

Synthesis, Structural Characterization, and Thermal Properties of the First Germanium N,N,N',N'-Tetraalkylguanidinates

Tianniu Chen,^{*,†} William Hunks,[†] Philip S. Chen,[†] Chongying Xu,[†] Antonio G. DiPasquale,[‡] and Arnold L. Rheingold[‡]

[†]Advanced Technology Development Division, Advanced Technology Materials Inc. (ATMI), 7 Commerce Drive, Danbury, Connecticut 06810 and ^{*}Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358, Urey Hall 5128, La Jolla, California 92093-0358

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Summary: The first examples of germanium N,N,N',N'-tetraalkylguanidinates have been prepared, and two of them have been structurally characterized. All of them exihibit high stability and volatility. Their potential as low-temperature precursors for MOCVD of Ge and Ge_xTe_y films has been explored.

Volatile germanium complexes have attracted considerable attention because of their potential applications as precursors for metal organic chemical vapor deposition (MOCVD), metal organic vapor-phase epitaxy (MOVPE), or atomic layer deposition (ALD) of metallic germanium and germanium alloy films for graded SiGe buffer layers, strained silicon being implemented in the next generation of complementary metal oxide semiconductor (CMOS) field effect transistor (FET) technology, silicon-based photonics, and more efficient solar cells.¹⁻⁷ Recently the use of both germanium(II)⁸⁻¹¹ and germanium(IV)¹²⁻¹⁷ precursors for MOCVD/ALD of phase-change chalcogenide alloy films with the prototype of GeTe or Ge₂Sb₂Te₅ (GST), which

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undergo a thermally induced crystalline-amorphous phase transition for data storage, has been demonstrated in the next-generation nonvolatile phase change random access memory (PRAM) to replace conventional dynamic and flash random access memory technology.^{18–23} However, there are some limitations associated with Ge(IV) precursors for MOCVD of Ge alloy films, such as high deposition temperatures, resulting poor film conformality and morphology, hazardous process conditions, and premature decomposition experienced when germane is present.¹²⁻¹⁷ In an

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(23) Akola, J.; Jones, R. O. *Phys. Rev. B* **2007**, *76*, 235207. (24) Synthesis of (TMG)₂GeCl₂ (1). Method A: (Me₂N)₂C=NH (HTMG) (93.2 mmol, 5.00 g) was dissolved in 100 mL of ether and then added slowly to the mixture of GeCl₄ (23.3 mmol, 5.00 g) in 10 mL of ether and NEt₃ (93.2 mmol, 9.43 g) at 0 °C, and the meiixture was stirred and warmed tomac_opb;its complementary NMR spectra are provided in the Supporting Information room temperature (RT) overnight. After filtration, the solvent was removed in vacuo, yielding off-white solid 1. Yield: 4.01 g (10.8 mmol, 46.4% based on GeCl₄). Method B: LiTMG (15.5 mmol, 11.3 g) was added to GeCl₄ (23.3 mmol, 5.00 g) in 100 mL of tomac_opb;its complementary NMR spectra are provided in the Supporting Information RT overnight. After filtration, the solvent was removed in vacuo, yielding off-white solid 1. Yield: 7.02 g (19.1 mmol, 82.0% based on GeCl₄). Anal. Calcd for GeN₆C₁₀H₂₄Cl₂: C, 32.29; H, ^{62.5} (10 Calc 10 Ci (10 Ci (10 Ci (10 Ci (10 Ci (10 Ci (10

(25) Synthesis of TMG)₂Ge(NMe₂)₂ (2). LiNMe₂ (6.08 mmol, 0.310 g) was added to complex 1 (2.96 mmol, 1.10 g) in 50 mL of ether slowly at °C, and the mciixture was stirred and warmed tomac_opb;its complementary NMR spectra are provided in the Supporting Information RT overlight. After filtration, the solvent was removed in vacuo, yielding off-white sticky solid **2**. Yield: 0.801 g (2.06 mmol, 69.6% based on 1). Anal. Calcd for GeN₈C₁₄H₃₆: C, 43.23; H, 9.33; N, 28.80. Found: C, 43.22; H, 9.34; N, 28.52. ¹H NMR (RT, 300 MHz, C₆D₆): δ 2.66 (24H, s, C(N(CH₃)₂)₂), 3.05 (12H, s, N(CH₃)₂), ¹³C{¹H} NMR (RT, 75 MHz, C_6D_6 : $\delta 40.14$ (C(N(CH_3)_2), 41.24 (N(CH_3)_2), 161.07 (C=N)

