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# Chemical Synthesis of Metastable Germanium−Carbon Alloys Grown Heteroepitaxially on (100) Si

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High-quality diamond-structured $Ge_{1-x}C_x$ alloys have been grown on (100) Si using ultrahigh-vacuum chemical vapor deposition techniques and novel chemical precursors. Two-dimensional growth of single-crystal heteroepitaxial layers (30−120 nm thick) of germanium−carbon alloys with carbon concentrations up to 7% has been achieved by reactions of $GeH_4$ with germylmethanes, $(GeH_3)_{4-x}CH_x$ ($x = 1-3$), at 470 °C. The composition of the materials was established by extensive Rutherford backscattering (RBS) carbon resonance analysis, and the layer crystallinity was characterized by cross-sectional transmission electron microscopy and RBS channeling experiments. RBS ion channeling revealed that the carbon primarily occupied substitutional sites in the diamond-like Ge lattice. Alloys with low carbon content displayed virtually perfect crystallinity whereas materials with high carbon incorporation had structural defects in the form of {111} stacking faults and microtwins. The thin film microstructure of a given alloy composition was independent of the precursor, but the efficiency of carbon incorporation increased dramatically as the number of $GeH_3$ moieties in the precursor increased. Further characterization by Auger electron spectroscopy and secondary ion mass spectrometry showed that the materials were pure and highly homogeneous, and electron energy loss spectroscopy indicated $sp^3$ hybridized diamond-like carbon. The synthesis and characterization of novel (trihalogermyl)methane compounds such as $(Br_3Ge)_3CH$ and $(Cl_2XGe)_2CH_2$ (X = Cl, Br, or I) and their reactions with $LiAlH_4$ to produce the corresponding hydrides is also reported.

## Introduction

Modern device design and fabrication is intimately associated with the concept of bandgap engineering. This concept has been extensively applied to realize practical goals such as the creation of light-emitting and laser diodes that emit light at specific wavelengths, faster transistors, and a series of other novel electronic devices using group III−V semiconductors. Integrated microelectronics, however, primarily rely on the unique properties of silicon and its native oxide. The synthesis of bandgap engineered epitaxial materials on Si is important for future generations of high-speed devices. The focus has been primarily on the Si−Ge equilibrium alloy system, and heterojunction bipolar transistors based on $Si_{1-x}Ge_x$ alloys and strained-layer superlattices have been successfully integrated with Si technology.[1−3]

Other crystalline group IV binary and ternary diamond-like alloys remain unexplored. A major limitation for their formation is the large difference in covalent radii among the elements, ranging from 0.77 Å for C to 1.40 Å for Sn. Another limitation is that the diamond structure is stable for Si and Ge at room temperature and normal pressures, metastable for C, and only stable up to near room temperature for α-Sn. For these reasons most alloys and ordered phases involving combinations of C, Si, Ge, and Sn are at best metastable. Only SiC with its numerous polytypes and Si−Ge are thermodynamically stable systems that have been thoroughly studied.

Despite the metastability of group IV alloys, intense efforts are under way to produce materials that might combine the unique and exciting properties that the group IV elements are known to possess. These properties include the highest thermal conductivity (diamond), high hole mobility (Ge), bandgap variation from 5.5 to 0 eV, and widespread technological applications (Si). A major challenge for group IV alloy or compound formation is the development of novel synthetic methods that can yield device quality materials under metastable conditions.

The successful creation of bandgap-engineered heterojunction bipolar transistors using $Si_{1-x}Ge_x$ alloys has led to tremendous interest in $Si_{1-x-y}Ge_xC_y$ alloys. Syntheses of a few compositions with low C content in the $Si_{1-x-y}Ge_xC_y$ alloy system have been achieved by kinetically favored, low-temperature chemical vapor deposi-

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tion (CVD) processes that utilize inorganic precursors[4−6] and by various beam deposition and implantation techniques.[7,8] The motivation of this work is to develop an epitaxial material that is lattice matched with Si and capable of bandgap engineering, compatible with group IV ULSI processing technology. The incorporation of carbon in sufficient amounts into SiGe alloys may result in an increase in the bandgap to values greater than those of SiGe and Si.[9] In addition, it may be possible to reduce the inherent lattice mismatch between SiGe and Si with the smaller size of carbon compensating for the larger size of germanium.[10]

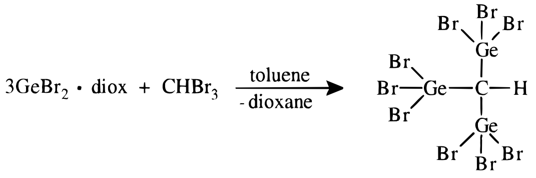
A closely related but much simpler binary material that has potential for Si-based bandgap engineering as well as lattice matching with Si substrates is the $Ge_{1-x}C_x$ alloy system. This thermodynamically unstable material may have compositions with bandgaps larger than those of current SiGe systems, which would then have important applications in high-speed heterojunction bipolar transistors and optoelectronics. In addition, the presence of carbon in the lattice should theoretically reduce the lattice mismatch between Ge and Si that limits the growth of pure Ge epitaxial layers on Si.

$Ge_{1-x}C_x$ hybrids of diamond and germanium are much harder to prepare than $Si_{1-x-y}Ge_xC_y$ alloys because of the metastability of the Ge−C bond in the solid state with respect to Ge and graphite. As a result of this instability, the equilibrium solubility of C in Ge is negligible at all temperatures and pressures, and a crystalline GeC analog of SiC has not yet been prepared. Routes to produce random alloy compositions in the form of epitaxial thin films are of much interest because virtually nothing is known about $Ge_{1-x}C_x$. Impurity (Sb) mediated growth of epitaxial $Ge_{1-x}C_x$ thin films with carbon concentrations of approximately 1 at. % by molecular beam epitaxy (MBE) methods was recently reported,[11,12] and another MBE study also resulted in similar materials.[13] Most recently, a detailed investigation using similar synthetic techniques described deposition of Ge−C films on Si that contained small epitaxial domains imbedded in an amorphous matrix.[14] Electron microscope analysis of the crystalline regions indicated a lattice parameter indistinguishable from that of pure Ge.[14]

Our work has been directed toward the development of new low-temperature synthetic methods involving ultrahigh-vacuum chemical vapor deposition (UHV-CVD) and germanium−carbon precursors to grow crystalline Ge−C alloys with substantial carbon incorporation (5−10 at. %). Success would allow us to study systematically the effects of varying carbon content on the lattice constant and the band structure. Successful syntheses of high-quality heteroepitaxial $Si_{1-x-y}Ge_xC_y$ ($y = 0.01-0.06$) alloys by chemical vapor deposition have utilized silylmethanes such as $CH_3SiH_3$ and $C(SiH_3)_4$ as precursors.[5,6] Analogous germylmethanes might then be ideal precursors for deposition of $Ge_{1-x}C_x$ alloys that contain substantial amount of carbon. We have explored in detail reactions of $GeH_4$ with three different Ge−C molecules, namely, methylgermane, digermylmethane, and trigermylmethane, to deposit single-crystal-quality heteroepitaxial Ge/C alloys with C concentrations of up to 7%. In this report we describe the material resulting from these reactions and the corresponding deposition procedures. We also describe the synthesis of $(GeH_3)_3CH$ (**1,** trigermylmethane) via reduction of the novel tris(tribromogermyl)methane ($(GeBr_3)_3CH$, **2**) as well as new and convenient synthetic methods to produce $GeH_3CH_3$ (**3**, methylgermane) and $(GeH_3)_2CH_2$ (**4**, digermylmethane).

