Ether-like Si-Ge hydrides for applications in synthesis of nanostructured semiconductors and dielectrics

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Hydrolysis reactions of silyl-germyl triflates are used to produce ether-like Si–Ge hydride compounds including H₃SiOSiH₃ and the previously unknown O(SiH₂GeH₃)₂. The structural, energetic and vibrational properties of the latter were investigated by experimental and quantum chemical simulation methods. A combined Raman, infrared and theoretical analysis indicated that the compound consists of an equal mixture of linear and gauche isomers in analogy to the butane-like H₃GeSiH₂SiH₂GeH₃ with an exceedingly small torsional barrier of ~0.2 kcal mol⁻¹. This is also corroborated by thermochemistry simulations which indicate that the energy difference between the isomers is less than 1 kcal mol⁻¹. Proof-of-principle depositions of O(SiH₂GeH₃)₂ at 500 °C on Si(100) yielded nearly stoichiometric Si₂Ge₂O materials, closely reflecting the composition of the molecular core. A complete characterization of the film by RBS, XTEM, Raman and IR ellipsometry revealed the presence of Si_{0.30}Ge_{0.70} quantum dots embedded within an amorphous matrix of Si–Ge–O suboxide, as required for the fabrication of high performance nonvolatile memory devices. The use of readily available starting materials coupled with facile purification and high yields also makes the above molecular approach an attractive synthesis route to H₃SiOSiH₃ with industrial applications in the formation of Si–O–N high-*k* gate materials in high-mobility SiGe based transistors.

Introduction

Silicon dioxide (SiO₂) is the most prominently used gate dielectric for microelectronics devices incorporating elemental silicon and Si-rich Si_{1-x}Ge_x alloy semiconductors. However, as CMOS dimensional scaling has progressed, the sizes of Si-based transistor structures have been considerably reduced requiring alternate dielectrics to ensure device reliability and the intended performance gains expected on account of Moore's Law. Within the last ten years silicon oxynitride (SiON) layers with thickness of <5 nm were introduced to replace conventional SiO₂ in its role as a gate insulator.1-3 These materials offer substantial improvements over the oxide counterpart including fewer interface defects and the ability to act as barriers to conventional B, P and As dopants diffusing from the polycrystalline Si gate into the substrate.⁴ The stoichiometric Si₂N₂O analog has a higher dielectric constant than either SiO₂ or SiON and it is more likely to form a chemically robust, ordered structure adjacent to the Si interface.5-7 Therefore this material could be used to further mitigate current leakage and suppress dopant penetration while maintaining high gate capacitance over the reduced length scales anticipated in modern devices. In recent work we presented a preliminary account of the formation of Si₂N₂O films at low temperatures via reactions of disiloxane H₃SiOSiH₃ and a large excess of NH₃ according to the reaction shown by eqn (1).8

$$H_{3}SiOSiH_{3} + 2 NH_{3} \rightarrow Si_{2}N_{2}O(s) + 6 H_{2}$$
(1)

The Si₂N₂O phase can be viewed as an assembly of Si-O-Si building blocks linked together at the Si sites by trigonal nitrogen centers. In our above synthesis approach the molecular Si-O-Si cores of H₃SiOSiH₃ deliver both the compositional and bonding configuration at the nanoscale required to form the desired solidstate material. In contrast to the formation of conventional silicon oxynitride gate dielectrics via reactions of NH₃ with SiH₄^{2,3} (or chlorosilane derivatives), the above process has the advantage to readily guarantee reproducibility of composition on a large production scale because precise control of the NH₃ activity is not required in the reaction medium. This is particularly attractive from a processing perspective and it is primarily due to the fact that disiloxane represents the limiting reagent while nitrogen derived from NH₃ is incorporated only to the degree required to achieve the compound stoichiometry. This dramatically reduces the complexity of the process, since precise conditions of the reaction are no longer critical and the problem is reduced to the simplest possible interaction involving the precursor and an ambient of ammonia.

Recently we have shown that $H_3SiOSiH_3$ can also be used as a single source to fabricate light emitting films comprised of Si nanoparticles embedded in an amorphous SiO₂ matrix.⁹ The latter may have potential application in optoelectronics including flat panel displays as well as charge storage devices such as nonvolatile memory. In our prior work amorphous films of SiO_x (x < 2) were first deposited at 750–850 °C on Si(100) substrates *via* the unimolecular decomposition of the compound. This was followed by rapid thermal annealing to crystallize the excess silicon and generate distinct Si nanoparticles

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with tunable sizes (1 and 10 nm), discrete shapes, and uniform distributions throughout the amorphous SiO_2 matrix. The resultant nanostructures exhibit room-temperature photoluminescence (PL) and the emission energy increases with decreasing crystal size in accordance with quantum confinement concepts. Important benefits of optically active silicon nanostructures enclosed in amorphous SiO_2 include improved reliability, chemical and electrical stability, full compatibility with existing complementary metal–oxide–semiconductor techniques, and the possibility of generating strong emission across the entire range of visible light.

In the above examples the common highlight is the use of a completely inorganic (C-H free) and volatile H₃SiOSiH₃ precursor with built-in Si-O-Si atomic arrangements that allow stoichiometric control at the atomic level ensuring formation of highly homogeneous materials with controllable quality and composition leading to the desired properties. In view of the success in using siloxane to directly prepare functional materials based on Si, our present work seeks to expand this technology concept by replacing the -SiH₃ groups with -SiH₂GeH₃ groups in the ether-like backbone to yield O(SiH₂GeH₃)₂, thereby enabling new applications in the area of Si-Ge photonics and dielectrics. For example the highest performance nonvolatile flash-memory devices are fabricated using $Si_{1-x}Ge_x$ alloy nanocrystals, or so called quantum dots, embedded in amorphous high-k dielectric media including SiON and SiO2.10-13 The writing/erasing speed of these devices was found to be faster and the retention times of the encoded information significantly longer by several orders of magnitude compared to more conventional device architectures. The SiGe quantum dots are typically grown by CVD reactions of SiH₄ and GeH₄ via a self assembly mechanism producing a random distribution of individual grains at 600 °C. This is followed by a thermal oxidation of the layers at 800 °C to generate the target nanostructures and the corresponding oxide matrix yielding areal densities and nominal dot sizes in the range of 10¹¹ cm⁻² and 5-10 nm, respectively. It is widely reported that the performance of flash memories incorporating these materials can be engineered by tuning the composition of the alloy and optimizing the shape and size of the corresponding nanocrystals.

