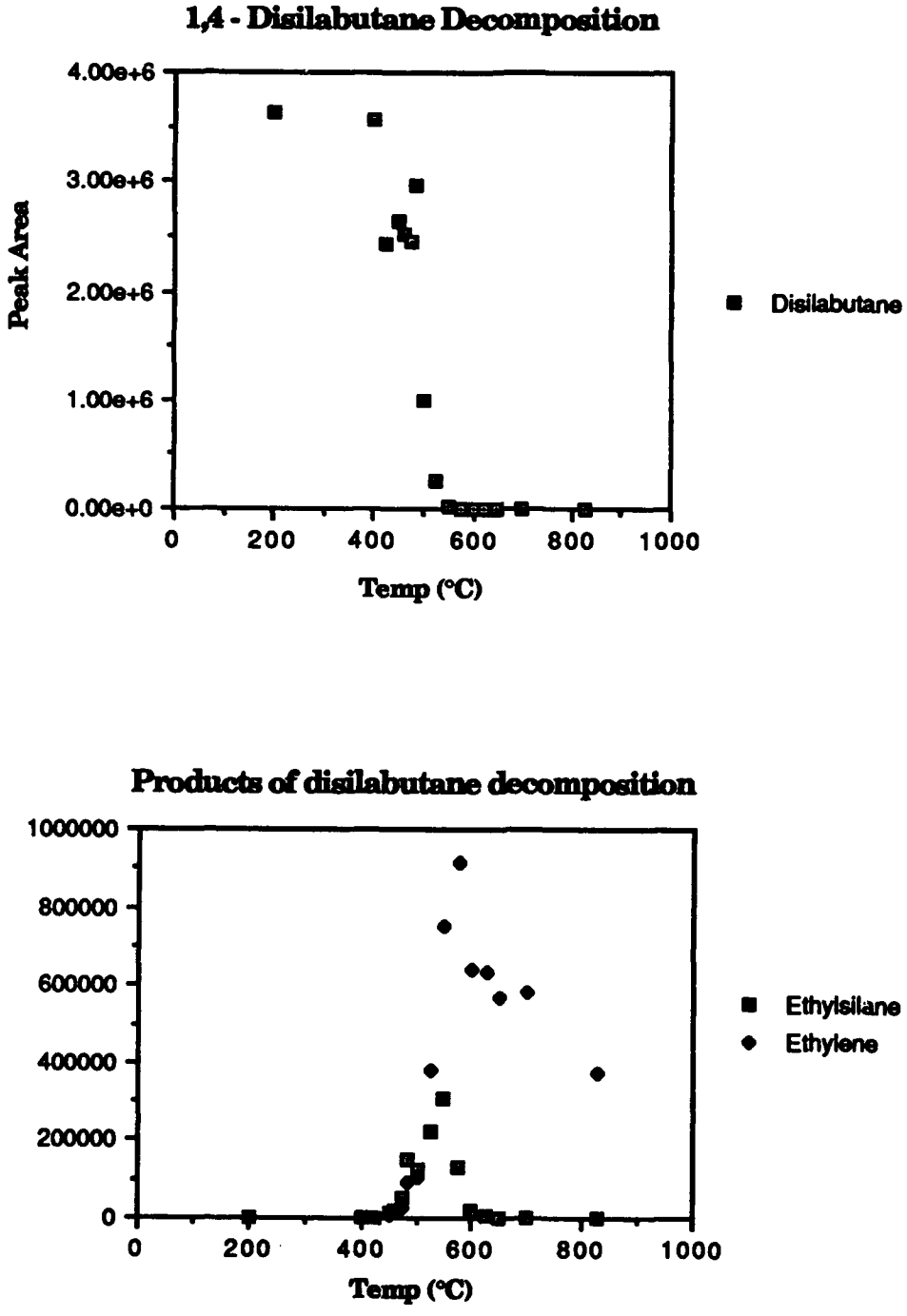
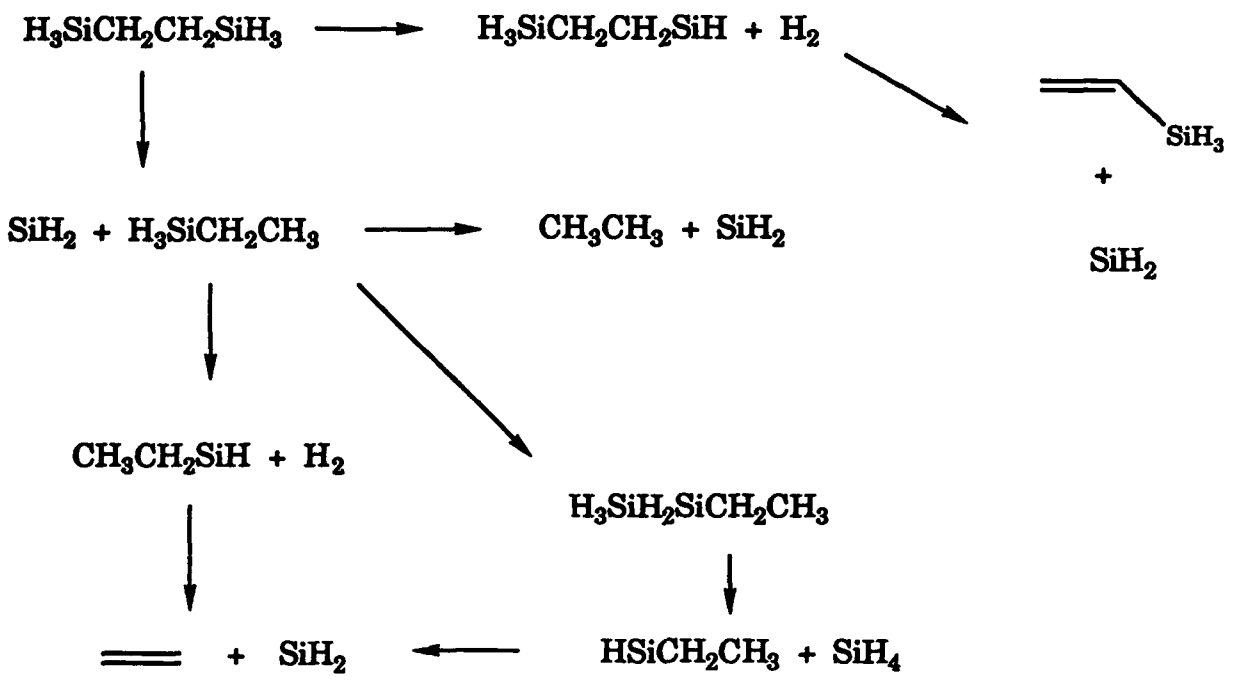


