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N-Substituted Hexamethyldisilazanes as New Substances for the Synthesis of Functional Films in the System Si–Ge–C–N–H

S. V. Sysoev[a], L. D. Nikulina[a], A. O. Kolontaeva[a], M. L. Kosinova[a], A. A. Titov[a], V. I. Rakhlin[b], I. P. Tsyrendorzhieva[b], A. V. Lis[b], and M. G. Voronkov[b]

[a] *Nikolaev Institute of Inorganic Chemistry, Siberian Branch, Russian Academy of Sciences, pr. Akademika Lavrent'eva 3, Novosibirsk, 630090 Russia*
e-mail: marina@niic.nsc.ru

[b] *Favorskii Irkutsk Institute of Chemistry, Siberian Branch, Russian Academy of Sciences, ul. Favorskogo 1, Irkutsk, 664033 Russia*

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Abstract—*N*-Organylbis(trimethylsilyl)amines of the general formula $RN(SiMe_3)_2$ (R = Me_3Si, Et_3Ge) were synthesized by reaction of sodium bis(trimethylsilyl)amide with the corresponding trialkylsilyl(germyl) halide. Their IR, UV, and ^1H, ^{13}C, and ^{29}Si NMR spectra were studied, and saturated vapor pressures and thermal stabilities were determined. The possibility of using the $RN(SiMe_3)_2$ compounds as precursors in chemical vapor deposition of films with specified composition was estimated by thermodynamic modeling.

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Organosilicon compounds are promising as starting materials for the preparation of substances used in various fields of science and technics. An example of their application in microelectronics is their use as dry vacuum resists [1–3]. Some organosilicon compounds are used to obtain ultrathin aligning films for the manufacture of display devices [4]. Much attention is given to the synthesis of volatile organosilicon compounds for the preparation of films and coatings based on silicon nitride, carbide, and carbonitride (SiC_xN_y) by plasma-enhanced chemical vapor deposition (PECVD) [5–8]; SiC_xN_y films possessing various sets of functional properties were obtained. Introduction of germanium atoms into molecules of organosilicon compounds could give rise to new functional materials with specific optical and electric properties, as well as to biologically active substances [9, 10].

We previously studied reactions of N,N-disubstituted carboxylic acid amides with iodotrimethylsilane and obtained a series of aminosilanes: Me_3SiNEt_2, $Me_3SiNNAll$, $Me_3SiNHPh$. These compounds may be recommended for use as pre-cursors of silicon carbonitride films in chemical vapor deposition (CVD) processes [11].

In the present work we examined specificity of the synthesis of *N*-organylbis(trimethylsilyl)amines of the general formula $RN(SiMe_3)_2$ (R = Me_3Si, Et_3Ge) and their physicochemical parameters as precursors for the preparation of thin-layer structures by vapor deposition. The target compounds were synthesized by reaction of sodium bis(trimethylsilyl)amide with trimethylsilyl or triethylgermyl halide in toluene. The products were colorless gel-like substances with a specific odor, which readily liquefied on heating. Their yield and purity depended on the initial organyl halide and solvent nature. The yield of **I** was 82%, and the yield of **II** was 77%.

$$(Me_3Si)_2NH + Na \xrightarrow{PhCH=CH_2} (Me_3Si)_2NNa,$$

$$(Me_3Si)_2NNa + R_3MHlg \rightarrow (Me_3Si)_2NMR_3,$$

R_3M = Me_3Si (**I**), Et_3Ge (**II**), Et_3Sn (**III**).