In this study we explore the possibility of producing $Si_{1-x}Ge_x$ alloy quantum dots surrounded by a dielectric matrix using the simplest single-source precursor O(SiH₂GeH₃)₂, akin to the prior work based on H₃SiOSiH₃. In the following we discuss the synthesis and fundamental properties of $O(SiH_2GeH_3)_2$ and its use in proof-of-concept depositions of Si₂Ge₂O materials which closely reflect the composition of the parent molecule. We show that the as-deposited films comprise of SiGe quantum dots embedded within an amorphous matrix of Si-Ge-O suboxide, as required for the envisioned applications, without the need for additional processing steps. The compound is conveniently obtained via simple hydrolysis of readily available and fairly inexpensive silyl-germyl triflate derivatives. The success of this approach prompted us to reconsider the synthesis of H₃SiOSiH₃ ultimately leading to the development of a practical process that can be readily scaled up to the industrial scale. The compound is easily separated from the byproducts in pure form and isolated in nearly quantitative, multigram yields, indicating that the process is amenable to large-scale production.

Results and discussion

Synthesis of H₃SiOSiH₃

Despite the common occurrence and widespread applications of organic disiloxanes a practical synthesis of the fully inorganic $H_3SiOSiH_3$ analog remains elusive. Several synthetic routes to $H_3SiOSiH_3$ have been previously reported, the most notable involving reactions of SiH₃I as the source of SiH₃ and irradiation of SiH₄ in the presence of HNO₃.¹⁴⁻¹⁶ These approaches have not been demonstrated to be practical for routine synthesis because they afford very limited yields and utilize highly reactive and unstable starting materials making isolation and handling difficult particularly in large-scale preparations. To circumvent these problems, for the initial growth studies using this compound, we developed an alternative synthetic route involving a single-step reduction of Cl₃SiOSiCl₃ with LiGaH₄, as described here for the first time by eqn (2).

$$2 \operatorname{Cl}_{3}\operatorname{SiOSiCl}_{3} + 3 \operatorname{LiGaH}_{4} \rightarrow 3 \operatorname{H}_{3}\operatorname{SiOSiH}_{3} + 3 \operatorname{LiCl} + 3 \operatorname{GaCl}_{3}$$
(2)

This approach provided yields ranging up to 25% for small laboratory-level preparations (see Experimental section) but we found that scaling up the process was not economically or logistically feasible and thus prohibitive, particularly from an industrial perspective. For example, the Cl₃SiOSiCl₃ reactant is not readily available and the LiGaH₄ counterpart is expensive to manufacture due to the high cost of the GaCl₃ starting material. Furthermore, LiGaH₄ once produced is also difficult to isolate and maintain in pure form owing to its instability at room temperature. Surprisingly, our attempts of similar reduction reactions involving the ubiquitous LiAlH₄ analog yielded no evidence of the target product, thus the use of LiGaH₄ as the reducing agent was absolutely critical to the synthesis of H₃SiOSiH₃. Another major drawback of the above approach was the propensity of the LiGaH₄ to decompose during the course of the experiment through sidereactions generating large H₂ over-pressures even at low reaction temperatures in the vicinity of -78 °C. This problem necessitated small scale preparations, and extremely delicate/stringent control of the reaction conditions such as temperature, pressure and solvent-reactant concentrations, yielding in turn a limited amount of the compound in the range of 1-2 g, which is adequate for CVD growth on small laboratory scale but not suitable for industrial processing.

In this study we find that the general approach developed for the synthesis of $O(SiH_2GeH_3)_2$ (as described in subsequent sections) represents a viable large-scale preparation of $H_3SiOSiH_3$ for applications in cost-effective fabrication of dielectrics. The compound is produced routinely and reproducibly *via* reactions of H_2O with silyl triflate ($H_3SiOSO_2CF_3$) as described by eqn (3). The latter is produced quantitatively by reacting phenylsilane with triflic acid ($HOSO_2CF_3$) *via* elimination of C_6H_6 . The reaction mechanism leading to $H_3SiOSiH_3$ could initially involve formation of unstable silanol (H_3SiOH) as a first step shown by eqn (4). This intermediate would then react with another silyl triflate molecule *via* condensation to form disiloxane while regenerating the parent triflic acid (see eqn (5)) which can in turn be recycled to produce more starting material $H_3SiOSO_2CF_3$ (eqn (6)), thereby reducing overall process cost (emphasized in bold in eqn (3) and (6)).

$2 \textbf{H}_3\textbf{SiOSO}_2\textbf{CF}_3 + \text{H}_2\text{O} \rightarrow \text{H}_3\text{SiOSiH}_3 + 2 \text{HOSO}_2\text{CF}_3$	• –	(3)
$H_{3}SiOSO_{2}CF_{3} + H_{2}O \rightarrow `H_{3}SiOH' + HOSO_{2}CF_{3}$		(4)
$\label{eq:H3SiOH} ``H_3SiOSO_2CF_3 \rightarrow H_3SiOSiH_3 + HOSO_2CF_3$		(5)
$HOSO_2CF_3 + C_6H_6SiH_3 \rightarrow H_3SiOSO_2CF_3 + C_6H_6$		(6)

The reactions of $H_3SiOSO_2CF_3$ were performed using an excess of the H_2O and the gaseous $H_3SiOSiH_3$ product was distilled and purified to obtain yields as high as 90–95%. IR and NMR were used as the primary means of characterization indicating that $H_3SiOSiH_3$ is devoid of impurities, including unreacted water. To further explore the above mechanism we conducted an analogous reaction involving methanol and silyl triflate, which yielded methyl siloxane¹⁷ in accordance with eqn (7).