Figure 4. Decomposition products of 1,4-disilabutane



Scheme 1. Possible decomposition pathways for 1,4 - disilabutane

In hopes of further elucidating the decomposition mechanism, the decomposition was carried out in the presence of 2-methyl-1,3-butadiene (isoprene). 1,3-Dienes are known to be efficient traps for silylenes and silenes (e. g., CH_2=SiH_2). Upon reaction with dienes, silylenes typically yield silacyclopentenes and silenes yield silacyclohexenes.[2] Neither ring system was found in the effluent from 1,4-disilabutane pyrolysis in the presence of isoprene. Instead, lower volatility compounds were present whose masses were consistent with isoprene oligomers. Isoprene oligomerization did not occur under identical conditions in the absence of 1,4-disilabutane. Pyrolysis experiments using dihydrogen rather than helium as carrier gas revealed no significant changes in the product distribution.

Decomposition of 2-methyl-1,3-disilapropane an isomer of 1,4-disilabutane, also produced ethylene and ethylsilane as the major products (Figure 5).

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2 Davidson, I.M.T.; Fenton, A.; Ijadi-Maghsoodi, S.; Scampton, R.J. *Organometallics*, **1984**, *3*, 1593-95

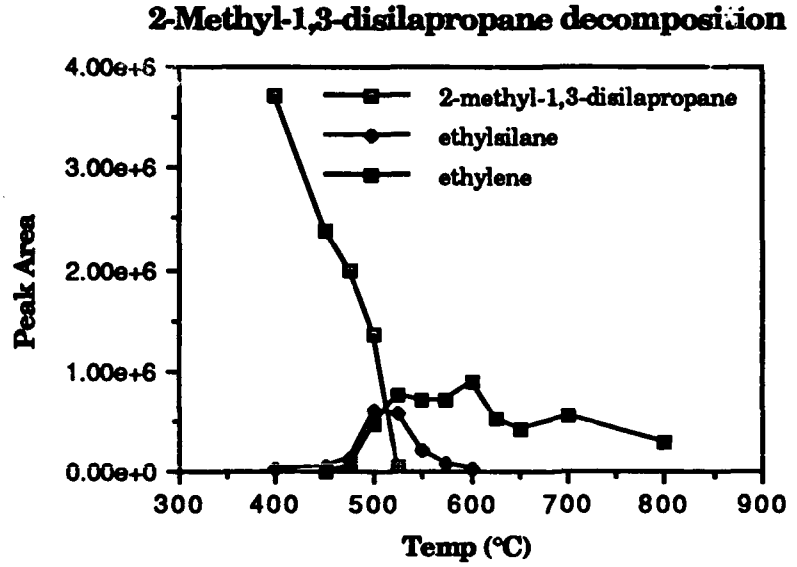

Figure 5. Product distribution as a function of temperature in the decomposition of 2-methyl-1,3-disilapropane

Decomposition of 1,3-disilacyclobutane produced methylsilane, dimethylsilane, trimethylsilane, 1,3-disilabutane, and ethylene as the major products (Figure 6).