## Results

**Precursor Synthesis.** We synthesized $(GeBr_3)_3CH$ (**2**) in 85% yield by complete insertion reactions of the $GeBr_2$·dioxane complex into the C−Br bonds of $HCBr_3$ as shown below.



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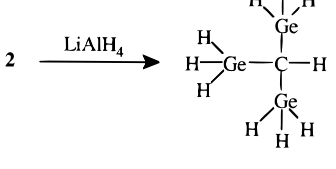
Compound **2** is a colorless, air-sensitive solid that is highly soluble in organic solvents and melts without decomposition at 150 °C. Its infrared spectrum is very simple. It shows two strong absorptions at 685 and 340 cm$^{-1}$ which are assigned to the Ge−C and Ge−Br stretching modes respectively. The other absorptions at 1020 cm-1 and 510 cm$^{-1}$ are attributed to C−H wagging and Ge−C bending modes. The compound is volatile in the mass spectrometer and it displays well-defined isotopic envelopes for ($M^+ - Br$) the strongest peak, ($M^+ - GeBr_3$) and ($M^+ - GeBr_4$). Additional evidence for **2** is provided by elemental analysis, as well as the $^{13}C$ (40.87 ppm, singlet) and $^1H$ (3.54 ppm, singlet) NMR spectra, which indicate the presence of a single carbon center bonded to one hydrogen atom. Reduction of **2** with $LiAlH_4$ under conditions similar to those used in the synthesis of $(SiH_3)_4C$[15] yield $(GeH_3)_3$-CH (**1**) in 15−20% yield.



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Compound **1** has also been isolated in very small quantities (2−3% yield) as a byproduct from the syn-

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thesis of $(GeH_3)_4C$.[16] It is a stable, colorless liquid, and its relatively high volatility, 20 Torr at 22 °C, makes it highly suitable for low-pressure CVD experiments.

In a similar manner, digermylmethane ($(GeH_3)_2CH_2$, **4)** was prepared by $LiAlH_4$ reduction of the corresponding $(GeX_3)_2CH_2$ (X = Cl, I) bis(trihalo)germylmethanes. The insertion reaction of the $GeCl_2$·dioxane complex into the C−I bonds of diiodomethane, $CH_2I_2$, gives primarily $(GeCl_2I)_2CH_2$ as a mobile liquid at 80% yield. This compound is, however, unstable. Over time, it decomposes via halide exchange to give other bis(trihalogermyl)methanes such as $(GeCl_3)_2CH_2$, $(GeCl_2I)CH_2(GeCl_3)$, and $(Ge_2Cl_3I_3)CH_2$ as indicated by NMR analysis. Mass spectroscopic examinations of the products reveal well-defined isotopic envelopes for the series of ions with composition $[CH_2Ge_2I_{5-x}Cl_x]^+$ ($x = 0-5$). The observation of these ions is likely to be a result of intermolecular halide scrambling in the gas phase. The molecules are also characterized by FTIR and NMR spectroscopies. In situ reduction of the bis(trihalogermyl)methane mixture with $LiAlH_4$ in butyl ether yields $(GeH_3)_2CH_2$ (**4**) in 30−35% yield. Compound **4** has been previously prepared by reaction of $KGeH_3$ with $I_2CH_2$ (2% yield) and by reduction of $(GeCl_3)_2CH_2$ (30% yield).[17] Our approach offers a more convenient synthetic method to **4** because routes to $CH_2(GeCl_3)_2$ are difficult and produce low yields of the compound.[18]

We obtained $CH_3GeH_3$ (**3**) by the reaction of potassium germyl ($KGeH_3$) and methyl iodide at nearly quantitative yields (a similar but lower yield preparation is described by Jolly et al.[19] ):

$$KGeH_3 + CH_3I \rightarrow KI + CH_3GeH_3 \qquad (3)$$

$KGeH_3$ requires special care because it decomposes explosively. For this reason we describe a new and safer synthetic route to **3** involving reductions of methyl trihalogermanes $CH_3GeI_{3-x}Cl_x$ ($x = 0-3$) with $LiAlH_4$. These are prepared by insertion of $GeCl_2$·dioxane into $CH_3I$ to yield a mixture of products in the approximate molar concentrations of $CH_3GeI_3$ (34%), $CH_3GeI_2Cl$ (40%), $CH_3GeICl_2$ (15%), and $CH_3GeCl_3$ (10%). These compounds have been identified by their $^1H$ NMR (singlets at 2.67, 2.22, 1.85, and 1.55 ppm, respectively)[18,20] and mass spectra ($M^+$ at $m/e = 469, 377, 286$, and 194, respectively). In situ reduction of the above mixture yielded **5** in 35% yield.

**Film Deposition and Characterization Using $GeH_3CH_3$.** The deposition process described here is similar to the one developed for epitaxial growth of $Si_{1-x-y}Ge_xC_y$ films at $T < 500$ °C.[5] The UHV-CVD system is a load-locked, resistively heated (with a three-zone resistance furnace) hot-wall CVD reactor, equipped with a differentially pumped mass spectrometer, fitted for in situ gas sampling. The pumping system consists of a turbomolecular pump that is used to obtain UHV before and after each deposition (base pressure of $(8-9) \times 10^{-9}$ Torr) and another corrosion-resistant turbo pump used during deposition. The single-crystal (100)-Si wafers were first RCA prepared in a clean room and then dipped in 10% hydrofluoric acid until the surface became hydroscopic. The substrates were loaded on a quartz boat, pumped in the load lock to $10^{-6}$ Torr and then passed into the reactor under a flow of ultrahigh-purity $H_2$. At this point, the pumping had been switched to the process pump, and the reactor had been heated to the deposition temperature, typically 450−500 °C, under a flow of $H_2$. A short time after the substrates were inserted into the preheated reactor, the reactants were introduced, intermixed with a large excess of $H_2$ through calibrated mass flow controllers. We find that, in addition to having UHV base pressure prior to deposition, commencement of growth almost immediately after the substrates have reached thermal equilibrium is an important condition for sustaining the clean interface that is essential for epitaxial growth.