 $H_3SiOSO_2CF_3 + CH_3OH \rightarrow H_3SiOCH_3 + HOSO_2CF_3$ (7)

Using an excess of methanol the above reaction produces highly pure methyl siloxane (H_3SiOCH_3) as confirmed by gas phase IR. The high volatility of the product allows facile separation from unreacted methanol *via* fractional distillation to isolate the compound in 63% yield.

Synthesis of $O(SiH_2GeH_3)_2$. The above hydrolysis approach was initially developed to synthesize the new $O(SiH_2GeH_3)_2$ (digermyldisiloxane) compound by combining H₃GeSiH₂SO₃CF₃, (the germylsilyl analog of the silyl triflate) with an excess of water. The digermyldisiloxane was isolated as a colorless, pyrophoric liquid with a vapor pressure of 10 Torr at 23 °C. Its molecular structure was elucidated by gas chromatography, mass spectrometry (GC-MS), infrared spectroscopy (FTIR), Raman, multinuclear NMR and quantum chemical simulations. The mass spectrum revealed the parent ion as an isotopic envelope centered at 223 amu with a fragmentation pattern consistent with the O(SiH₂GeH₃)₂ molecular structure. The ¹H and ²⁹Si NMR spectra showed a triplet at 3.05 ppm corresponding to the GeH₃ terminal ligands, a quartet at 5.09 associated with the SiH₂ protons, and singlet at -21.1 ppm due to the ²⁹Si. A 2D ¹H COSY spectrum revealed crosspeaks between the SiH_2 at 5.09 ppm and the GeH₃ at 3.05 ppm indicating the direct connectivity between the Ge and Si atoms in the -SiH₂GeH₃ fragment. A ¹H-²⁹Si HMQC showed that the SiH₂ atoms (5.09 ppm) are directly bound to the Si atom (-21.1 ppm) which further confirms the proposed molecular structure. In relation to the butane-like H₃GeSiH₂SiH₂GeH₃ analog, the SiH₂ and ²⁹Si resonances are shifted downfield to ppm values of 3.29 and -105, respectively, due to the presence of the highly electronegative oxygen atom. The IR spectra obtained from gaseous samples showed the Si-H, Ge-H and Si-O vibrational modes at 2153, 2069 and 1078 cm⁻¹, respectively, as expected for the proposed molecular structure. Fig. 1 compares the experimental spectrum with a simulated pattern indicating an excellent agreement between the principal features. The simulated spectrum was obtained by first calculating the individual spectra of the normal and gauche conformations shown in Fig. 2 and then adjusting their linear combination to best fit the experimental data as described in the following section. This fitting procedure was first developed in our prior work involving the closely related butane-like H₃GeSiH₂SiH₂GeH₃ where it was used to estimate the proportions of the linear and gauche isomers in the observed gas spectrum.¹⁸ We note in passing that the NMR spectra of this class of hydride compounds only provides direct evidence of



Fig. 1 Comparison of the simulated and experimental spectrum for $O(SiH_2GeH_3)_2$. The optimized spectrum labeled "THEORY" contains a mixture of 55% linear and 45% gauche isomers.



Fig. 2 Structural models of the "normal" and "gauche" isomers of the digermyl-disiloxane compound.

local bonding linkages, and not the geometric conformations of the molecular backbones. Accordingly, application of the fitting scheme to the IR spectrum of $O(SiH_2GeH_3)_2$ indicates that the compound exists as a nearly equal admixture (55 and 45%) of normal and gauche isomers. Thus this result suggests that the relative stabilities of the isomers might be comparable at room temperature.

A similar analysis of the Raman spectra obtained from a solution of $H_3GeSiH_2SiH_2GeH_3$ in C_6H_6 yielded a virtually identical

Table 1 Unscaled frequencies (in cm^{-1}) and mode assignments for the N (normal) and G (gauche) isomers. The italic entries correspond to modes with a common frequency and vibrational character. The largest frequency difference between the isomers is found in the antisymmetric Si–O stretches near 1080 cm⁻¹

n-O(SiH ₂ Gel	$(I_3)_2$	g-O(SiH ₂ GeI	H ₃) ₂	Primary mode assignments
N ₁	341	G ₁	341	Antisymmetric Si-Ge stretching
NT	262	G_2	349	Out-of-phase GeH ₃ & SiH ₂ wagging \perp to backbone
N_2	362	$G_{2'}$	362	In-phase GeH ₃ & SiH ₂ wagging \perp to backbone
N_3	470	G_3	470	In-phase GeH ₃ rocking to backbone
N_4	770	G_4	772	In-phase GeH ₃ wagging
N_5	803	G_5	797	Out-of-phase GeH ₃ wagging
N_6	869	G_6	872	In-phase GeH ₂ & SiH ₂ wagging
N_7	891	G_7	893	Out-of-phase GeH ₂ & SiH ₂ wagging
N_8	900	G_8	900	In-phase SiH ₂ wagging & "GeH ₂ " scissors
N_9	918	G_9	915	Out-of-phase SiH ₂ wagging & "GeH ₂ " scissors
N ₁₀	957	G_{10}	960	In-phase SiH ₂ scissors
N ₁₁	973	G_{11}	968	Out-of-phase SiH ₂ scissors
N ₁₂	1075	G_{12}	1089	Antisymmetric Si–O stretching
N ₁₃	2107	G_{13}	2113	In- and out-of-phase symmetric GeH ₃ stretching
N ₁₄	2122	G_{14}	~ 2127	In- and out-of-phase asymmetric GeH ₃ stretching
N ₁₅	2210	G ₁₅	~ 2210	In- and out-of-phase asymmetric SiH ₂ stretching
		G_{16}	2221	Isolated Si–H stretching

Table 2	As	signi	nent of the c	bse	erved I	Raman peak	s of	the O(S	GiH2GeH3)2
compour	ıd.	The	frequencies	in	italic	correspond	to	totally	symmetric
modes									

Frequency/cm ⁻¹	Assignment
344/355	Si–Ge stretch
465	GeH ₃ wag
607	Si-O stretch
748	SiH ₂ twisting relative to backbone
775	H wag to backbone
877	GeH ₂ scissors and wag \perp to backbone
937	In-phase SiH ₂ wag
2062	Ge–H stretch
2150	Si–H stretch

mixture a gauche (44%) and normal (56%) isomers in the liquid state. A representative depolarized spectrum after subtraction of the solvent is compared in Fig. 3 with the theoretical admixture. Note that the high frequency Raman shifts are dominated by the Ge–H and Si–H stretches at 2069 and 2153 cm⁻¹, in good agreement with the IR frequencies. The low-energy spectral range is very rich and shows a strong doublet at 350 cm⁻¹ that corresponds to Si–Ge stretches, not seen in the IR spectrum. The 350, 2069 and 2153 cm⁻¹ peaks have depolarization ratios much smaller than $\frac{3}{4}$, revealing their totally symmetric character. A more complete assignment of modes is given in Table 2 and discussed in detail in the following section.