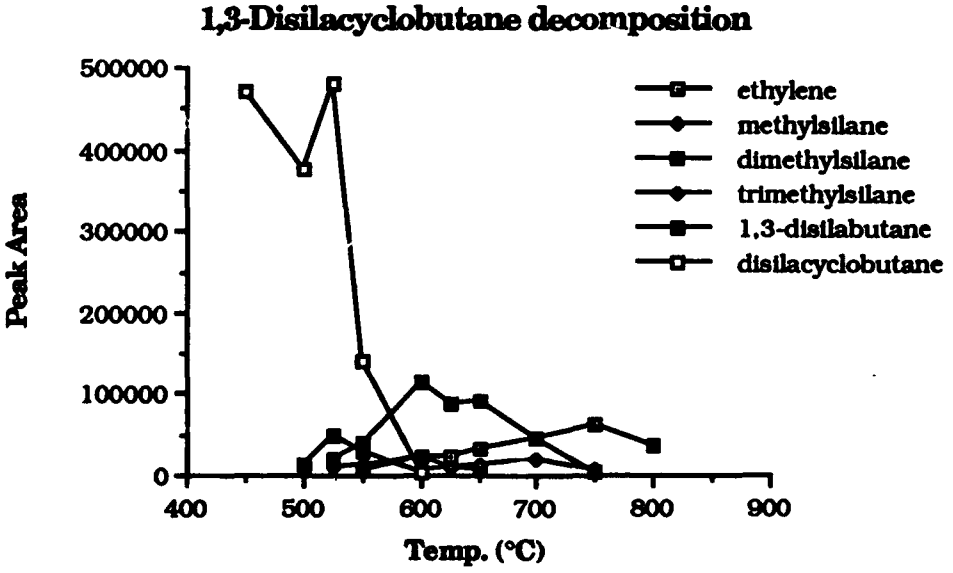

Figure 6. Product distribution as a function of temperature in the decomposition of 1,3-disilacyclobutane

These results are consistent with literature reports on the decomposition of this compound.[3]

The decomposition studies clearly shows that primary decomposition of the organosilanes proceeds at low temperature (<700°C). The nature of the film will therefore be determined by the identity of the reactive intermediates and stable by-products produced upon decomposition. As will be seen in the film growth studies, the production of a stable hydrocarbon by-product (e. g., ethylene) decreases the probability of silicon carbide growth at low temperature.

Film Growth

Film growth experiments were carried out with 1,1,3,3-tetrachloro-1,3-disilacyclobutane, 1,3-disilacyclobutane, and 1,4-disilabutane in the inverted vertical quartz reactor shown in Figure 7. There has been a recent report of chemical vapor deposition of beta-SiC from 1,3-disilacyclobutane.[4] To our knowledge there has been no previous work on beta-SiC deposition from 1,1,3,3-tetrachloro-1,3-disilacyclobutane. Due to the similarity seen in the decomposition of 1,4-disilabutane and 2-methyl-1,3-disilapropane film growth experiments were done only with the former compound which was available in much higher purity.

The Si substrate was given an *in-situ* surface cleaning in a hydrogen and HCl environment at 1060 °C for 10 minutes prior to film growth. After the cleaning procedure the reactor was purged with hydrogen and the substrate temperature was reduced to 100°C. After the substrate temperature reached 100°C, a 100 sccm flow rate of ethylene was introduced into the reactor for 4 minutes. After the ethylene flow stabilized, the temperature of the substrate was ramped from near room temperature to the film growth temperature. This sequence resulted in carbonization of the Si surface just prior to the start of the ß-SiC film growth. After 90 seconds the ethylene flow rate was either stopped or reduced to 5 sccm depending on the experiment and hydrogen carrier gas containing the reagent under investigation was introduced into the reactor. A graph summarizing this etch, carbonization, and growth procedure is shown in Figure 8.

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[3] Auner, N.; Davidson, I.M.T.; Ijadi-Maghsoodi, S.; Lawrence, F.T. *Organometallics*, **1986**, *5*, 431-435

[4] Larkin, D.J.; Interrante, L.V. *Chemistry of Materials* **1992**, *4*, 22-24.

