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Vapor Pressure of Tetrakis(dimethylamino)germanium

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The vapor pressure of tetrakis(dimethylamino)germanium (CAS RN 7344-40-3) was measured using the static method in the technologically important temperature range (278 to 308) K. The experimental data were fitted with the Clarke and Glew equation. To our knowledge, this is the first time that the vapor pressure measurements for this compound are reported.

Introduction

Metalorganic vapor phase epitaxy (MOVPE) and other epitaxial techniques use a broad variety of organometallic precursors. The knowledge of the essential physical and chemical parameters of such compounds is necessary for precise application of these materials during technological processes. In particular, volatility data and a detailed vapor pressure equation are essential for controlled precursor dosimetry and thermodynamic analysis of MOVPE growth.[1−3] At the pressures typical of organometallic precursors, often less than 1000 Pa, the accurate determination of vapor pressure is not an easy task. It is not unusual for measurements made by different methods or in different laboratories to differ relative to each other by tens of percent or even orders of magnitude. Contamination of the sample by a gas or a volatile liquid is a common source of error, and maintaining an accurately calibrated pressure gauge below 1000 Pa is always difficult. Organometallic precursors present additional challenges because many are pyrophoric, toxic, or sensitive to moisture and oxygen. Special care is needed for their safe handling and for avoiding the uncertainties caused by their decomposition products. As a consequence, experimental vapor pressure data for these compounds either show significant scatter or are unavailable. Our laboratories have been involved in systematic measurement of vapor pressure of new as well as recently available high quality precursors used for MOVPE. The vapor pressure data of the precursors of Ga, Al, Sb, Zn, Si, In, Y, Zr, and Ge ($Ge(OCH_3)_4$ and $Ge(OC_2H_5)_4$) were published in our previous works.[4−10] In this work, we report the vapor pressure data for tetrakis(dimethylamino)germanium, $Ge[N(CH_3)_2]_4$, in the technologically important interval (273 to 308) K. $Ge[N(CH_3)_2]_4$ is the precursor used for the growth of Ge−Te and Ge−Sb−Te alloys which are under intense investigation for applications in the field of optical and electrical storage due to their fast reversible crystalline-to-amorphous phase transition induced by either laser or electrical pulses. Phase-change materials are now successfully employed in the optical data storage and are becoming promising candidates for the future electronic storage applications.[11]

Experimental Section

$Ge[N(CH_3)_2]_4$ was supplied by SAFC Hitech−Sigma Aldrich in a stainless steel container under nitrogen atmosphere. The metal mass fraction impurities as determined by ICP-MS were less than $1 \cdot 10^{-7}$, and organic impurities as determined by FT-NMR were less than $2 \cdot 10^{-5}$. The container was equipped with VCR fittings allowing direct connection to the degassing and measuring apparatuses that were kept under high vacuum. This avoided any contamination of $Ge[N(CH_3)_2]_4$ by oxygen or moisture during the degassing and vapor pressure measurements. The thorough degassing was performed by a multistage vacuum distillation as described in detail in ref 9.

Apparatus and Procedure. Vapor pressure measurements were performed using the static method with an apparatus internally denoted as STAT4. The apparatus and measuring procedure were previously described in detail.[12] Therefore, only a short description is given.

The pressure was measured by a capacitance diaphragm absolute gauge MKS Baratron 690A11TRA (MKS Instruments Inc., USA). Its measuring upper limit is 1333 Pa. The temperature of the pressure sensor was kept at $T = 318$ K by the self-controlling temperature system. The calibration of the gauge performed by the manufacturer at 11 equally spaced pressures from (0 to 1333) Pa with a maximum relative deviation of 0.03 % is traceable to the National Institute of Standards and Technology (NIST). Additional calibration focusing on the beginning of a pressure span was performed in the Czech Metrology Institute. The uncertainty of the pressure reading is estimated to be less than 0.05 %. The sample temperature was measured by a platinum resistance thermometer Pt100 in a four-wire connection. The thermometer was calibrated at the ice point and/or by comparison to the standard platinum resistance thermometer (SPRT). This SPRT was calibrated to the ITS-90, and its calibration was traceable to NIST. The uncertainty of the temperature measurement was estimated to be less than 0.02 K. All temperatures reported here are based on the international temperature scale ITS-90. The apparatus STAT4 is fully automated. The overall uncertainty in the vapor pressure measurement using the STAT4 apparatus is adequately described

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Table 1. Experimental Data on Vapor Pressure of Liquid $Ge[N(CH_3)_2]_4$[a]

T/K	p/Pa	Δp/Pa
278.15	11.92	0.31
278.15	11.98	0.36
283.15	16.93	−0.04
283.15	16.96	−0.01
288.15	24.05	−0.41
288.15	23.98	−0.48
293.15	33.99	−0.83
293.15	33.88	−0.94
298.15	48.28	−0.72
298.15	48.25	−0.74
302.95	67.87	0.59
302.95	67.90	0.63
308.17	96.12	2.20
308.17	96.10	2.18

[a] $\Delta p = p - p^{\text{calcd}}$, where p^{calcd} is calculated from the Clarke and Glew eq 1 with parameters given in Table 2.