CVD synthesis of crystalline $Si_{1-x-y}Ge_xC_y$ ($y = 0.02$) has been achieved by reactions of silane with methylsilane, which is the simplest silicon−carbon molecule containing a preformed Si−C bond. We envisaged that a convenient route to $Ge_{1-x}C_x$ with low C concentrations might involve reactions of the analogous methylgermane with germane gas. Gaseous $GeH_3CH_3$ did not show any indications of decomposition at temperatures as high as 750 °C under our deposition conditions. However, it reacts readily with $GeH_4$ on (100)Si to yield single-crystal heteroepitaxial Ge−C alloys at 470 °C and $2 \times 10^{-4}$ Torr. The duration of the deposition time was typically 2−3.5 h, yielding films with thickness ranging from 30 to 125 nm. The deposition rate decreased from 0.6 to 0.2 nm/min as the C content increased from 2 to 7 at. %. The C concentration in the films was dependent on the gas ratio of $CH_3GeH_3$ and $GeH_4$ with the higher ratio resulting in higher C incorporation in the films. We determined that an approximate $GeH_3CH_3$:$GeH_4$ reactant ratio of 1:1 was needed to obtain 6 at. % C incorporation, whereas a much lower ratio of 1:15 resulted in 2 at. % carbon.

The carbon concentration in all samples was determined by Rutherford backscattering spectroscopic analysis utilizing an elastic carbon resonance reaction $^{12}C(\alpha,\alpha)^{12}C$ with a 4.28 MeV beam of $He^{2+}$ ions. This technique enhances the carbon signal 125-fold and quantifies C contents as low as 0.5% (it is the preferred and most accurate method for measuring C content in semiconductor alloys). We acquired the RBS spectra with the sample normal to the beam and also with the sample inclined at 30°. The low-angle data allowed us to differentiate the surface carbon from the bulk signal. The surface carbon was then subtracted from the bulk in order to obtain the most accurate carbon measurement. Figure 1 shows typical resonance profiles for various samples with different carbon contents that were modeled using the program RUMP. Ion-channeled spectra of selected samples were also obtained and showed a substantial decrease in the carbon signal relative to the channeled signal, indicating that the carbon primarily occupied substitutional sites in the diamond-like Ge lattice.

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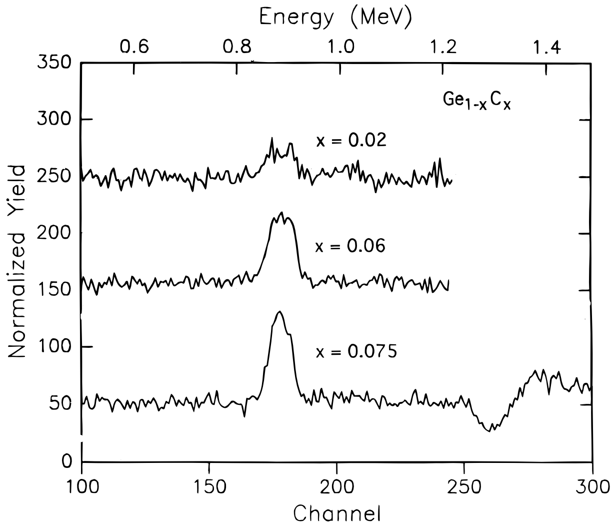

**Figure 1.** Rutherford backscattering spectrometry (RBS) carbon random spectra for $Ge_{1-x}C_x$ alloys, $x = 0.02, 0.06, 0.075$. Spectra obtained with 4.3 MeV He ions utilizing $^{12}C(\alpha,\alpha)^{12}C$ resonance reaction that allows measurement of C contents as low as 0.5%.

RBS in the random and channeling modes utilizing 2 MeV $He^{2+}$ ions were also used to determine thickness, Ge concentration, and crystallinity. Figure 2a shows the RBS random and the (100) channeled spectra for a sample containing 1.5−2% carbon. The measured value for $\chi_{min}$ ranges from 0.12 to 0.25 with the higher value obtained near the Si interface. The dechanneling observed close to the interface indicates the presence of crystal defects that do not extend throughout the layer. The dechannelling increased with increasing carbon content. Figures 2b,c show the RBS-channeled spectrum for samples of $Ge_{0.97}C_{0.03}$ and $Ge_{0.95}C_{0.05}$ with $\chi_{min}$ of 0.36 and 0.42, respectively. The latter spectrum shows dechanneling throughout the layer and suggests much higher defect densities.

Complementary transmission electron microscopy observations were made by using a 400 kV JEM-4000 EX high-resolution electron microscope (HREM). All samples showed layers that were entirely crystalline and heteroepitaxial. For the low-carbon samples, defects in the form of {111} stacking faults and twins were observed primarily near the $Ge_{1-x}C_x$/Si interface, but the remainder of the layer was comparatively defect-free. For the higher C samples (4−7 at. %), stacking faults were observed throughout the layer, confirming the dechanneling indicated by the ion channeling experiments. A typical high-resolution cross-sectional electron micrograph of the interface region demonstrating the heteroepitaxial growth of a high-quality $Ge_{0.98}C_{0.02}$ film is shown in Figure 3. Selected-area electron diffraction (SAED) patterns showed that the material had the diamond cubic structure. An example for $Ge_{0.97}C_{0.03}$ is shown in Figure 4. Optical diffractogram analysis (by Fourier transform of the lattice-fringe images) revealed an average lattice parameter slightly lower than that of pure Ge, suggesting that the carbon occupied substitutional sites in the Ge lattice. Diffraction data of samples containing 5−6% C indicated a lattice constant $a = 0.554$ nm ($a_{Si} = 0.543$ nm, $a_{Ge} = 0.565$ nm).

Examinations by electron energy loss spectroscopy (EELS) using a Phillips 400ST field emission gun