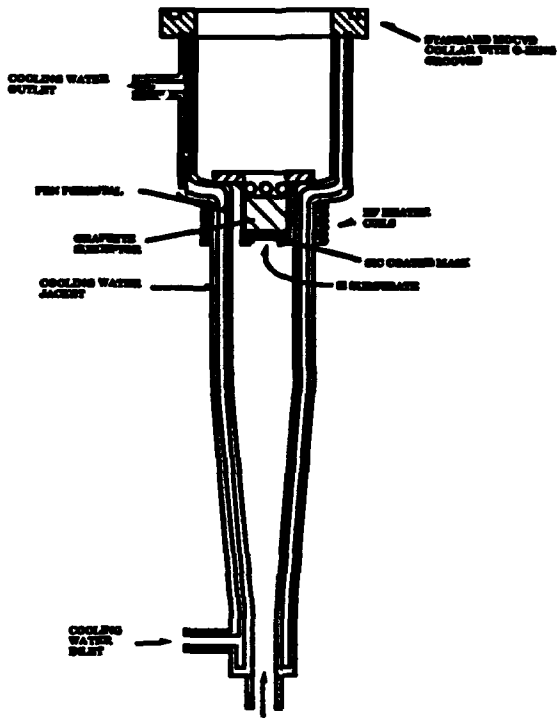

Figure 7. Schematic of the inverted vertical reactor used in the deposition of ß-SiC.

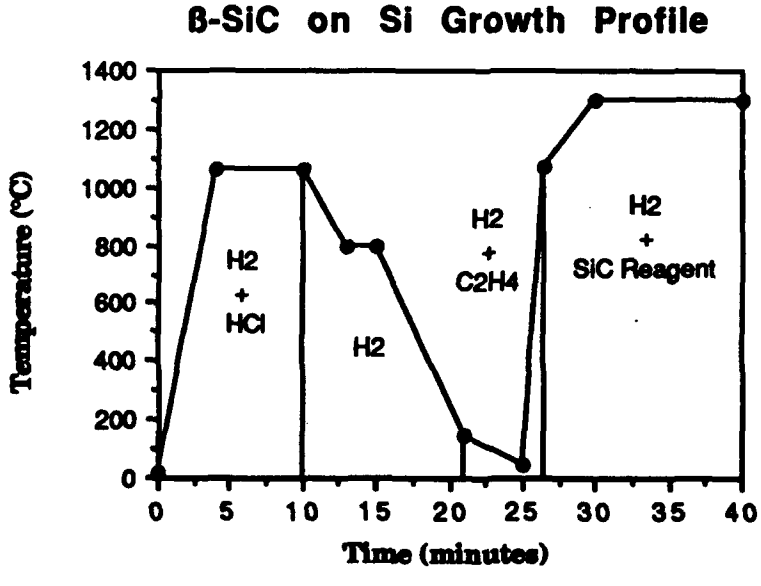

Figure 8. Reactor conditions profile for the growth of ß-SiC on silicon substrates.

Substrate temperatures were varied from 1000 to 1300°C. Carrier gas flow rates through the bubbler were adjusted to obtain similar growth rates (~1μm/hour) with each reagent. Flow rates were initially estimated based on approximate vapor pressures derived from boiling points, then adjusted based on the growth rates observed in the early experiments. Figure 9 summarizes growth runs.

1,4-Disilabutane Deposition Conditions

Run #	Substrate Temperature	Diluent Gas	C_2H_4 Flow Rate	Reagent Carrier Gas Flow Rate
92019	1000 °C	3.0 slm H_2	0.0 sccm	3.0 sccm
92018	1200 °C	3.0 slm H_2	0.0 sccm	3.0 sccm
-	1300 °C	3.0 slm H_2	0.0 sccm	3.0 sccm
92005	1300 °C	3.0 slm H_2	5.0 sccm	3.0 sccm
92008	1300 °C	3.0 slm Ar	0.0 sccm	3.0 sccm

1,1,3,3-Tetrachloro-1,3-disilacyclobutane Deposition Conditions

Run #	Substrate Temperature	Diluent Gas	C_2H_4 Flow Rate	Reagent Carrier Gas Flow Rate
91086	1000 °C	2.6 slm H_2	0.0 sccm	400 sccm
91085	1200 °C	2.6 slm H_2	0.0 sccm	400 sccm
91087	1300 °C	2.6 slm H_2	0.0 sccm	400 sccm
92001	1300 °C	2.6 slm H_2	5.0 sccm	400 sccm
92011	1300 °C	2.6 slm Ar	0.0 sccm	400 sccm

1,3-Disilacyclobutane Deposition Conditions

Run #	Substrate Temperature	Diluent Gas	C_2H_4 Flow Rate	Reagent Carrier Gas Flow Rate
92016	1000 °C	3.0 slm H_2	0.0 sccm	3.0 sccm
92014	1200 °C	3.0 slm H_2	0.0 sccm	3.0 sccm
92015	1300 °C	3.0 slm H_2	0.0 sccm	3.0 sccm
92016	1300 °C	3.0 slm H_2	5.0 sccm	3.0 sccm
92017	1300 °C	3.0 slm Ar	0.0 sccm	3.0 sccm

Figure 9. Deposition conditions for beta-SiC films

The quality of the deposited films was determined by visual inspection, reflectance Fourier Transform Infrared Spectroscopy (FTIR), and X-ray diffraction (XRD). Film roughness was determined using a Dectak II surface profilometer.