Quantum chemical simulations of $O(SiH_2GeH_3)_2$. In this section we describe the theoretical analysis of the vibrational spectra and elucidate the thermochemistry of both the normal and gauche $O(SiH_2GeH_3)_2$ isomers. All quantum chemical simulations were conducted using density functional theory at the B3LYP level and a standard 6-311N++G(3df,3pd) basis set as implemented in the Gaussian03 code.¹⁹ Tight convergence conditions were employed in all of the structural optimizations with no symmetry constraints applied to either molecule. Our results indicate that both normal and gauche isomers are asymmetrical tops possessing rotational constants *A*, *B* and *C* (in GHz) of (2.46, 0.33, 0.29) and (4.14, 0.28, 0.27), respectively, while their corresponding



Fig. 3 Experimental and theoretical Raman spectrum for the $O(SiH_2GeH_3)_2$ compound. The theoretical data were corrected as discussed in the text.

optimized geometries exhibited C_{2v} and C_1 symmetry. In both cases the spectrum of vibrational frequencies was positive definite, indicating that the equilibrium structures are both dynamically stable. The Si–Ge, Si–H and Ge–H bond lengths (2.392, 1.484 and 1.538, respectively) were identical to within ~ 0.002 Å, and closely matched those that we reported in our earlier work on the butane-like H₃GeSiH₂SiH₂GeH₃ isomers.¹⁸ This is also true of the hydride bond angles, for which we find very typical tetrahedral values such as ∠HSiO ~109.4 ± 0.2°, ∠HGeSi ~110.7°, ∠HSiH ~108.1° and ∠HGeH ~108.1°. The Si–O bond lengths of the isomers were also



Fig. 4 Calculated infrared vibrational spectra of the normal (top panels) and gauche (bottom panels) $O(SiH_2GeH_3)_2$ isomers. The mode assignments and unscaled frequencies corresponding to the modes labeled N_i (normal) and G_i (gauche), are listed in Table 1.

found to be identical (and equal to 1.645 Å), however, the Si–O–Si angle in the gauche (147.1°) was found to be about 3° smaller than in its normal counterpart (150.1°). We note that the above structural parameters are very similar to those typically observed in condensed oxide phases such α -quartz in which $b_{\text{sio}} \sim 1.61$ Å and \angle SiOSi $\sim 144-146^{\circ}$.

Fig. 4 shows plots of the calculated spectra of n-O(SiH₂GeH₃)₂ and g-O(SiH₂GeH₃)₂ (top and bottoms panels, respectively) showing the high- and low-frequency regions individually. All of the principal vibrational features are labeled N_i (normal) and G_i (gauche) and the corresponding normal mode assignments are provided in Table 1. We note that with a few exceptions, such as modes 2 and 14–16, the label numbers reflect distinct vibrational modes shared by the two molecular isomers.

The high-frequency (>2000 cm⁻¹) spectral features in both isomers originate from the Si–H and Ge–H stretches centered approximately at 2100 and 2200 cm⁻¹, respectively. The symmetric Ge–H stretches are found near 2110 cm⁻¹ (labeled N₁₃ and G₁₃, respectively). The higher intensity asymmetrical Ge–H counterparts occur near 2124 cm⁻¹, however, in the lower symmetry gauche conformer these are split over a narrow range of frequencies centered on the values indicated by tildes. The symmetric and asymmetric SiH₂ stretches virtually coincide in the normal isomer (feature N₁₅ near 2210 cm⁻¹), while the corresponding modes in the gauche isomer are again split into an envelope of multiplets centered on the same frequency. The only distinct feature associated with the gauche isomer is a set of lone Si–H stretching modes near 2221 cm⁻¹ (feature G₁₆).

The weak low-frequency Si–Ge skeletal modes $\{N_1, G_1\}$ occur at the same frequency (341 cm⁻¹) in both isomers. In contrast, the strong asymmetric Si–O skeletal vibrations $\{N_{12}, G_{12}\}$ exhibit the largest frequency difference (~15 cm⁻¹) between the two isomers, and therefore play a key role (see below) in distinguishing between the two conformations. The low-frequency non-skeletal vibrational structure, also shown in Fig. 4, is considerably more complex and involves symmetric and antisymmetric Si–H/Ge–H wagging, rocking and scissoring vibrations, both in- and out-ofphase in relation to the oxygen center. Our analysis closely follows that employed in our work on the *n*- and *g*-isomers of the H₃GeSiH₂SiH₂GeH₃ compound. In the latter case, we found that the most symmetric vibrations in the normal isomer were split and/or shifted in the gauche counterpart. This is likely due to the strong coupling of these modes through the butane-like molecular backbone. In the ether-like $O(SiH_2GeH_3)_2$ analog we find that the non-skeletal vibrations occur at essentially the same frequencies (to within 2–5 cm⁻¹) in both isomers, but with quite different relative intensities in general (see Table 1). For example, the GeH₃ wagging modes (N₅ and G₅) are much weaker in the lower symmetry gauche isomer than in the normal counterpart.