(26) Synthesis of (TMG)₂Ge(NEt₂)₂ (3). LiNEt₂ (25.3 mmol, 2.00 g) was added to complex 1 (12.0 mmol, 4.50 g) in 50 mL of ether slowly at 0 °C, and the mciixture was stirred and warmed tomac_opb;its complementary NMR spectra are provided in the Supporting Information RT overnight. After filtration, the solvent was removed in vacuo, (c) a solution of the second t, N(CH₂CH₃)₂), 2.67 (12H, s, C(N(CH₃)₂)₂, 3.41 (8H, q, N(CH₂CH₃)₂). $^{13}C{^{1}H}$ NMR (RT, 75 MHz, C₆D₆): δ 16.7 (N(CH₂CH₃)₂), 40.0 (C(N(CH₃)₂)₂), 40.7 (N(CH₂CH₃)₂), 160.2 (C=N).

^{*}To whom correspondence should be addressed: Tel: (203) 739-1405. Fax: (203) 830-2123. E-mail: tchen@atmi.com.

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ongoing effort to design and synthesize microelectronic materials to enable increased transistor performance, the N, N, N', N'-tetramethylguanidinate (TMG) ligand is introduced for the first time for the development of volatile, thermally robust Ge(IV) precursors as potential sources for low-temperature MOCVD processes.

We report here the synthesis of the first series of germanium N, N, N', N'-tetraalkylguanidinates: (TMG)₂GeCl₂ (1), $(TMG)_2Ge(NMe_2)_2$ (2), and $(TMG)_2Ge(NEt_2)_2$ (3) (Scheme 1).²⁴⁻²⁷ Complexes 1 and 2 are also the first structurally determined monomeric group 14 N,N,N',N'tetraalkylguanidinate complexes. The only other group 14 N, N, N', N'-tetraalkylguanidinate complex with a determined structure is the dimeric mixed-ligand Sn(II) complex $\{(\eta^3-Cp)Sn[\mu_2-N=C(NMe_2)_2]\}_2$ reported by Wright and his co-workers.²⁸ Furthermore, complex 1 (its complementary NMR spectra are provided in the Supporting Information) could potentially serve as a "synthon" for a variety of mixed-ligand germanium(IV) complexes. In addition, the formation of complex 1 using GeCl₄ with either [LiTMG]₆²⁹⁻³¹ or HTMG in the presence of triethylamine as an HCl scavenger provides multiple scalable routes toward mixed-ligand group 14 complexes for precursor development.