1,4-disilabutane and 1,1,3,3-tetrachloro-1,3-disilacyclobutane gave similar results in the film growth experiments. Both reagents gave poor quality films at the lower temperatures (1000°C). Films at these temperatures were rough, non-transparent and did not show interference fringe patterns in the FTIR spectra. Both reagents gave high quality films at 1300°C. Films were specular with clear XRD patterns showing the presence of crystalline beta-silicon carbide. (Figure 10).

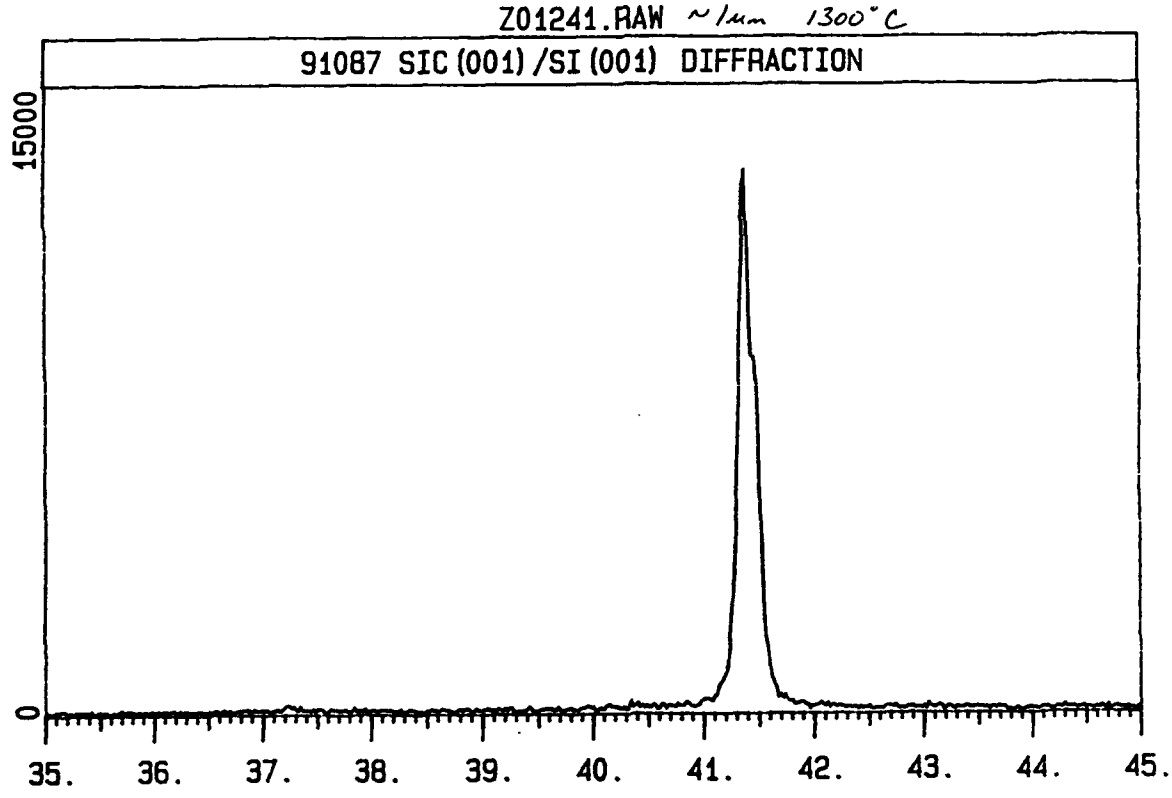

Figure 10. X-ray diffraction pattern of beta-SiC film deposited from 1,1,3,3-tetrachloro-1,3-disilacyclobutane

The best film was grown from tetrachlorodisilacyclobutane at 1300°C. An X-ray rocking curve measurement on this film showed the full width at half maximum (FWHM) to be 0.4° (Figure 11). A film grown with this reagent and a co-feed of ethylene (C_2H_4) showed the same FWHM but an improvement in visual specularity.