The simulated low-frequency spectra (Fig. 4) were next used to estimate the relative admixture γ of the isomers $(100\gamma = \%$ normal and $100(1-\gamma) = \%$ gauche) in the observed spectrum of the $O(SiH_2GeH_3)_2$ compound. A best fit is obtained by simultaneously varying the admixture parameter γ , the intensity of the simulated spectrum relative to that observed β , and the global frequency scale factor η which produces the best match in peak positions over the entire low-frequency range (300–1300 cm⁻¹). The optimization is carried out numerically by minimizing the following objective function (see eqn (8) below):

$$O(\beta,\gamma,\eta) = \sum_{k} \left[E_{\exp}(\omega_{k}) - \beta \left(\gamma \ I_{n}(\eta\omega_{k}) + (1-\gamma) \ I_{g}(\eta\omega_{k}) \right) \right]^{2}$$
(8)

yielding values $\gamma = 0.55$, $\beta \sim 1.4$ and $\eta = 0.9948$, which were then employed to create the synthetic spectrum labeled as "Theory" in Fig. 1 above. We note that the frequency scale factor ~0.995 obtained here for the ether-like compounds is similar to the value of ~0.990 obtained in our prior work on butane-like SiGe hydrides using the B3LYP/6-311++g(3df,3pd) level of theory. The best fit admixture implies nearly equal fractions of the two isomers (55% normal and 45% gauche) suggesting that their thermodynamic stability is comparable. A preliminary estimate of their relative stability is afforded by the static-molecule electronic energies at the B3LYP/6-311++g(3df,3pd) level of theory, which yielded identical energies to within a few milliHartree (E_0 (normal) = $-4814.430220E_h$ and E_0 (gauche) = $-4814.430147E_h$). A corresponding thermochemical estimate was obtained using the well-known CBS-QB3 level of theory, which reproduces experimental heats of formation to within a few kcal mol⁻¹. CODATA atomic heats of formation were combined with the molecular enthalpy estimates from CBS-QB3 to obtain standard heats of formation of -62.03 and -62.20 kcal mol⁻¹ for the normal and gauche isomers, respectively, corroborating the existence of equal isomeric proportions suggested by the independent spectral fitting procedure.

The analysis of the Raman spectrum proceeds along the same lines as the discussion of the infrared absorption. In Table 2 we show the assignment of the main Raman lines. The theoretical spectrum in Fig. 3 was corrected by the same scale factors as those used above in the IR calculations (0.979 for frequencies above 1500 cm⁻¹ and 0.995 for frequencies below 1500 cm⁻¹). The theoretical Raman intensities were normalized to the 876 cm⁻¹ line for the top panel and to the 2062 cm⁻¹ mode for the lower panel of Fig. 3. The observed doublet near 350 cm⁻¹ can be used to independently determine the normal/gauche admixture. Each of the isomers produces two Si-Ge Raman peaks, corresponding to in-phase and out-of-phase stretches of the two Si-Ge bonds. However, the predicted Raman intensity is much higher for the in-phase vibration, so that the Raman spectrum of a single isomer should be essentially dominated by one peak. The observation of a doublet is naturally explained by the combined contribution from the in-phase Si-Ge stretches in the normal and gauche isomers, respectively, which according to the theoretical simulations are separated by 7.5 cm⁻¹. A fit of the experimental Raman spectra using the theoretically predicted Raman intensities for the two modes yields a gauche isomer concentration of 44%, in remarkable agreement with the IR analysis, above. Further spectroscopic evidence for the coexistence of the two isomers is obtained from the high-energy Raman spectrum in the region of Ge-H stretches, which experimentally is represented by a single, relatively broad peak but is clearly split into two main peaks in the simulation of the normal isomer. The combination of the two isomers produces a complex broader structure, as seen in Fig. 3, which explains the experimental observation if the peaks are further broadened by effects such as isotopic disorder, particularly in the case of the Ge atoms.

To further elucidate the relative stabilities of the isomers we also calculated the potential energy surface (PES) of the $O(SiH_2GeH_3)_2$ molecule as a function of the Ge-Si-Si-Ge backbone torsion angle. This is similar in spirit to our earlier calculations for the butane-like GeSiSiGe hydride in which the linear (normal) conformation corresponds to a torsion angle of 180° while the gauche modification occurs at ~66°. In the present work we modified the Z-matrix to explicitly incorporate the Ge-Si-Si-Ge torsion angle, and then optimized all remaining structural degrees of the freedom, including the bond lengths and band angles involving the oxygen atom. Our results indicate that the optimized position of the oxygen along the PES curve is always found to be such that the repulsion between its lone-pairs and the remaining "SiH₂GeH₃" framework is minimal. Fig. 5 compares the torsional PES of $O(SiH_2GeH_3)_2$ with that of $H_3GeSiH_2SiH_2GeH_3$. We note that while the energy-torsion profiles are plotted on a common horizontal axis, the actual torsion angle of O(SiH₂GeH₃)₂ is 180° out-of-phase with that of H3GeSiH2SiH2GeH3.18 This is consistent



Fig. 5 Relaxed PES as a function of the molecular backbone torsion angle for $O(SiH_2GeH_3)_2$ (solid curve, A) and the butane-like hydride $H_3GeSiH_2SiH_2GeH_3$ (dotted curve, B) (ref. 18). In both cases the plots show that the gauche (g) isomer is metastable compared to its linear (n) counterpart, but only slightly so in the ether-like compound. Note the different vertical energy scales for compounds A and B, and that the torsion angle for the butane-like molecule is 180° out-of-phase with that of the ether-like compound (see ref. 18).

with the convention that the "normal" conformation is the one in which all backbone atoms are co-planar. Thus, in Fig. 5 the butanelike torsion is plotted as " $t - 180^{\circ}$ " to allow the PES profiles of the two molecules to be easily compared. The results show that the global minimum corresponds to the "normal" configurations, while in both molecules the "gauche" configurations are local minima. Using the DFT B3LYP/6-311G++(3df,3pd) description we obtain $\Delta E_{n-g} \sim 0.4$ kcal mol⁻¹ for the H₃GeSiH₂SiH₂GeH₃. However, a significantly smaller value of $\Delta E_{n-g} \sim 0.05$ kcal mol⁻¹ is computed for O(SiH₂GeH₃)₂ indicating that the forward and reverse barriers are of comparable magnitude (~0.2 kcal mol⁻¹). On statistical grounds this implies that the populations of normal and gauche isomers are expected to be the same, which is consistent with the experimental comparison of the vibrational spectra with the theoretical ~ 50/50 mixture proposed above.