The IR spectra of compounds **I** and **II** are given in Table 1. Absorption bands were assigned according to [12, 13]. Bands typical of vibrations of the Si–N–Si fragment in disilazanes were observed in the region

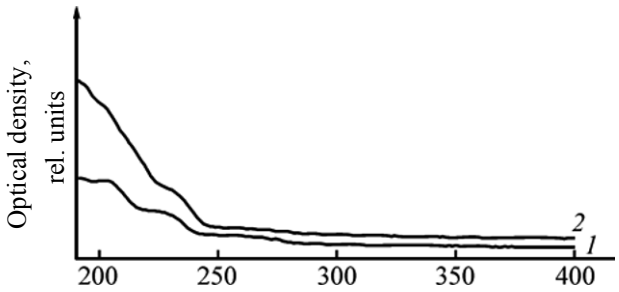

Fig. 1. UV spectra of compounds (*1*) **I** and (*2*) **II**.

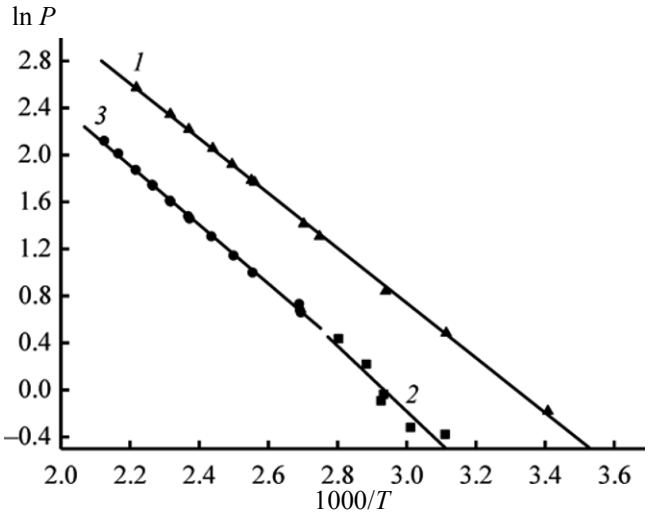

Fig. 2. Temperature dependences of saturated vapor pressure of (*1*) $N(SiMe_3)_3$ and (*2*, *3*) $Et_3GeN(SiMe_3)_2$.

837–962 cm^{-1}. Strong bands in the regions 1252–1257 and 1354–1460 cm^{-1} resulted from stretching and bending vibrations of the Si–C bonds. Stretching vibrations of the C–H bonds gave rise to absorption at 2874–2956 cm^{-1}. Compounds **I** and **II** displayed in the UV spectra absorption maxima at λ 200–270 nm (Fig. 1).

Table 1. IR spectra (ν, cm^{-1}) of compounds **I** and **II**

I	II	Assignment
2956	2955	ν_{asim} (CH) in CH_3
2902	2907	ν_{sim} (CH) in CH_3
	2874	ν_{asim} (CH_2) in CH_2CH_3
		ν_{sim} (CH_2) in CH_2CH_3
1439	1460	δ (Si–CH_3), δ (Si–CH_2–CH_3)
1406	1431	
1354		
	1379	δ_{asim} (CH_2) in CH_2CH_3
1257	1252	ν(Si–C)
	1007	
918	962	ν(Si–N–Si)
844	916	
	879	
	837	
766	758	$\delta_{wagging}$ (NH) + rocking vibrations
		(– CH_3) in $Si(CH_3)_x$
679	698	twisting, in-plane,
	673	and out-of-plane
620	617	vibrations in amines
	575	vibrations of the M(Ge)–N bond,
397	382	composite lattice vibrations

The temperature dependences of saturated vapor pressure of compounds **I** and **II** were determined by the static method with the aid of a glass membrane pressure gauge [14] (Fig. 2). Processing of the experimental data with the sum of squared normalized pressure deviations as target function [15] gave temperature dependences of saturated vapor pressure in the form $\ln P = A - B/T$, and thermodynamic parameters of vaporization processes (enthalpy and entropy of vaporization at the mid temperature in the examined range) were determined. The results are collected in Table 2. Compounds **I** and **II** turned out to be fairly stable within the examined temperature range, as followed from good agreement between the data on vapor pressure obtained upon heating and cooling. The plots shown in Fig. 2 allowed us to estimate the temperature and heat effect of the transition of $Et_3GeN\cdot(SiMe_3)_2$ from jellous to liquid state: T = 340±3 K, ΔH = 15±8 kJ mol^{-1}. Qualitative volatility parameters of organometallic compounds can be obtained by integral thermal analysis; the corresponding data are shown in Fig. 3. It is seen that the temperature of maximal weight loss for compound **II** is higher than for compound **I**, which is consistent with the obtained quantitative data on vapor pressure.