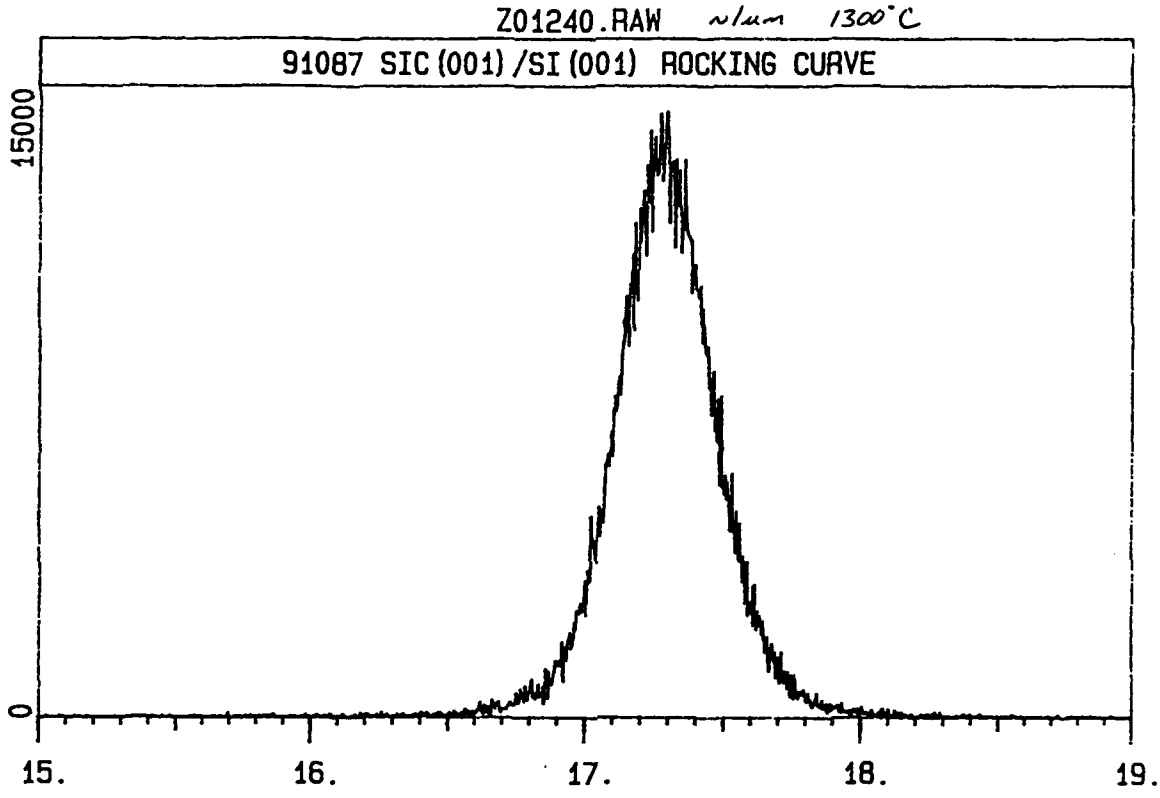

Figure 11. X-ray rocking curve of beta-SiC film deposited from 1,1,3,3-tetrachloro-1,3-disilacyclobutane

1,3-disilacyclobutane gave significantly different results than the other reagents. Films were slightly lower quality at 1300°C than with the other reagents yet a polycrystalline beta-SiC film could be grown from this reagent at 1000°C. This was the only film grown at 1000°C which showed interference patterns in the FTIR spectrum (Figure 12).