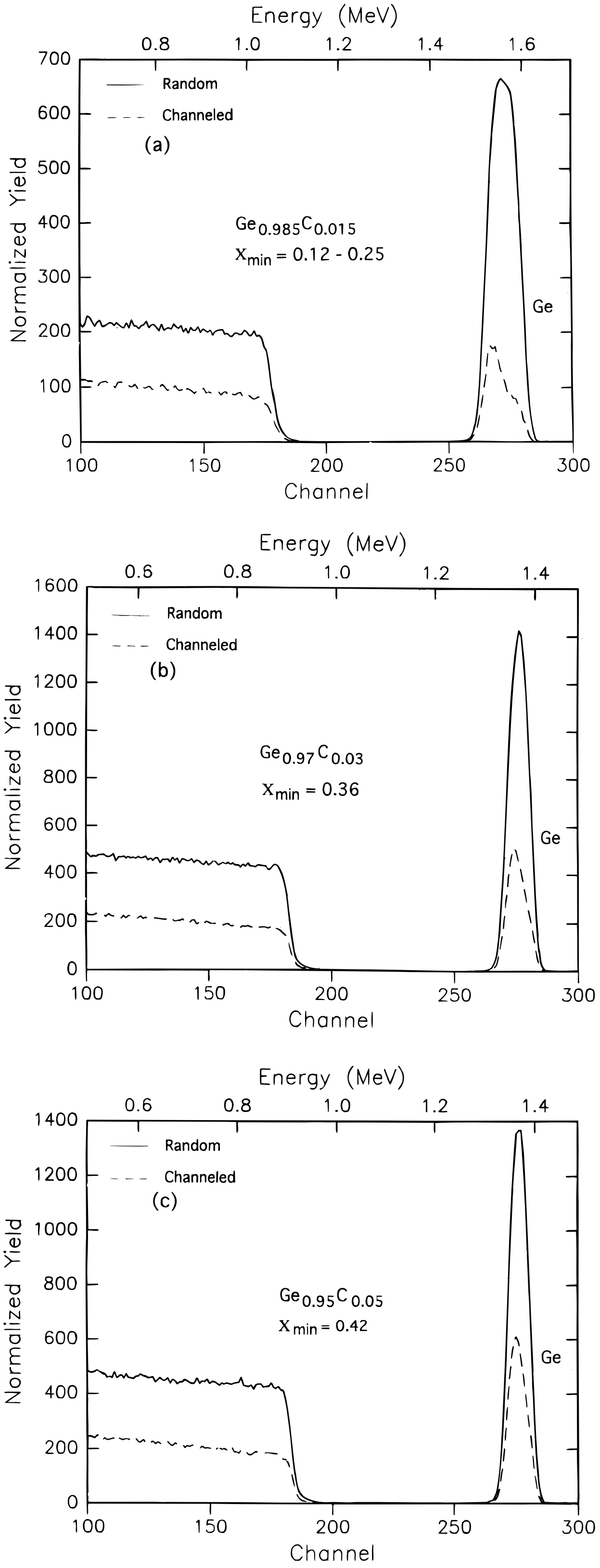

**Figure 2.** The 2.0 MeV $He^{2+}$ random and (100) channeled spectra for (a) $Ce_{0.985}C_{0.015}$ , (b) $Ge_{0.97}C_{0.03}$, and (c) $Ce_{0.95}C_{0.05}$. Dechanneling observed near interface in spectrum (a) suggests the presence of misfit dislocations. Dechanneling increased with increasing carbon content as visible in (b) 3% C and (c) 5% C.

transmission electron microscope (TEM) equipped with a parallel electron energy loss spectrometer confirmed the presence of carbon throughout the film and sug-

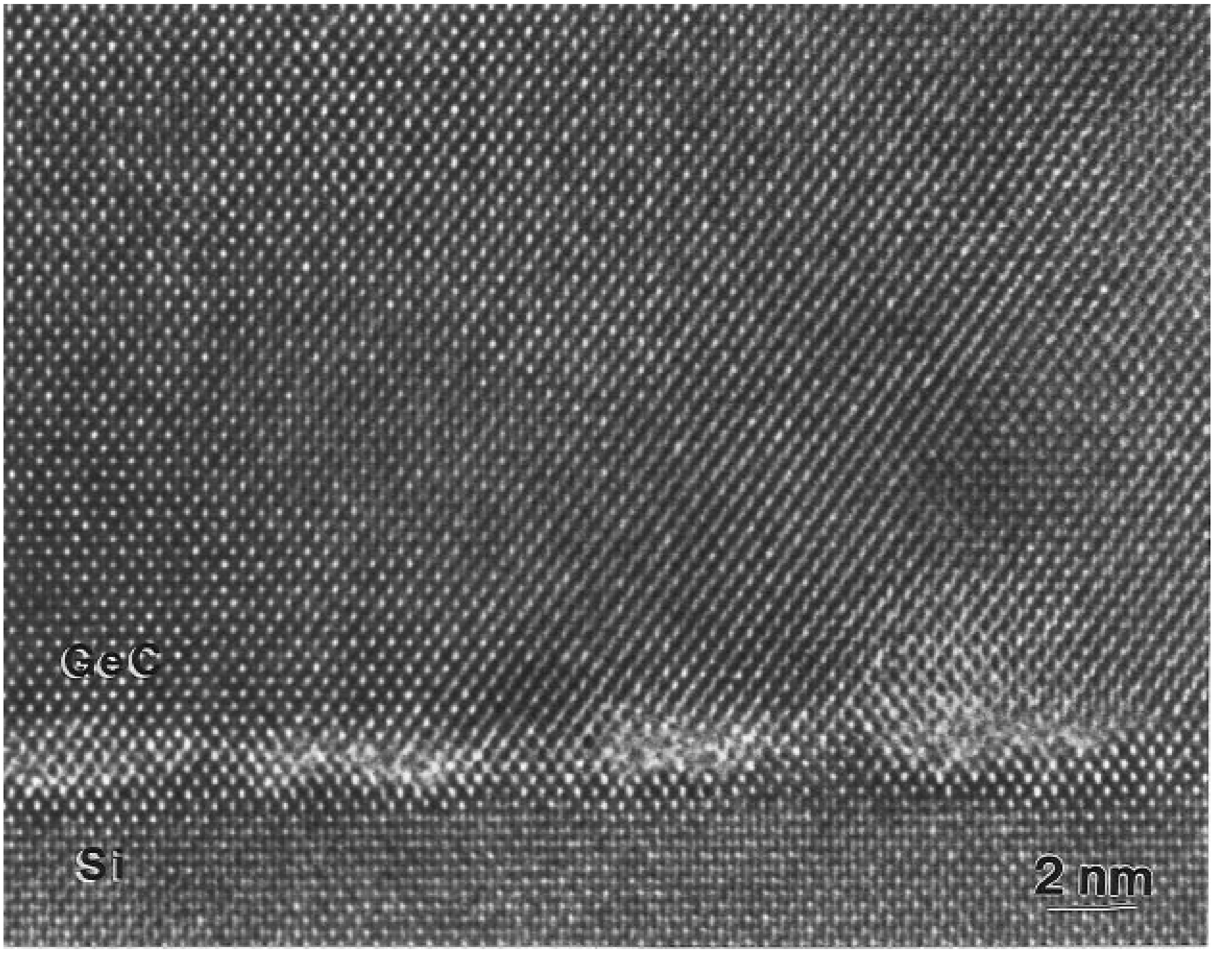

**Figure 3.** Cross-sectional transmission electron micrograph showing interface of $Ge_{1-x}C_x$/Si layer with 98 at. % Ge and 2 at. % C. Material prepared by reaction of $CH_3GeH_3$ with $GeH_4$ at 470 °C. Low growth temperature and relatively low growth rate of 0.5−0.6 nm/min yield nearly perfect epitaxy.