Thermodynamic modeling provides an efficient method for the determination of optimal conditions for chemical vapor deposition (CVD). It makes it possible to predict the composition of deposited phase complexes and partial pressures of components of the equilibrium gas phase upon vide variation of the

Table 2. Thermodynamic parameters of vaporization of compounds **I** and **II**

Compound	ln *P*(Topp) = A – B/*T*		ΔH_{vap}, kJ mol^{-1}	$\Delta S°_{vap}$, J mol^{-1} K^{-1}	Temperature, °C
	A	B			
$Et_3GeN(SiMe_3)_2$	17.77	6072	50.5±0.3	92.7±0.7	50–200
$N(SiMe_3)_3$	18.07	5474	45.5±0.2	95.1±0.4	20–178

conditions (temperature, pressure) and compositions of the initial gas mixture. The calculation procedure is based on minimization of the ratio of the Gibbs energy of a flow system to the amount of non-deposited element (e.g., hydrogen or inert gas), which is described in detail in [16]. It was believed that a condensed phase has a constant composition and that gaseous substances conform to the ideal gas law. As initial data we used standard thermodynamic parameters of individual substances: $\Delta_f H°$, $S°$, $C°_p = f(T)$. Unfortunately, thermodynamic parameters of ternary compound (silicon carbonitride), germanium carbide and nitride, and their possible compounds with hydrogen are unknown. The set of consistent thermodynamic parameters for all compounds was taken the Electronic Technics Materials Database (Nikolaev Institute of Inorganic Chemistry, Novosibirsk).

Thermodynamic modeling of chemical vapor deposition in the system Si–C–N–H was performed over a wide temperature range (300–1300 K) at a pressure of 0.01 to 10 mm using $N(SiMe_3)_3$ as initial compound in a mixture with an inert gas and hydrogen. Here, the input flows of the precursor and carrier gas were treated as flows of elements, and an additional gas flow (He, H_2) was assumed to be possible in the deposition zone.

The CVD diagram in Fig. 4 shows temperature ranges for deposition of different phase complexes under conditions ensuring thermal decomposition of the reagent alone or its decomposition in an inert gas. In the low-temperature region, joint deposition of silicon carbide and nitride with carbon should be observed. The process in the presence of hydrogen in the low-temperature region should result in deposition of silicon carbide and nitride without impurity of carbon. Figure 5 shows the CVD diagram in the system $N(SiMe_3)_3$–H_2. Increase of the overall pressure extends temperature range of phase equilibria. Deposition of silicon nitride may be expected in the low-temperature process with the use of ammonia.

Thus the examined compounds are promising as precursors for chemical vapor deposition of various functional thin-layer structures from the viewpoints of both their physicochemical properties (saturated vapor pressure, thermal stability) and the possibility for formation of silicon carbonitride (SiN_xC_y) over a fairly wide range of conditions.