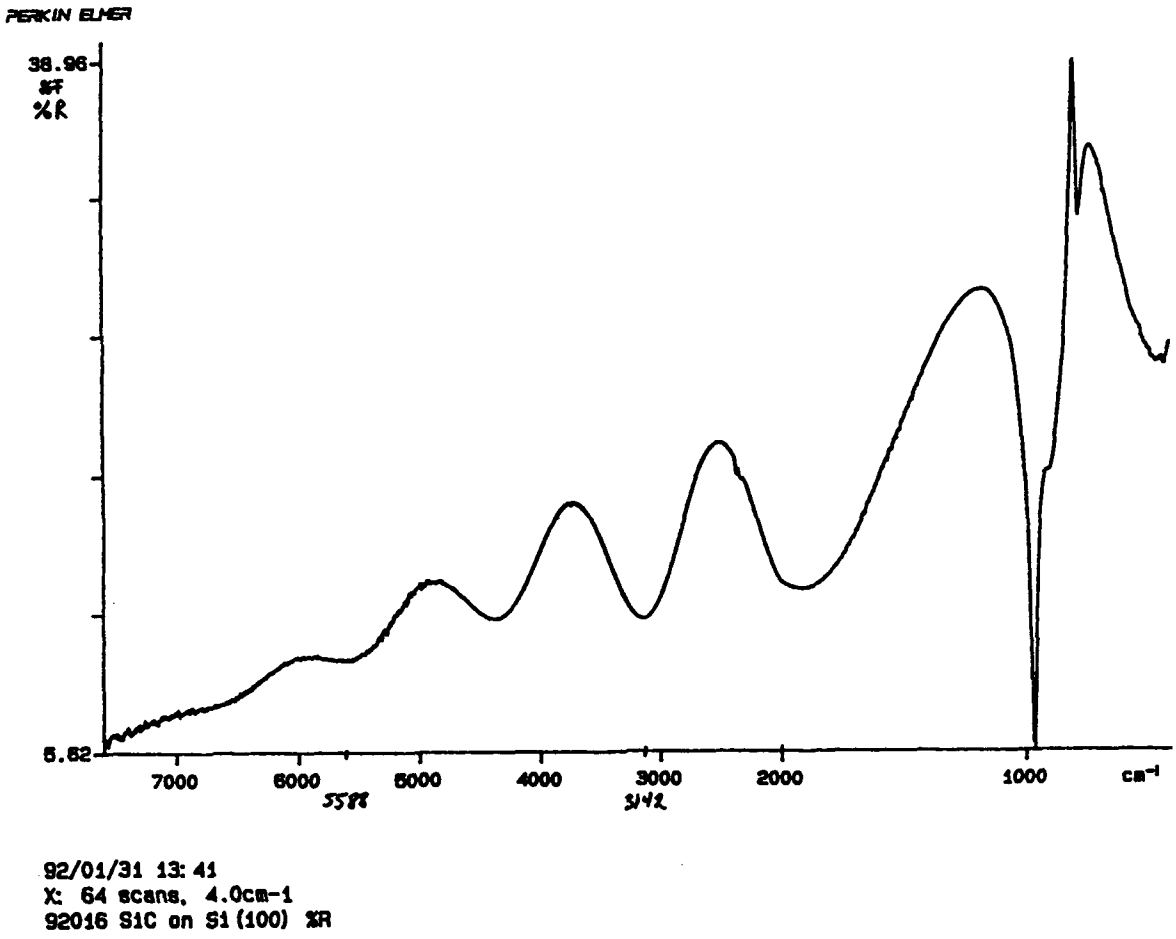

Figure 12. FTIR interference patterns from SiC film deposited at 1000°C from 1,3-disilacyclobutane

The lower quality of the films deposited at 1300°C is not understood. Impurities in the source gas or changes in decomposition pathways could be contributing to the decline in quality.

Technical Feasibility

Organosilanes offer a rich chemistry that can be exploited for specific process requirements. For example, using 1,4-disilabutane, silicon films can be grown at low temperature, carbon-doped silicon films at intermediate temperature and stoichiometric silicon carbide films at high temperature. The results of this study demonstrate that the molecular structure of the source reagent and surface mediated reactions are both important in the growth of ß-SiC. Detailed decomposition studies will be carried out in Phase II to build the paradigms for rational design of source reagents.

Deposition of ß-SiC from 1,3-disilacyclobutane at 1000°C, 300° lower temperature than with other source reagents, offers the potential of integrating silicon and silicon carbide device structures. Lower deposition temperatures are apparently possible due to the relief of ring strain upon decomposition. Other strained ring compounds may be envisioned that will decompose to yield more reactive intermediates that could yield crystalline silicon carbide at even lower temperature. Phase II will focus on the quality of thin film growth from stoichiometric precursors on silicon and silicon carbide substrates. Elementary devices will be built in SiC/Si structures for evaluation and comparison with previous work.

Since the organosilanes provide all the necessary silicon for silicon carbide, silane can be eliminated from the process. Elimination of silane from the process reduces the risk and hazards thereby reducing the capital and facility requirements. Replacement of silane by the organosilanes that do not contribute large amounts of carbon in tungsten (from the reduction of tungsten hexafluoride) or polysilicon film growth is an important opportunity. Collaborations will be established for evaluation of the reagents in Si-based applications in Phase II.

Experimental

Source Reagent Syntheses

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 was 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 crude product was collected. Impurities detected by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) were 1,1-bis(silyl)ethane and ethylsilane. Distillation of the mixture at 45-46° yielded the desired 1,4-disilabutane in >99% purity.

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°.

1,3-disilacyclobutane

Sublimed tetrachlorodisilacyclobutane (3.16g 0.014 ,moles) was added to a small addition funnel and an additional portion (10.0 g, 0.044 moles) was addded to a 125 mL Wheaton bottle in the drybox. Lithium aluminum hydride (2.6 g, 0.068 moles) was loaded into a solids addition tube. The solids addtition tube and the addition funnel were attached to a 500 mL 3-neck r.b. flask and removed to the hood. 25 mL of tetraglyme was used to dissolve the tetrachlorodisilacyclobutane in the funnel and another 100 mL of 4-glyme used to dissolve the 10 g. 100 mL of 4-glyme was added to the reaction flask which was then cooled to ~5 °C in an ice/water bath. The $LiAlH_4$ was added to the cold 4-glyme in small portions. Meanwhile, a trap was attached to the system, evacuated and dried with a heat gun. The trap was cooled to -78°C and the system was vented through this trap. The solutions of tetrachlorodisilacyclobutane were added dropwise via the addition funnel over 30 min. The reaction mixture was then stirred for an additional hour at room temperature. The trap was then cooled to -196 °C and the volatiles were transferred by several evacuate-equilibrate cycles. The volatiles were then transferred from the trap to a Kontes ampule. Yield: 1.9 g, 0.021 moles, 37%. GC/MS of the resulting colorless liquid revealed two impurities. An impurity which is more volatile than the product is likely a ring-opened species, while one of lower volatility appears to be $H_2Si(CH_2)_2SiHMe$.