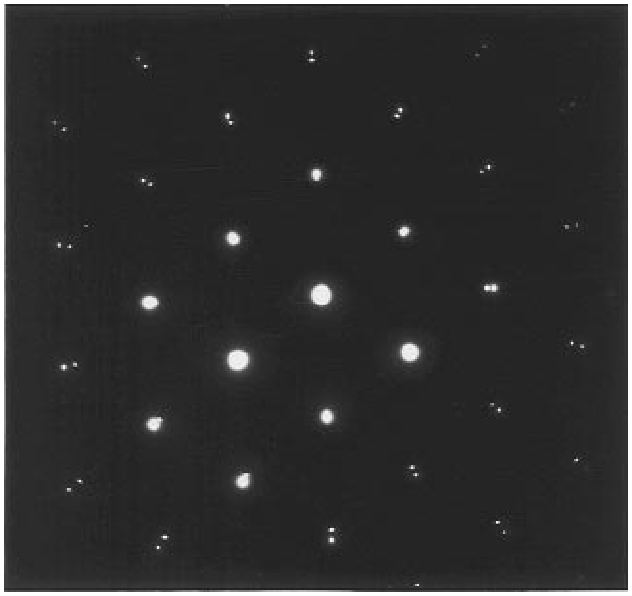

**Figure 4.** Typical selected area electron diffraction pattern of $Ge_{0.97}C_{0.03}$/Si showing highly ordered $Ge_{1-x}C_x$ layer with diamond cubic structure.

gested that the C was $sp^3$ hybridized. Systematic analysis of areas less than 2 nm in diameter using cross-sectional TEM samples of specimens with high carbon contents (approximately 7 at. % C) revealed that the carbon K-shell ionization edge featured a broad peak that is attributable to $\sigma^*$ transitions. It clearly did not contain any $\pi^*$ transitions, which are characteristic of $sp^2$ hybridization.

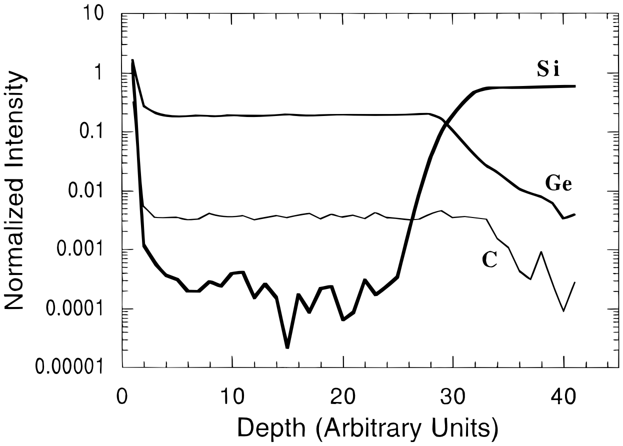

**Figure 5.** SIMS profile of C, Ge, and Si in $Ge_{0.97}C_{0.03}$.

Secondary ion mass spectrometry (SIMS) results from selected films showed that the Ge and C elemental contents were constant throughout the films and that the samples were essentially free of impurities. A representative SIMS profile of a $Ge_{0.97}C_{0.03}$ film is presented in Figure 5. Auger elemental profiles confirmed the presence of carbon and also showed that the films were pure and highly homogeneous.

**Film Deposition by Use of $(GeH_3)_2CH_2$ and $(GeH_3)_3CH$.** Our second approach for depositing $Ge_{1-x}C_x$

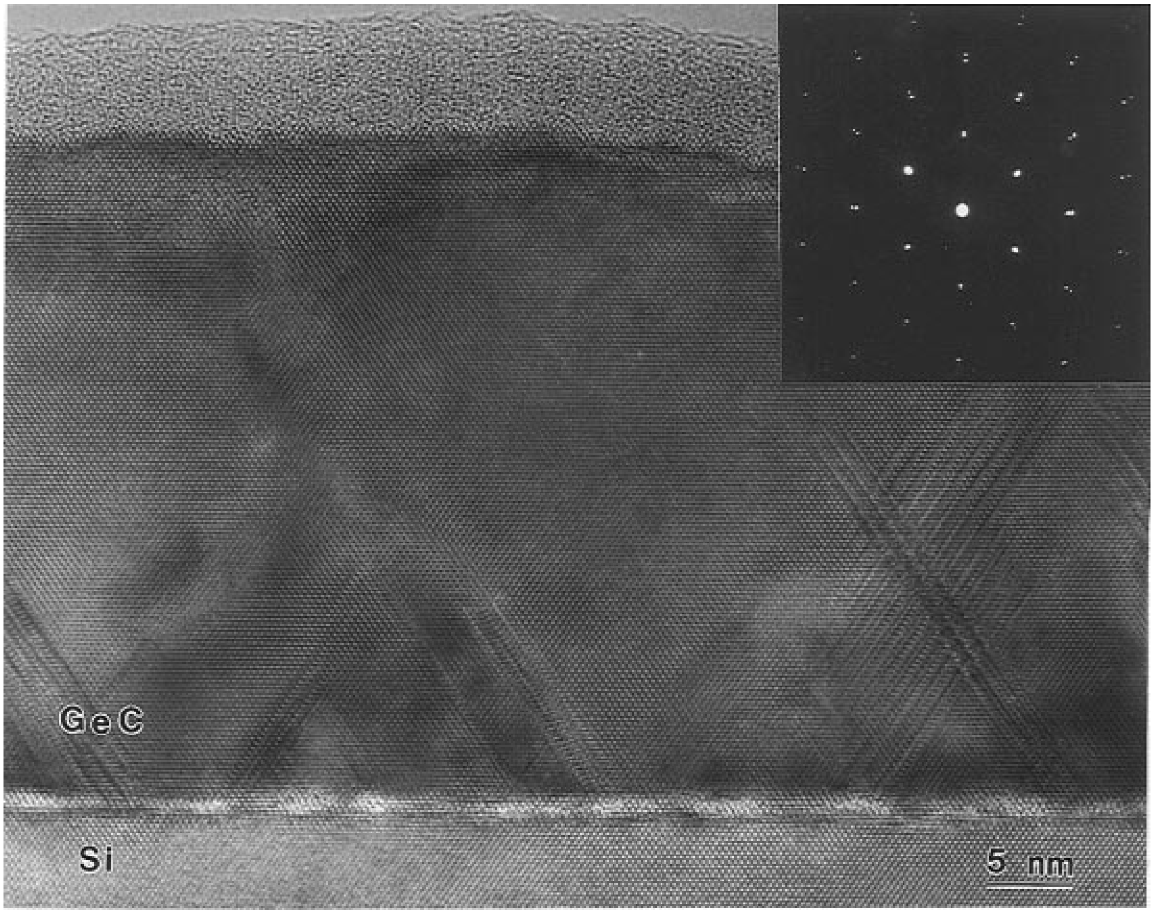

**Figure 6.** Cross-sectional high-resolution TEM micrograph demonstrating defect structure of a $Ge_{0.96}C_{0.04}$ layer on (100) Si. Stacking faults and twins are typical defects. Corresponding selected area diffraction pattern is also shown (inset).

alloys utilized reactions of $GeH_4$ with $(GeH_3)_2CH_2$ or $(GeH_3)_3CH$. The advantage of this approach is that the precursors contain less C−H bonds than does methylgermane and they are expected to permit lower deposition temperatures and also provide materials with greater C content (the stability of C−H bonds requires higher reaction temperatures).