Formation of SiGe nanocrystals in amorphous Si–Ge–O matrix. Deposition studies of $O(SiH_2GeH_3)_2$ was conducted on an Si(100) substrate using a molecular beam epitaxy (GS-MBE) chamber maintained at a base pressure of 3×10^{-10} Torr. The substrates were first outgassed at 650 °C under UHV to remove surface contaminants and then flashed at 1050 to 1200 °C for 20 s to desorb the native oxide from their surface. Gaseous $O(SiH_2GeH_3)_2$ was introduced onto the substrate surface at 500 °C through an injection manifold using a high precision needle valve. This arrangement allowed a constant flow to be maintained yielding a growth pressure of 5×10^{-5} Torr. The duration of the depositions was typically up to 90 min, producing layers that exhibited a visual appearance indistinguishable from that of the underlying Si wafer.

The bulk elemental content of the samples was determined by simulations of the Rutherford backscattering spectra (RBS). The Si and Ge concentrations were measured at 2 MeV (see Fig. 6) and a resonance nuclear reaction at 3.05 MeV was used to establish the precise oxygen content. For all films grown at 500 °C the composition was found to be 35-37% Si, 45-43%Ge and 20% O closely matching the Si₂Ge₂O composition of the O(SiH₂GeH₃)₂ precursor. Transmission electron microscopy (XTEM) observations of representative films showed the presence of fairly uniform layers exhibiting undulated surfaces, amorphous



Fig. 6 Representative 2 MeV RBS spectrum of a ~250 nm thick $Si_xGe_yO_z$ film on Si(100), yielding a composition of 35% Si, 45% Ge and 20% O. Thick gray and thin black lines represent measured data and simulated fit, respectively.

interfaces and average thicknesses in the range ~200 and 400 nm. The latter values are consistent with RBS estimates of the thickness and correspond to samples grown for 45 and 90 min at a growth rate of 3–4 nm min⁻¹. The high-resolution micrographs revealed the formation of well-defined and well-separated crystalline nanoparticles evenly distributed within an amorphous matrix with an average size of 4-5 nm (see Fig. 7). Using selected area diffraction patterns of the bulk layer and that of the Si substrate as an internal calibration standard, the unit cell parameter of the cubic structure of these grains was determined to be 5.58 Å. This value corresponds to a Si_{1-x}Ge_x alloy with composition x = 0.7 on the basis of Vegard's Law, which assumes linear interpolation between the lattice constants of elemental Si and Ge vs. atomic content. The presence of crystalline dots with Si_{0.30}Ge_{0.70} composition was also corroborated by Raman scattering experiments. Fig. 8 contains an overlay of representative spectra obtained for several films exhibiting the typical peak lineshape of crystalline $Si_{1-x}Ge_x$ alloys, consisting of Ge-Ge, Si-Ge and Si-Si bands. An analysis based on the known compositional dependence of the Raman bands²⁰ yielded $x \sim 0.64-0.73$, in excellent agreement with the diffraction measurements.

The observed composition of the SiGe nanocrystals suggests a specific reaction path for the assembly and final composition of the "nanoparticle + matrix" film shown in the XTEM micrograph of Fig. 7. Here we envision an oxygen condensation mechanism in which two or more precursor molecules react to form larger



Fig. 8 Raman spectrum of the Si–Ge–O material showing the characteristic Ge–Ge, Si–Ge and Si–Si vibrational bands observed in crystalline Si–Ge alloys.

diethoxymethane-like units *via* stoichiometric elimination of the well-known digermylsilane $SiH_2(GeH_3)_2$ compound according to eqn (9), and shown schematically in Fig. 9.

$$2 \operatorname{O}(\operatorname{SiH}_2\operatorname{GeH}_3)_2 \to \operatorname{SiH}_2(\operatorname{OSiH}_2\operatorname{GeH}_3)_2 + \operatorname{SiH}_2(\operatorname{GeH}_3)_2 \qquad (9)$$

The process can be envisioned as an isodesmic reaction sequence in which the bond enthalpy lost in breaking the Si-O and Si-Ge bonds is recovered when the diethoxymethane-like and digermylsilane product are formed. The steps involved in an actual reaction process likely involve discrete scission reactions in which individual Si-Ge (~300 kJ mol⁻¹) and Si-O (~370 kJ mol⁻¹) bonds, are broken in turn. In this scenario, the hypothetical SiH₂(OSiH₂GeH₃)₂ species polymerizes on the hot surface to form an amorphous Si-Ge-O suboxide while the SiH₂(GeH₃)₂ dissociates to produce $Si_{0.33}Ge_{0.66}$ alloy crystallites, with a composition very close to the experimental observation. In previous work we have carried out detailed deposition studies of SiH₂(GeH₃)₂ on Si(100) over a temperature range from 400-600 °C. At temperatures less than 450 °C we found that the compound produces monocrystalline and perfectly uniform Si_{0.33}Ge_{0.66} layers with atomically smooth surfaces, while for T > 450 °C we invariably formed arrays of self-assembled and perfectly coherent quantum dots possessing a composition of $Si_{0.33}Ge_{0.66}$ close to that observed ($Si_{0.30}Ge_{0.70}$) in this study. In view of these observations the outcome of our present O(SiH₂GeH₃)₂ depositions carried out under similar temperature/pressure conditions is perhaps not surprising-the common feature being the strong driving force to produce



Fig. 7 (a) XTEM micrograph showing nanocrystals of $Si_{0.30}$ Ge_{0.70} embedded in amorphous Si–Ge–O suboxide matrix. (b) The image on the right is an enlarged view of an individual crystallite showing the (111) lattice planes. (c) SAED pattern of the nanocrystals (rings) and the Si in (110) projection.



Fig. 9 Condensation reaction described by eqn (9) shown here as an isodesmic sequence, including a possible transition state structure suggested by preliminary quantum chemical calculations (Si, Ge, O and H atoms are drawn as gold, blue, red and white spheres, respectively).