The monomeric solid-state structures of 1 and 2 were determined by single-crystal X-ray diffraction studies and are illustrated in Figures 1 and 2, respectively. The Ge^{IV} centers in both complexes occupy a distorted-tetrahedral coordination geometry that is composed of two nitrogen atoms and two chlorine atoms in 1 while it is composed of four nitrogen atoms in 2, two of which come from the TMG ligands and the other two from dimethylamido groups. The N-Ge-N angles between TMG ligands in 2 are larger due to the different ligand effects imposed by Cl and NMe2, respectively $(\angle N1-Ge1-N4 = 107.17(9)^{\circ} \text{ in } 1; \angle N3-Ge1-N4 =$ $120.12(6)^{\circ}$ in 2). The germanium-nitrogen bond lengths of Ge-N=C units in 1 (Ge1-N1 = 1.777(2) Å. Ge1-N4 = 1.768(2) Å) and 2 (Ge1-N3 = 1.8268(14) Å, Ge1-N4 = 1.8135(13) Å) are shorter than the reported bond lengths in the Ge^{IV} diphenylketimine Ge(N=CPh₂)₄ (1.872(5) Å),³² while they are more comparable to those in the Ge-N-N units in the Ge^{IV} hydrazide Ge(NMeNMe₂)₄ (1.828(2) and 1.834(2) Å).³³ The bond lengths of C=N in the terminal TMG ligands in 1 (N1-C1 = 1.303(3), N4-C6 = 1.302(3)Å) and 2 (N3-C5 = 1.277(2), N4-C10 = 1.284(2) Å) lie within the scope of few reported data on bridged-chelating TMG ligands in $\{Cp_2Gd[\mu^{-1}\eta:^2\eta - N = C(NMe_2)_2]\}_2$ (1.247) (8) Å)³¹ and {(η^3 -Cp)Sn[μ_2 -N=C(NMe₂)₂]}₂ (1.294(5) Å).²⁸ The Ge-N=C angles in 1 (Ge1-N1-C1 = $128.54(17)^{\circ}$, $Ge1-N4-C6 = 129.67(18)^{\circ}$ and 2 (Ge1-N3-C5 = $133.04(12)^{\circ}$, Ge1-N4-C10 = $129.77(12)^{\circ}$) are readily distorted, which are consistent with the corresponding observed angles in Ge(N=CPh₂)₄ (123.8(6) and 130.1(6)°)³² and most likely dependent on the packing effects in the solid state. Therefore, when the dichloride groups in 1 are replaced by dimethylamide groups in 2 or diethylamide groups in 3, the low melting point solid 1 (mp 52.9 °C) turns into the lower melting solid 2 (mp 46.7 °C) and the pale yellow liquid 3, which can be distilled at 60 °C under 60 mTorr of vacuum.

⁽²⁷⁾ Single-crystal X-ray diffraction: data collection was performed on a Bruker diffractometer with CCD detectors, equipped with a cryogenic nitrogen cold stream and using graphite-monochromated Mo K α radiation (0.71073 Å). The structures were solved by direct methods and refined anisotropically with the SHELXL-97 program suite. Crystallographic data for **1** (CCDC 728312) (colorless, 0.30 × 0.30 × 0.20 mm): GeN₆C₁₀H₂₄Cl₂, M_r = 371.84, monoclinic, a = 10.0347(9) Å, b = 11.4752(10) Å, c = 14.8505(14) Å, $\beta = 97.796(2)^\circ$, U = 1694.2(3) Å³, T = 100(2) K, space group P2₁/n, Z = 4, 6971 reflections collected, 3651 unique ($R_{int} = 0.0201$), which were used in all calculations. The final $R_w(F^2)$ value was 0.0952 (all data). Crystallographic data for **2** (CCDC 728313) (colorless, 0.12 × 0.08 × 0.08 mm): GeN₈C₁₄H₃₆, $M_r = 389.10$, monoclinic, a = 8.6692(4) Å, b = 15.7430(7) Å, c = 14.9497(7) Å, $\beta = 100.3190(10)^\circ$, U = 2007.32(16) Å³, T = 100(2) K, space group P2₁/n, Z = 4, 15 557 reflections collected, 3645 unique ($R_{int} = 0.0216$), which were used in all calculations. The final $R_w(F^2)$ value was 0.0637 (all data).

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Figure 1. Thermal ellipsoid plot of 1 showing 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ge1-N1 = 1.777(2), Ge1-N4 = 1.768(2), Ge1-Cl1 = 2.1957(7), Ge1-Cl2 = 2.1954(7), N1-C1 = 1.303(3), N4-C6 = 1.302(3); N1-Ge1-N4 = 107.17(9), N1-Ge1-Cl1 = 113.98(7), N4-Ge1-Cl1 = 113.43(7), N1-Ge1-Cl2 = 108.39(7), Ge1-N1-C1 = 128.54(17), Ge1-N4-C6 = 129.67(18).