Table 2. Parameters of Clarke and Glew Equation 1 at the Reference Temperatures θ =298.15 K and Pressure $p^0 = 10^5$ Pa

$\Delta_l^g G_m^0$	$\Delta_l^g H_m^0$	($T_{\min}$ to $T_{\max}$)	σ^a
(J·mol^{-1})	(J·mol^{-1})	K	Pa
18892.84 ± 15.75	49619.61 ± 401.42	278 to 308	1.06

[a] σ is the standard deviation of the fit defined as $\sigma = [\sum_{i=1}^{n}(\Delta p)_i^2/(n - m)]^{1/2}$, where Δp is the difference between the experimental and the smoothed values; n is the number of experimental points used in the fit; and m is the number of adjustable parameters of Clarke and Glew eq 1.

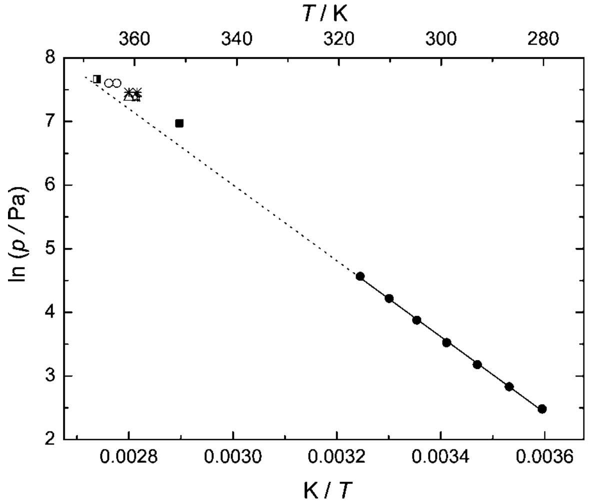

Figure 1. Comparison of vapor pressure for $Ge[N(CH_3)_2]_4$ obtained in this work with the literature values. ●, this work (experimental values); —, this work (smoothed values); ···, this work (extrapolated values); ○, Anderson;[13] Δ, Bürger and Sawodny;[19] ■, Mack;[16] ☆, Pacl et al.;[17] ∗, Rejhon et al.;[18] ◧, Lee et al.[14]

by the expression $\sigma(p/\text{Pa}) = 0.005(p/\text{Pa}) + 0.05$. This expression was derived based on the calibration measurements with naphthalene.[12] The uncertainty can be higher in cases when the compounds of lower purity or stability are investigated.

Results and Discussion

The vapor pressure measurements of $Ge[N(CH_3)_2]_4$ were performed in the temperature interval (278 to 308) K by varying the temperature at random to detect systematic errors caused by possible decomposition or insufficient degassing of the sample. When the pressure at selected temperatures, at which the experiments were performed repeatedly, did not change with the number of measuring cycles, the sample was considered completely degassed, and the final set of data was recorded. Two experimental points were obtained for each temperature. $Ge[N(CH_3)_2]_4$ undercooled readily which allowed us to determine the vapor pressure for the liquid phase well below the reported melting temperature 287.15 K.[13,14] The sample solidified when cooled below approximately 275 K. When the solid sample was heated with a rate of 3 K·min^{-1}, it obviously melted at 290 K (see Figure S1 in Supporting Information).

The experimental data on vapor pressure listed in Table 1 were fitted with the Clarke and Glew equation[15]

$$R \ln\left(\frac{p}{p^0}\right) = -\frac{\Delta_l^g G_m^0(\theta)}{\theta} + \Delta_l^g H_m^0(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) \qquad (1)$$

where p is the vapor pressure; p^0 is a selected reference pressure; θ is a selected reference temperature; R is the molar gas constant ($R = 8.314472$ J·K^{-1}·mol^{-1}); $\Delta_l^g G_m^0$ is the difference in molar Gibbs energy between the gaseous and the liquid phase at the selected reference pressure (the gaseous phase is supposed to have characteristics of ideal gas at the pressure p^0); and $\Delta_l^g H_m^0$ is the vaporization enthalpy. Given the temperature range studied, the use of the Clarke and Glew eq 1 with two parameters is adequate. The advantage of this equation lies in a physical significance of the fitted parameters. The parameters of the Clarke and Glew eq 1 together with the standard deviation of the fit, σ, are presented in Table 2.

To our knowledge, there is no previous work reporting vapor pressure measurements on $Ge[N(CH_3)_2]_4$. Only values reported at single or two temperatures, often obtained in studies devoted to synthesis of $Ge[N(CH_3)_2]_4$, were found in the literature.[13,14,16−19] These values are reported in the temperature range (355 to 362) K that is well above the upper temperature limit of this study (T = 308 K). As extrapolating the vapor pressure equation far beyond the temperature range for which its parameters are applicable can lead to serious errors, in particular when only a two constant equation such as as eq 1 is employed, the comparison with the literature values cannot a priori be conclusive. Still, the comparison displayed in Figure 1 using ln p as a function of $1/T$ representation shows qualitative agreement among our and the literature data. The relative deviations range from (10 to 40) %. As the normal boiling temperature, T_{nbp}, is one of the basic characteristics of a compound used as input in many correlations and estimation methods, $T_{\text{nbp}} = 482$ K was calculated using eq 1. Given the length of extrapolation, this value compares satisfactorily with that reported by Anderson,[13] $T_{\text{nbp}} = 476$ K, which is adopted by different physicochemical databases used today and also chemical suppliers.

Conclusions

Vapor pressure data for liquid $Ge[N(CH_3)_2]_4$ in the temperature range typically used in MOVPE were obtained. To our knowledge, this the first study on vapor pressure for this compound.

Supporting Information Available:

Detection of the melting temperature of $Ge[N(CH_3)_2]_4$ in the static apparatus (Figure S1). This material is available free of charge via the Internet at http://pubs.acs.org.

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