 $Si_{0.33}Ge_{0.66}$ quantum dots. In this case the nano-structures are intergrown within the dielectric medium comprised of polymerized $SiH_2(OSiH_2GeH_3)_2$ as suggested by the reaction in eqn (9).

Finally, we note that the reaction depicted by eqn (9) implies a composition of Si₃Ge₂O₂ (or Si_{1.5}GeO) for the amorphous matrix and Si_{0.33}Ge_{0.66} for the nanocrystals, with the two components occurring in a 1 : 1 ratio. The lower density of nanocrystals potentially occurring in our actual films can be accounted for by assuming that some fraction of the O(SiH₂GeH₃)₂ molecules react at the surface to form a stoichiometric suboxide with formula Si₂Ge₂O *via* release of 5 moles of H₂. Thus, the combined action of the latter direct reaction with the condensation reaction in eqn (9) would produce 2 + M moles of suboxide with composition Si $\left(\frac{3+2M}{2+M}\right)$ Ge $\left(\frac{2+2M}{2+M}\right)$ O for every mole of SiGe₂ (Si_{0.33}Ge_{0.66}). For example, M = 0 corresponds to a 1 : 1 mixture of Si₃Ge₂O₂ (Si_{1.5}GeO) "matrix" and SiGe₂ nanocrystals, while M = 2 yield

(Si_{1.5}GeO) "matrix" and SiGe₂ nanocrystals, while M = 2 yields a film with a 4 : 1 ratio of Si₇Ge₆O₄ (Si_{1.75}Ge_{1.5}O) "matrix" and SiGe₂ nanocrystals.

To test these ideas we have carried out far-infrared studies of the vibrational properties of the samples using spectroscopic ellipsometry. Fig. 10 shows the imaginary part of the infrared dielectric function of a typical film. The IR response of $Si_{1,x}Ge_x$ crystals is very weak, so that the observed signal can be assigned to the amorphous matrix. In amorphous SiO₂ and GeO₂ the asymmetric stretch, symmetric stretch and rocking movements of the O atom in the Si–O–Si and Ge–O–Ge bonds produce three distinct absorption bands, which appear at 1082, 800 and 455 cm⁻¹ in SiO₂ and 857, 556 and 278 cm⁻¹ in GeO₂, respectively.²¹ The spectrum in Fig. 10 shows at least six different absorption bands, suggesting different local environments for the O atoms, as expected for an oxide matrix incorporating Ge and Si atoms. Some of the observed peaks can be directly related to the SiO₂ and GeO₂ spectra. For example, the 1030 cm⁻¹ band is close in frequency and



Fig. 10 Imaginary part of the dielectric function of the Si–Ge–O material showing several absorption features in the spectral range corresponding to IR-active vibrations in SiO₂ and GeO₂ glasses.

lineshape to the asymmetric stretch in SiO_2 , and there is clearly a peak below 300 cm⁻¹ (which unfortunately is beyond the spectral range of our ellipsometer) which can be assigned to the rocking O motion in a Ge–O–Ge bond. A complete study would require detailed vibrational calculations, but it is already apparent from this brief analysis that the IR spectrum is consistent with our conclusion above that the oxide matrix contains both Ge and Si atoms.

Conclusions

In this study we have reported the synthesis of ether-like SiGe hydrides including H₃SiOSiH₃ and O(SiH₂GeH₃)₂ using hydrolysis reactions involving silyl-germyl triflates. In the case of H₃SiOSiH₃ the overall process represents a new and practical synthetic route utilizing convenient reaction conditions. The compound is obtained for the first time in nearly quantitative yields and is readily purified to achieve semiconductor grade material for further applications in CVD fabrication of Si-O-N microelectronic components. The second, previously unknown $O(SiH_2GeH_3)_2$ was characterized experimentally using FTIR, Raman, mass spectroscopy and NMR, and studied in detail using state-of-theart first principles quantum chemical simulation methods. Theory predicts that the compound exists as two energetically identical isomers, closely related to the linear and gauche conformations observed in butane-like molecules, separated by a very small torsional barrier of ~0.2 kcal mol⁻¹. The observed vibrational spectra are found to correspond to a mixture of 55% linear and 45% gauche isomers, in accord with the thermodynamic expectations. The $O(SiH_2GeH_3)_2$ molecule was then employed to deposit Si₂Ge₂O materials on Si(100) at 500 °C. The composition, structure and nano-morphology of the films was characterized by RBS, XTEM, Raman and IR ellipsometry, which revealed the presence of Ge-rich Si_{0.30}Ge_{0.70} quantum dots (diameter ~5 nm) embedded within an amorphous matrix of Si-Ge-O suboxide possessing a composition between Si15GeO and Si175Ge15O depending on the precise density of nanoparticles present. The strategic synthesis of the new $O(SiH_2GeH_3)_2$ compound, and its subsequent deposition on Si(100) corroborates the notion that the precursor molecule confers its composition to the film via complete incorporation of its core. Collectively, our work represents a potentially useful framework for the development of new Si-Ge-O based dielectric materials, beginning at the molecular level.

Experimental

General considerations

All manipulations were carried out under inert conditions using standard high vacuum line and drybox techniques. Dry, air-free solvents were distilled from either anhydrous CaCl₂ or sodium benzophenone ketyl prior to use. The NMR spectra were collected on an Inova 500 MHz spectrometer. Samples were dissolved in deuterated benzene, and all nuclei were referenced either to the signal of TMS [Si(CH₃)₄] or the residual solvent peak as indicated below. Gaseous infrared spectra were obtained in 10-cm cells fitted with KBr windows. Gas chromatography mass spectrometry (GC-MS) data were obtained using a JEOL JMS-GC Mate II spectrometer. Lithium tetrahydroaluminate, phenyl trichlorosilane, trifluoromethane sulfonic acid, lithium hydride (Aldrich), gallium trichloride and hexachlorodisiloxane (Alfa Aesar), and electronic grade germane gas (donated by Voltaix, Inc.) were used as received. Deionized water was thoroughly degassed to remove all of the dissolved atmospheric oxygen prior to use. Phenylsilane, lithium tetrahydridoogallane and germylsilyl trifluoromethanesulfonate were prepared according to literature procedures.²²⁻²⁴ All starting materials were checked by NMR spectroscopy to verify their purities. Potassium germyl (KGeH₃) was synthesized in monoglyme by reaction of gaseous GeH4 with a finely dispersed sodium-potassium (80% K) alloy. Note: the Teflon bar that was used to stir the GeH₄/Na-K/monoglyme solution was encapsulated in glass owing to the high reactivity of Teflon with Na-K alloys. Caution: all reactions should be conducted with uttermost care. Any silane byproducts are pyrophoric and potentially explosive.