Figure 2. Thermal ellipsoid plot of 2 showing 30% thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Ge1-N1 = 1.8312(14), Ge1-N2 = 1.8317(14), Ge1-N3 = 1.8268(14), Ge1-N4 = 1.8135(13), N3-C5 = 1.277(2), N4-C10 = 1.284(2); N1-Ge1-N2 = 100.91(6), N1-Ge1-N3 = 115.30(6), N2-Ge1-N4 = 116.32(8), N3-Ge1-N4 = 120.12(6), Ge1-N3-C5 = 133.04(12), Ge1-N4-C10 = 129.77(12).

Table 1. STA Data of Complexes 1–3

complex	T_{50} (°C)	onset temp (°C)	residual mass (%)
$Ge(NMe_2)_4^{a,b}$	115	104	7
1 ^b	230	210	3
2^b	207	190	0
3^b	222	203	0

^{*a*}Included for comparison. ^{*b*}Sample size (mg): 7.57, Ge(NMe₂)₄; 10.03, **1**; 9.57, **2**; 10.03, **3**.

The temperatures of 50% mass (T_{50}) loss derived from thermogravimetric analysis (TGA) in simultaneous thermal analyses (STA) experiments for the novel germanium N,N, N',N'-tetraalkylguanidinates **1–3** are given in Table 1. T_{50} values have been demonstrated to correlate with the



Figure 3. TGA curves of precursors 1-3 and $Ge(NMe_2)_4$.



Figure 4. Arrhenius plot showing Ge growth rate (log scale) in GeTe films as a function of the inverse substrate temperature for precursors $Ge(NMe_2)_4$ vs 2 in H₂.

volatility of the sample and are used to compare relative volatilities.^{34,35,36} The TGA plots (Figure 3) show the precursors are stable up to vaporization temperatures with minimal mass residuals, indicating substantial vapor-phase stability and exceptionally clean transport characteristics. The combination of a lower T_{50} and lower onset temperature strongly indicates their suitability for MOCVD/ALD applications.

Both germanium and binary GexTey films were deposited using precursor **2**, which shows the best combined volatility and thermal stability among the three tetramethylguanidinates, in the presence of H₂ and in a temperature range of 240–320 °C (Figure 4). The commercially available Ge^{IV} precursor Ge(NMe₂)₄ was also investigated under the same experimental conditions for comparison. The growth rate of Ge was monitored by wavelength dispersive X-ray fluorescence (XRF), and the growth rates of Ge films using **2** are lower than those using Ge(NMe₂)₄ in our process. However, the growth rates of **2** are in line with the reported growth rates of Ge films using Ge(NMe₂)₄ and higher than those using Ge(N(SiMe₃)₂)₄.¹² Our preliminary growth rates of Ge (0.3 Å/min) during

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MOCVD of GeTe films using complex **2** suggests it is an alternative low-temperature Ge precursor as compared to $Ge(NMe_2)_4$, especially when the substrate temperature is as low as 240 °C. The lower temperature is of greater interest for the growth of GeTe films because the tellurium precursors usually are not thermally stable at 350 °C and higher.^{21,37}

In summary, the first examples of monomeric group 14 N, N, N', N'-tetraalkylguanidinates have been prepared and structurally characterized. Complex 1 was shown to be a useful and versatile starting material for the design of Ge^{IV} MOCVD precursors 2 and 3. Complex 2 is highly stable in the vapor phase, displays substantial vapor pressure, and was explored as a potential Ge CVD precursor. Complex 2 exhibited comparable Ge growth

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rates at low deposition temperatures versus the commercially available precursor in the MOCVD of Ge_xTe_y films, for potential applications in MOS-FETs, selective growth of Ge films directly on Si substrates, optoelectronic devices, III/V integration on Si, and the integration of microelectronics with optical components (photodiodes) into a single chip.

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Supporting Information Available: Figures giving ¹H and ¹³C NMR spectra of the new compound **1** and CIF files giving X-ray crystallographic data for **1** and **2**. This material is available free of charge via the Internet at http://pubs.acs.org.