EXPERIMENTAL

The concentrations of carbon, hydrogen, nitrogen, and silicon were determined by burning with the aid of

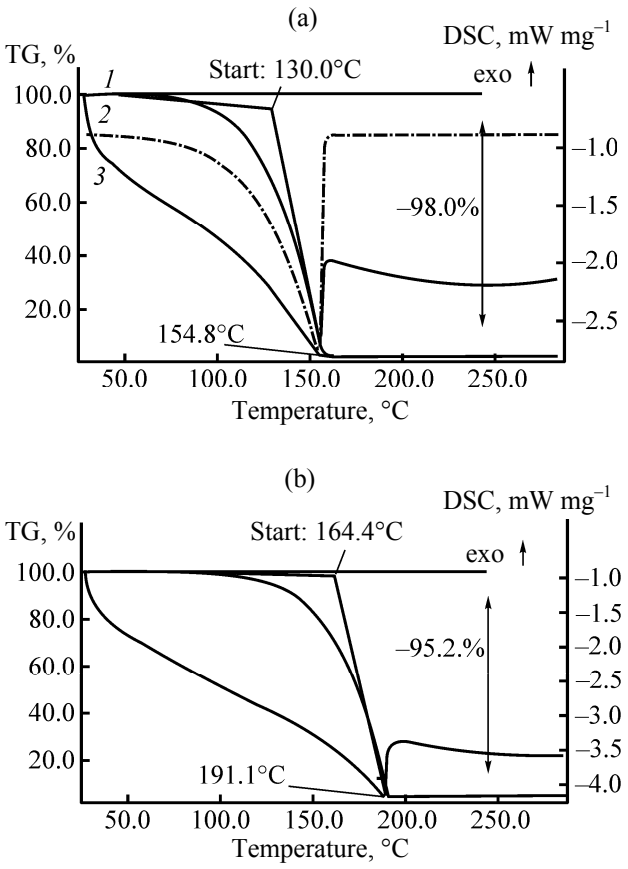

Fig. 3. Thermal analysis of compounds (a) **I** and (b) **II**: (*1*) TG, (*2*) DTG, and (*3*) DSC.

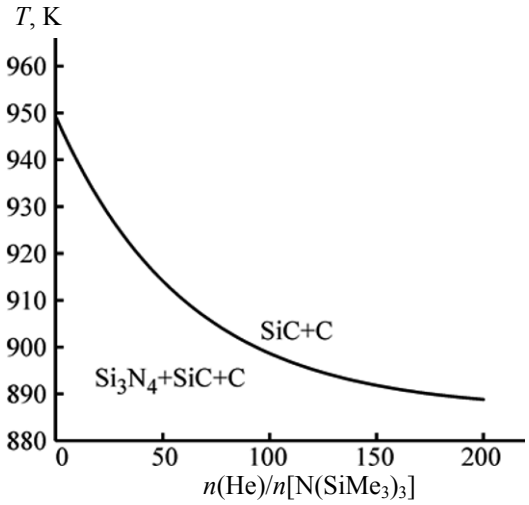

Fig. 4. CVD diagram of the system $N(SiMe_3)_3$–inert gas; pressure 0.01 mm.