Gaseous $(GeH_3)_2CH_2$ (**4**) is much less stable thermally than $CH_3GeH_3$ (**3**). It decomposes readily at 540 °C with growth rates higher than 1.5 nm/min to form germanium−carbon films of composition $Ge_{0.85}C_{0.15}$. The films are, however, rough and do not adhere well to the substrate. The layer morphology and microstructure is indicative of islandlike, three-dimensional nucleation during growth. Although thermal decomposition of the precursor below 500 °C is negligible, reactions with $GeH_4$ at 470 °C result in deposition of high-quality films with an average growth rate of 0.2 nm/min. Low growth rates provide two-dimensional, layer-by-layer growth, which is important for the development of perfectly epitaxial defect-free materials. The films obtained here are smooth, continuous, and essentially indistinguishable from the underlying Si substrate. Examinations of the surface morphology by atomic force microscopy showed surface regularity compatible with single-crystal Si. Cross-sectional transmission electron microscopy revealed heteroepitaxial growth with relatively few defects and confirmed that the films were relatively smooth and homogeneous in thickness. For high carbon samples (C = 4 at. %), however, stacking faults were observed throughout the layer as shown in Figure 6. Layers of 25−40 nm thickness are typically obtained in 2−3 h, and it appears that the film thickness as well as the growth rate decreased with increased C content. The carbon concentration ranged from 2 to 5 at. % with the higher $(GeH_3)_2CH_2{:}GeH_4$ precursor ratio resulting in higher carbon incorporation. The composition was established by use of RBS carbon resonance analysis as previously described, and SIMS spectra verified the presence of carbon and showed constant elemental content throughout the layer. Furthermore, $(GeH_3)_2CH_2$ (**4**) is a much more effective carbon source for Ge−C growth than $CH_3GeH_3$ (**3**). The amount of $(GeH_3)_2CH_2$ gas that was required to introduce 5 at. % C in the Ge−C film was substantially smaller, nearly 50-fold less, than that required of $GeH_3CH_3$ in order to produce materials of the same composition.

Deposition of $Ge_{1-x}C_x$ via reactions of trigermylmethane, $(GeH_3)_3CH$, with $GeH_4$ also provided high-quality heteroepitaxial $Ge_{1-x}C_x$ layers on Si. The main advantage here is the extraordinary ability of this molecule to introduce large concentrations of substitutional carbon (5−6 at. %) when reacted with a large excess of $GeH_4$ below 500 °C. Reaction mixtures containing 1% by volume of the precursor in $GeH_4$ resulted in $Ge_{0.94-0.95}C_{0.06-0.04}$ alloy compositions at growth rates and layer thicknesses virtually identical with those observed in deposition from mixtures containing $(GeH_3)_2CH_2$ or $CH_3GeH_3$. The same structural and analytical procedures employed previously were used to show that the films deposited by this method grew epitaxially and that the entire layer was crystalline, pure and highly homogeneous. Figure 7 shows a sample of $Ge_{0.95}C_{0.05}$.

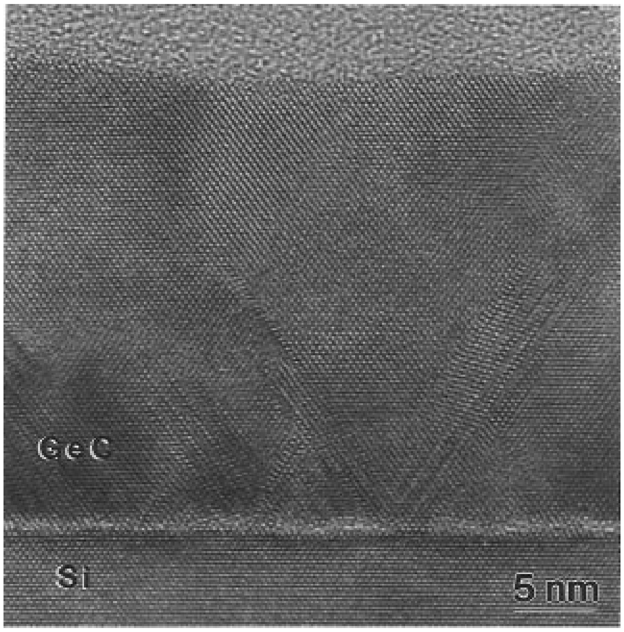

**Figure 7.** Cross-sectional view of $Ge_{0.95}C_{0.05}$ sample grown by reaction of $(GeH_3)_3CH$ with $GeH_4$ at 470 °C, with growth rate of 0.2 nm/min. Low growth rate and relative smooth film surface indicate layer-by-layer growth.

## Discussion

Our deposition results show that low temperature growth of crystalline $Ge_{1-x}C_x$ is now possible by use of the unique combination of UHV-CVD and germanium–carbon chemical precursors. The islandlike 3-D nucleation typically observed during growth of Ge films has been suppressed by the incorporation of carbon. The mechanism for the island suppression can be attributed to strain relief via better lattice matching of the epilayer to the silicon substrate because the smaller size of C compensates for the larger Ge. We have determined from electron diffraction data that the $Ge_{1-x}C_x$ lattice constants decrease slightly as the value of x is increased and are in general smaller than that of Ge, as expected from Vegard's law. Confirmation that carbon is incorporated in the lattice is provided by ion channeling-blocking experiments and EELS. The presence of only $\sigma^*$ electronic transitions in the EELS spectra suggests that C is primarily $sp^3$ hybridized and part of the diamond-like Ge structure.

To achieve our goal of lattice matching with Si, an alloy composition of at least $Ge_{0.90}C_{0.10}$ is required. We have not yet achieved a cohesive layer of single crystalline material with C content greater than 7 at. %. It is remarkable, however, that even C concentrations as low as 1.5–2.0% can have substantial impact on the structure and the growth behavior of the material. Controlled deposition experiments involving thermal decomposition of $GeH_4$ at growth conditions identical to those for $Ge_{1-x}C_x$ resulted in three-dimensional growth of thick incommensurate layers of pure Ge as indicated by carbon resonance RBS experiments and TEM observations. Typical growth rates ranged from 4.5 to 5.5 nm/min, whereas those for $Ge_{0.95}C_{0.045}$ obtained from 1% by volume $(GeH_3)_3CH$ in $GeH_4$ were substantially lower at approximately 0.2 nm/min. During the growth of the $Ge_{1-x}C_x$ films, we also observed that the growth rate decreased as the C concentration was increased, ranging from 0.5–0.6 nm/min for 1.5% C to 0.2 nm/min for 5–6% C. Speculatively, we attribute this decrease to a reduced adsorption probability as the concentration of the C-containing species at the growth front increases. The growth rate and the crystal quality of layers with the same composition were virtually the same for all precursors. The effectiveness of carbon incorporation increased dramatically, however, as the number of $GeH_3$ groups increased from one in methylgermane to three in trigermyl methane. We determined that the increase in the number of $GeH_3$ groups (fewer C–H bonds) results in lower thermal stability and presumably higher reactivity of the molecules, which may explain the high efficiency of carbon incorporation. We are currently directing our efforts to growing higher carbon content alloys and our target composition is 10 at. % C which is expected to produce lattice-matched $Ge_{1-x}C_x$ according to Vegard's law. Future work from a precursor standpoint will focus on improvement of the synthesis of $(GeH_3)_4C$, which has thus far been obtained with only 4% yield. This low yield may limit its application as a practical source for large-scale industrial syntheses of $Ge_{1-x}C_x$. Although our bis(germyl) and tris(germyl)methanes are synthesized in substantially higher yields (35% and ~15%, respectively) via single-step reduction experiments of the corresponding halides, and their use to prepare device-quality low carbon concentration Ge–C alloys has been demonstrated, $(GeH_3)_4C$ is expected to be a more highly effective carbon source for low-temperature Ge–C growth because it lacks strong C–H bonds. We anticipate that the use of tetragermylmethane will result in higher carbon incorporations which may be necessary to influence the bandgap. The optical properties of the $Ge_{1-x}C_x$ materials are currently being investigated using photoluminescence and modulation spectroscopy.