Synthesis of H₃SiOSiH₃ *via* reduction of Cl₃SiOSiCl₃. A solution of Cl₃SiOSiCl₃ (8.83 g, 31 mmol) in butyl ether (40 mL) was added slowly under reduced pressure (10 Torr) to a mixture of LiGaH₄ (3.75 g, 56.4 mmol) in 100 mL of butyl ether with stirring at –50 °C. The procedure involved the addition of several drops of Cl₃SiOSiCl₃/butyl ether to the reaction mixture with subsequent trapping of any volatiles through –78 and –196 °C traps under dynamic vacuum. Once all the Cl₃SiOSiCl₃ had been added, the reaction flask was allowed to slowly warm to room temperature with continuous trapping over the course of 2 h. Gas-phase IR revealed the presence of pure H₃SiOSiH₃ (4.3–8 mmol, 15–25% yield) in the –196 °C trap, and butyl ether in the –78 °C trap.

Synthesis of H₃SiOSiH₃*via* reactions of triflates. Distilled water was thoroughly degassed (1.4 g, 78 mmol) and then slowly added to a 100 mL flask containing H₃SiSO₃CF₃ (23.04 g, 128 mmol) held at -35 °C and 10 Torr pressure. An immediate increase in pressure to 30 Torr was observed and the volatiles were passed through traps held at -78 °C and -196 °C. The reaction flask was then slowly warmed to room temperature under dynamic pumping through -78 °C and -196 °C traps for 1 h. Gas-phase IR indicated the presence pure (SiH₃)₂O in the -196 °C trap (4.5 g, -90% yield), while the -78 °C contained the HSO₃CF₃ byproduct.

Synthesis of CH₃OSiH₃. Degassed CH₃OH (0.52 g, 16.3 mmol) was slowly added to a 100 mL flask containing

 $H_3SiSO_3CF_3$ (2.90 g, 16.0 mmol) at -35 °C and 10 Torr generating an immediate increase in pressure to 90 Torr. The volatiles were immediately passed through traps at -78 and -196 °C. The reaction flask was slowly warmed to 23 °C with continuous pumping through -78 and -196 °C traps for 1 h. Gas-phase IR indicated the presence of unreacted methanol in the -78 °C trap, while the -196 °C trap contained pure CH_3OSiH_3 (0.62 g, 63% yield).

Synthesis of O(SiH₂GeH₃)₂. Distilled water was thoroughly degassed (0.40 g, 22.2 mmol) and then slowly added to a 100 mL flask containing H₃GeSiH₂SO₃CF₃ (3.21 g, 12.6 mmol) at -35 °C under reduced pressure (~2 Torr). The reaction flask was slowly warmed to 23 °C while stirring for 1 h. The volatiles were fractionally distilled under dynamic vacuum through U-traps held at -30 and -196 °C. The latter was empty, while the former contained pure O(SiH₂GeH₃)₂ as a clear, colorless liquid (1.0 g, ~70% yield). Vapor pressure: ~10 Torr (23 °C). IR (gas cm⁻¹): 2153 (vs), 2069 (vs), 1148 (vw), 1078 (s), 953 (m), 886 (s), 863 (s), 791 (vs), 763 (vs), 466 (w), 356 (w). ¹H NMR (500 MHz, C₆D₆): δ 3.05 (t, 6H, GeH₃), δ 5.09 (q, 4H, SiH₂). ²⁹Si NMR: δ-21.1. GC-MS: m/z isotopic envelopes centered at 223 (M⁺), 193 (SiOGe₂H_x⁺), 176 $(SiGe_2H_x^+)$, 150 $(Si_2OGeH_x^+)$, 119 $(SiOGeH_x^+)$, 102 $(SiGeH_x^+)$, 75 (GeH_x⁺), 31 (SiH_x⁺), 16 (O⁺). The Raman measurements on the benzene solutions were measured at room temperature in the back-scattering configuration using a 532 nm laser line. The incident power was ~2 mW and the light was focused on the surface of the cuvette using a 10× objective. The scattered light was analyzed with a single-state 0.5 m monochromator equipped with 1800 lines/mm gratings and detected with a liquid-nitrogen cooled CCD detector. The spectral resolution is approximately 4 cm⁻¹. Similar experimental conditions were used for film measurements.

Ellipsometric measurements. Spectroscopic ellipsometry measurements were carried out at room temperature using an Infrared Variable Angle Spectroscopic Ellipsometer manufactured by J. A. Woollam Co. The IR-VASE system is based on a Fourier-Transform Infrared Spectrometer and covers the 0.04 eV to 0.62 eV range. The measurements were performed at three angles of incidence (55, 65 and 75 °). The Si–Ge–O samples were modeled as a three-layer system consisting of a Si substrate, Si-Ge-O film and a surface layer. The dielectric function of the Si substrate, with a resistivity of 0.01-0.02 ohm cm, was measured separately and used in tabulated form. The surface was modeled as a SiO_2 layer and the optical constants from Woollam software database were used in tabulated form. The IR dielectric function of the Si-Ge-O film was described using an optical dispersion model consisting of several Lorentzian oscillators and a parametric oscillator. The Lorentzian line shapes describe the various vibrational modes, whereas the parametric oscillator describes the lowest direct gap in the material. All adjustable parameters in the model, including the thicknesses of the surface and film layers are fitted using a proprietary Marquardt-Levenberg algorithm provided by the ellipsometer's manufacturer. A point by point fit is then used to extract the dielectric function of the material. Agreement of this dielectric function with the optical dispersion model guarantees Kramers-Kronig consistency between the real and imaginary parts of the experimental dielectric function.

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