1,1-bis(trichlorosilyl)ethane

A 3 L r.b. flask was oven dried, equipped with a large dry-ice condenser and gas adapters and purged with nitrogen. 20 mL (0.2 mol) of CH_3CCl_3 and 91 mL (0.9 mol) of $HSiCl_3$ were added to the flask. The condenser was charged with dry ice/isopropanol and then 100 mL of acetonitrile was added to the flask. 115 mL of triisopropylamine (0.6 mol) was added to the flask with stirring, which resulted in an exothermic reaction. After the temperature subsided, the flask was kept at ~60 °C using a heating mantle. Heating was stopped after 7 hrs and the solution left stirring overnight. Reflux was continued the following day. Analysis of an

aliquot by GC/MS suggested that the reaction was not complete and the reaction was stirred at room temp for two more days.

Addition of 500 mL of ether caused precipitation of Pr_3NHCl. The mixture was filtered through a fritted Schlenk filter using a wide-guage PTFE cannula. The solid was washed with 200 mL of ether and N2 purge was used to dry the solid. The solid was removed and weighed, yielding 59.5 g (55% of theoretical). The ether and volatile solvents were stripped from the reaction mixture by bubbling nitrogen through the flask and venting through a liquid N_2 trap. The liquid remaining was distilled under vacuum (45-47°/0.5 torr) to give ~10ml of a mixture of the desired product and Pr_3N. This mixture was used in the next reaction without further purification.

1,1-bis(silyl)ethane

In the drybox $LiAlH_4$ (4g, 0.105 moles) was loaded into a solids addition tube and the tube put onto a 2 L flask equipped with gas adapters. The flask was removed to the hood and 200 mL of tetraglyme was added. The $LiAlH_4$ was added to the tetraglyme in portions, while stirring, and the resulting suspension was cooled to 0°C with an ice bath. An all-glass connection was made from the flask to a liquid nitrogen trap which was purged and then opened to the system as the path to an oil bubbler vent-line. The mixture of $CH_3CH(SiCl_3)_2$ and Pr_3N (~10 mL) was added to this suspension dropwise via a narrow gauge cannula. The flask which contained the $CH_3CH(SiCl_3)_2$ was rinsed with 10 mL of tetraglyme and this also added to the reaction flask. The product was then vacuum transferred to the liq N_2 trap. During this step the contents of the reaction flask were maintained at room temperature, and the time the system spent under dynamic vacuum was limited so that product loss could be minimized. 4-5 ml of the desired product was isolated.

ß-SiC Film Growth

An inverted vertical reactor was used to deposit nominally undoped 3C-SiC on Si(100) substrates. Three inch diameter Si(100) wafers were cut into 1 inch squares. A Barrel Asher was used to remove organics from the surface of the Si wafers. The oxygen plasma cleaning lasted for 25 minutes at 250 W. The sample

was placed in a Nalgene beaker with 1:1 HF:deionized (D.I.) water solution for 1 minute at room temperature to remove any surface oxide before the wafer was placed into the reactor.

After the wafer completed the *ex-situ* cleaning process described above, it was mounted in the reactor. The reactor went through three pump and purge cycles with argon. The reactor leak rate was approximately 1 mTorr/min. The system was then purged with hydrogen at a flow rate of 2900 sccm for 30 minutes.

The Si substrate was given an *in-situ* surface cleaning in a hydrogen and HCl environment at 1060 °C for 10 minutes prior to film growth. The hydrogen flow rate was 2900 sccm and the HCl flow rate was 10 sccm. The HCl flow rate was turned off and the substrate temperature was decreased after the 10 minute etch.

After 6 minutes a 100 sccm flow rate of ethylene was introduced into the reactor for 4 minutes. This resulted in a carbonization of the Si surface just prior to the start of the 3C-SiC film growth. The temperature of the substrate during this time was ramped from near room temperature to the film growth temperature.

The temperature of the substrate was varied between 1000 °C and 1300 °C. After 90 seconds the ethylene flow rate was either stopped or reduced to 5 sccm depending on the experiment. Hydrogen carrier gas was bubbled through the desired source reagent at the rates shown in Figure 9.