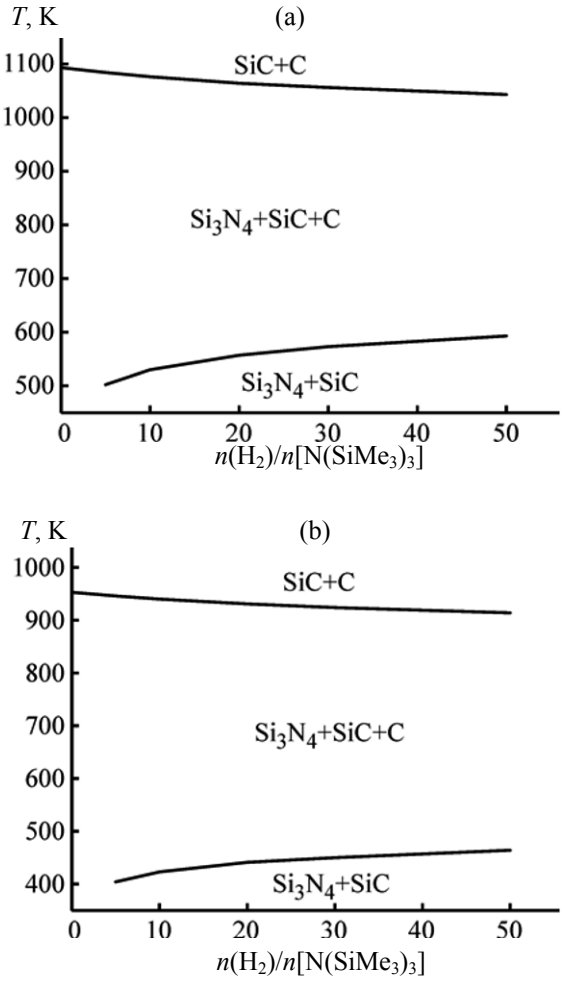

Fig. 5. Temperature ranges for phase complexes in the system $N(SiMe_3)_3$–H_2 at different hydrogen flow rates at a residual pressure of (a) 1 and (b) 0.01 mm.

a Thermo Finnigan Flash EA 1112 Series C,H,N analyzer. The IR spectra (375–7800 cm^{-1}) were recorded from samples placed between KBr plates on a Scimitar FTS 2000 (Digilab) spectrometer with Fourier transform (resolution 1 cm^{-1}). The UV spectra (λ 190–400 nm) were measured on a Shimadzu UV-3101PC scanning spectrophotometer from films applied to an optically transparent quartz support. The refractive indices were determined by spectrophotometry. The ^1H, ^{13}C, and ^{29}Si NMR spectra were recorded on a Bruker DPX 400 instrument at 400.13, 100.58, and 79.46 MHz, respectively, from solutions in $CDCl_3$ using tetramethylsilane as reference. Thermal analysis was performed in a helium atmosphere using a Netzsch STA 409 thermal analyzer. The saturated vapor pressures were measured by static method with the aid of a glass membrane pressure gauge [14].

Tris(trimethylsilyl)amine (I). A mixture of 36 g (0.22 mol) of hexamethyldisilazane and 22 ml of styrene was added dropwise under stirring to a suspension of 5.1 g (0.22 mol) of metallic sodium in 250 ml of boiling toluene. The mixture was stirred for 3 h on heating under reflux, 24 g (0.22 mol) of chlorotrimethylsilane was slowly added, the mixture was stirred for 4 h under reflux, the solvent was distilled off, and the precipitate was filtered off. Vacuum distillation of the filtrate gave 41.6 g (82%) of compound **I** with bp 98–100°C (13 mm); published data [17]: bp 216°C (760 mm). ^1H NMR spectrum: δ 0.21 ppm, s (27H, CH_3). ^{13}C NMR spectrum: δ_C 5.34 ppm (CH_3). ^{29}Si NMR spectrum: δ_{Si} 2.34 ppm. Found, %: C 46.19; H 10.98; N 5.38; Si 37.54. $C_9H_{27}Si_3N$. Calculated, %: C 46.28; H 11.65; N 6.00; Si 36.07.

Triethylgermylbis(trimethylsilyl)amine (II) was synthesized in a similar way from 31 g (0.19 mol) of hexamethyldisilazane and 45 g (0.19 mol) of bromotriethylgermane using 4.4 g (0.19 mol) of metallic sodium and 20 ml of styrene. Vacuum distillation gave 47 g (77%) of compound **II** with bp 100–105°C (2 mm). ^1H NMR spectrum, δ, ppm: 0.14 s (18H, $SiCH_3$), 1.30 q (6H, CH_2), 1.11 t (9H, CH_3). ^{13}C NMR spectrum, δ_C, ppm: 5.65 ($SiCH_3$), 8.60 (CH_2), 9.64 (CH_2CH_3). ^{29}Si NMR spectrum: δ_{Si} –2.2 ppm. Found, %: C 45.73; H 10.61; N 3.68. $C_{12}H_{33}GeSi_2N$. Calculated, %: C 45.02; H 10.39; N 4.37.

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