## Conclusion

We have shown that low-temperature UHV-CVD reactions of germylmethanes $(GeH_3)_{4-x}CH_x$ ($x = 1-3$) with germane result in heteroepitaxial germanium–carbon films in which the carbon occupies substitutional sites in the Ge diamond-like lattice. The carbon content in the films ranges from 1.5 to 7 at. %, the highest carbon content yet observed in crystalline $Ge_{1-x}C_x$ alloys. This is also the first example of crystalline Ge–C alloys obtained by chemical methods. From the precursors used in this study, the most efficient carbon incorporation is achieved by reaction of $GeH_4$ with a novel $CH(GeH_3)_3$ molecule having the least number of strong C–H bonds. This molecule is obtained in good yield by reduction of the newly synthesized tris(tribromogermyl) methane, $(GeBr_3)_3CH$.

## Experimental Procedure

**General Procedures.** Reactions were performed under prepurified nitrogen with standard Schlenk and drybox techniques. Solvents were distilled from sodium benzophenone ketyl prior to use. $^1H$ (300 MHz) and $^{13}C$ (125.7 MHz) NMR spectra were collected on a Varian Gemini 300 spectrometer and were referenced to the solvent resonances ($C_6D_6$, $^1H$ $\delta$ 7.17, $^{13}C$, $\delta$ 128.0). FTIR spectra were recorded on a Nicolet Magna-IR spectrometer either in Nujol mull or in a 10 cm gas cell with KBr windows. Elemental analyses were performed by Desert Analytics (Tucson, AZ). Electron impact mass spectra were collected on a Finnigan-MAT Model 312 mass spectrometer (IE = 70 eV, source $T$ = 225 °C). Iodomethane (Aldrich), diiodomethane (Aldrich), benzyltriethylammonium chloride (Aldrich), tribromomethane (Aldrich), and ultrahigh-purity germane (Voltaix) were used as received. Lithium aluminum hydride (Aldrich) was purified from diethyl ether prior to use. $GeX_2$·dioxane (X = Br, CI) were synthesized as described previously.[23]

We synthesized $GeBr_4$ at nearly quantitative yields in a thick-wall Schlenk tube equipped with a high-vacuum Teflon valve. The tube was charged with stoichiometric quantities of Ge powder and purified $Br_2$ and then placed in a muffle furnace with the closed lower portion at the hot zone and the upper half outside the furnace. The temperature was slowly raised to 520 °C while $Br_2$ was refluxing on the side of the Schlenk reactor, which was constantly cooled by a water jacket to prevent overheating of the valve. The sample was maintained at 520 °C until the refluxing liquid changed from red to clear, indicating that the $Br_2$ had completely reacted. The clear $GeBr_4$ liquid was isolated, purified by trap-to-trap distillation and characterized by infrared spectroscopy.

**Preparation of $(GeBr_3)_3CH$ (2) .** Neat tribromomethane (0.525 g, 2.08 mmol) was added to a suspension of $GeBr_2$·dioxane (2.05 g, 6.40 mmol) in toluene (60 mL). The mixture was stirred at 85 °C for 3 days during which time most of the solid dissolved. The mixture was then filtered while hot. Concentration and cooling of the resulting solution produced several crops of a colorless solid to give a total yield of 1.77 g (1.86 mmol, 89%), mp 148−150 °C. IR (Nujol) 1016 (m, CH bend), 684 (vs, GeC str), 509 (s, GeC bend), 334 (vs, GeBr str). EIMS (*m*/*e*) isotopic envelopes centered at 870 ($Br_8Ge_3CH^+$), 638 ($Br_6Ge_2CH^+$), 557 ($Br_5Ge_2CH^+$), 478, ($Br_4Ge_2CH^+$), 395 ($Br_3Ge_2CH^+$), 325 ($Br_3GeCH^+$), 244 ($Br_2GeCH^+$), 233 ($Br_2Ge^+$) and 153 ($BrGe^+$). $^1H$ NMR $\delta$ 3.54 (s, *CH*). $^{13}C$ NMR $\delta$ 40.87 ppm. Anal. Calcd for $(Br_3Ge)_3CH$: Br, 75.7. Found: Br, 75.5.

**Reduction of 2 with $LiAlH_4$.** A flask was charged with tris(tribromo)germylmethane (**2**, 5.0 g, 5.26 mmol), benzyltriethylammonium chloride (0.25 g, 1.1 mmol) and $LiAlH_4$ (2.0 g, 52.7 mmol) in 1,2,3,4-tetrahydronaphthalene (THN, 60 mL). The mixture was stirred under nitrogen at ambient temperature for 3 days, followed by stirring at 60 °C for 5 h. The volatiles were then passed through traps held at −45, −78, and −196 °C. A small quantity of $(GeH_3)_3CH$ (**1**) and THN was collected at −45 °C, pure $(GeH_3)_3CH$ (**1**) was collected at −78 °C, and a mixture of germane and methylgermane (**3**) was collected at −196 °C. **1:** (0.79 mmol, 15% yield), vapor pressure 22 Torr at 25 °C. IR (gas phase) 2935 (w, CH str), 2140 (sh, GeH str), 2079 (vs, GeH str), 2006 (sh, GeH str), 1263 (vw), 1034 (m, CH wag), 880 (s, $GeH_3$ asym def), 840 (vs, $GeH_3$ sym def), 749 (vs, GeC str), 708 (s), 555 (vw). $^1H$ NMR $\delta$ −0.60 (dect, $J = 3.90$ Hz, *CH*), $\delta$ 3.83 (d, $J = 3.90$ Hz, *$GeH_3$*). $^{13}C$ NMR $\delta$ −28.46. EIMS (*m*/*e*) 222−244 ($CHGe_3^+$).

**Synthesis of $(GeH_3)_2CH_2$ (4) via Reduction of Bis(trihalogermyl)methanes.** Neat diiodomethane (7.7 g, 28.7 mmol) was added to a suspension of $GeCl_2$·dioxane (13.3 g, 57.4 mmol) in hexane (125 mL), and the mixture was refluxed at 85 °C for 20 h until most of the solid was dissolved. The mixture was filtered hot and the solvent was removed in vacuo yielding 12.9 g (23.3 mmol, 81%) of a pale yellow oil. Analysis of the oil revealed $(GeCl_2I)_2CH_2$ as the major product (60% yield) and other minor products of the form $(GeI_{5-x}Cl_x)_2CH_2$. ($^1H$ NMR, $CDC1_3$): $\delta$ 3.35 ($C1_6Ge_2CH_2$), $\delta$ 3.30 ($C1_5IGe_2CH_2$), $\delta$ 3.05 ($C1_4I_2Ge_2CH_2$), $\delta$ 2.82 ($C1_3I_3Ge_2CH_2$). EIMS (*m*/*e*): halide scrambling with isotopic envelopes centered around 794 ($H_2CGe_2I_5^+$), 702 ($H_2CGe_2I_4Cl^+$), 610 ($H_2CGe_2I_3Cl_2^+$), 518 ($H_2CGe_2I_2Cl_3^+$), 428 ($H_2CGe_2ICl_4^+$), and 336 ($H_2CGe_2C1_5^+$). IR (neat) 3010−2900 m, 1728 w, 1465 vw, 1408 vw, 1362 vw, 1119 m, 1078 m, 881 w, 829 w, 695 s, 664 s, 559 m, 434 vs, 407 vs.

A solution of the above mixture (12.0 g, 21.6 mmol) in dibutyl ether (60 mL) was added, dropwise, to a suspension of $LiAlH_4$ (3.3 g, 87.0 mmol) in dibutyl ether (150 mL) which was cooled to 0 °C. The mixture was stirred for 24 h at room temperature. The volatiles were then passed through traps held at −65, −116, and −196 °C. The −196 °C trap retained methylgermane (**3**), the −116 °C trap retained digermylmethane (**4**, 33%), and the −65 °C trap retained dibutyl ether.

Compound **4**: IR (gas phase, this work) 2920−2990 (w, CH str), 2088 (vs, GeH str), 1145 (vw, $CH_2$ twist), 1052 (m, $CH_2$ wag), 960 (sh, $GeH_3$ asym def), 886 (vs, $GeH_3$ asym def), 840 (vs, $GeH_3$ sym def), 763 (s, $CH_2$ rock), 680 (vs, GeC str), 468 (w, $GeH_3$ rock). IR (gas phase, Jolly et al. [17]) 3000 (st), 2160 (sh), 2100 (vs), 1380 (w), 1140 (w), 1050 (mw), 960 (br, sh), 880 (br), 840 (vs), 775 (br, m), 680 (s). $^1H$ NMR $\delta$ 3.66 (t, $J =$ 3.90 Hz, $GeH_3$), $\delta$ 0.244 (sept, $J = 3.90$ Hz, $CH_2$). $^{13}C$ NMR $\delta$ −19.77. Vapor pressure 70 Torr at 25 °C.

**Synthesis of $GeH_3CH_3$ (3) via Reduction of $GeI_{3-x}Cl_xCH_3$ ($x = 0-3$).** Iodomethane (3.31 g, 23.3 mmol) was syringed into a suspension of $GeCl_2$·dioxane (5.4 g, 23.3 mmol) in hexane (150 mL). The mixture was refluxed under nitrogen at 85 °C for 24 h and during this time most of the solid dissolved. The mixture was then filtered hot and the hexane was removed in vacuo leaving a pale yellow oil. Analysis of the oil revealed a mixture of products of the form $GeI_{3-x}Cl_xCH_3$ ($x = 0-3$). $^1H$ NMR showed $H_3CGeC1_3$ (34.4%), $H_3CGeC1_2I$ (39.2%), $H_3CGeClI_2$ (15.4%), and $H_3CGeI_3$ (11.0%) based on integration of the $^1H$ signal. $^1H$ NMR ($CDCl_3$) $\delta$ 2.67 ($GeC1_3CH_3$), $\delta$ 2.22 ($GeC1_2ICH_3$), $\delta$ 1.85 ($GeClI_2CH_3$), and $\delta$ 1.55 ($H_3CGeI_3$). EIMS (*m*/*e*) halide scrambling with isotopic envelopes centered at 469 ($H_3CGeI_3^+$), 377 ($H_3CGeI_2Cl^+$), 286 ($H_3CGeC1_2I^+$), and 194 ($H_3CGeC1_3^+$). IR (gas phase) 2982 (vw, CH str), 825 (s, $CH_3$ rock), 633 (m, GeC str), 442 (vs, GeCI str). This spectrum matches that of $GeCl_3CH_3$. IR (neat, KBr plates) 2940 (CH str), 1464 (w, $CH_3$ def), 1417 (w, $CH_3$ def), 808 (vs, $CH_3$ rock), 739 (sh, GeC str), 692 (m, GeC str), 603 (m, GeC str), 403 (s, GeCl str). These vibrations correspond to the $GeI_{3-x}Cl_xCH_3$ ($x = 0-3$) products.

A solution of $LiAlH_4$ (0.27 g, 7.1 mmol) in dibutyl ether (50 mL) was added slowly to a solution of $GeI_{3-x}Cl_xCH_3$ ($x = 0-3$) in dibutyl ether (70 mL) at 0 °C. The mixture was stirred for 9 h at room temperature. The volatiles were then passed through traps held at −78 and −196 °C. The −78 °C trap retained dibutyl ether and the −196 °C trap retained $H_3CGeH_3$ (0.13 g, 33%). IR (gas phase) 2950 (m, CH str), 2084 (vs, GeH str), 1430 (vw, $CH_3$ def), 1254 (w, $CH_3$ def), 848 (vs, $CH_3$ rock, $GeH_3$ def), 602 (s, GeC str), 510 (s, $GeH_3$ rock). IR (gas phase, Griffiths[24] ) 2947 (st), 2984 (vs), 1430 (w), 1254 (st), 847 (vs), 602 (vs), 506 (st).

**Synthesis of $GeH_3CH_3$ (3) by Reaction of $KGeH_3$ with $ICH_3$.** This route is more convenient and affords higher yields of the product than the synthesis reported by Jolly et al. $GeH_4$ gas (77.7 mmol) was condensed into a liter flask containing a mixture of 1:4 (by weight) Na/K alloy (3.8 g, 77.7 mmol K) in monoglyme (100 mL). The mixture was stirred using a glass coated magnetic bar at ambient temperature for 16 h, then degassed to remove the $H_2$, and filtered under $N_2$ to remove the unreacted Na. The monoglyme was pumped away to yield 8.23 g (71.7 mmol, 92%) of $KGeH_3$ as a pale yellow solid which was stored at −34 °C in the drybox (unrefrigerated $KGeH_3$ turns dark brown and decomposes explosively). Iodomethane (5.80 g, 41.0 mmol) was condensed into a 500-mL flask containing $KGeH_3$ (4.7 g, 41.0 mmol) and diglyme (100 mL). The mixture was stirred at room temperature for 15 min and the volatiles were passed through traps held at −130, −161, and −196 °C. Pure $GeH_3CH_3$ (**3)** was collected in the −161 °C trap (35.1 mmol, 86%) and was characterized by gas-phase IR.

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