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Vapor pressure of germanium precursors

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ABSTRACT

The vapor pressure of two germanium precursors tetrakis(methoxy)germanium ($Ge(OCH_3)_4$, CASRN 992-91-6) and tetrakis(ethoxy)germanium ($Ge(OC_2H_5)_4$, CASRN 14165-55-0) was determined using a static method in the temperature range 259–303 K. The experimental vapor pressure data were fit with the Antoine equation. The mass spectra before and after degassing by vacuum distillation at low temperature are also reported and discussed.

1. Introduction

Metalorganic vapor-phase epitaxy (MOVPE) [1], metalorganic molecular beam epitaxy (MOMBE) and other epitaxial techniques use a broad variety of organometallic precursors. The correct and exact knowledge of the essential physical and chemical parameters is necessary for precise technological application of these materials during technological processes. In particular, volatility data and a detailed vapor pressure equation is essential for controlled precursor dosimetry. Our laboratory has been involved in systematic measurement of vapor pressure of new as well as recently available high-quality precursors used for MOVPE [2–6] for which the data on vapor pressure are missing and/or the data were measured a long time ago and reflect the state of purity and measuring techniques available then. Vapor pressure data obtained using the static method may also systematically deviate due to insufficient degassing of samples. In this work, we report the vapor pressure data for two germanium precursors tetrakis(methoxy)germanium ($Ge(OCH_3)_4$) and tetrakis(ethoxy)germanium ($Ge(OC_2H_5)_4$) in the technologically important interval 259–303 K. To our knowledge this is the first time that the vapor pressure data for these precursors are reported in this temperature range.

2. Experimental procedure

Both the studied precursors $Ge(OCH_3)_4$ and $Ge(OC_2H_5)_4$ were supplied by SAFC Hitech–Sigma Aldrich. $Ge(OCH_3)_4$ and $Ge(OC_2H_5)_4$ are liquids in the temperature range 259–303 K. The degassing of samples is a prerequisite for correct vapor pressure measurement using the static method. First, the samples were degassed by pumping down the vapor components above the sample at liquid nitrogen temperature (LNT) followed by heating up the sample to room temperature with the vacuum pump disconnected from the system. The sample was then kept at room temperature for some time in order to allow the system to reach equilibrium between the vapor and liquid phases. This cycle was repeated fifteen times for each sample. As the vapor measurements indicated that the samples were still not sufficiently degassed after this procedure (measured pressure at constant temperature was decreasing with the number of measuring cycles) we decided to use another method for degassing—multistep vacuum distillation at low temperatures. The distillation apparatus is shown in Fig. 1. The material is evaporated from the cell placed at higher temperature (T_1, evaporation temperature) and transported to the cell placed at lower temperature (T_2, condensation temperature) at which the sample condenses and non-condensable gases are pumped out. In two subsequent steps, during which T_2 (evaporation temperature) $>T_3$ (condensation temperature) and T_3 (evaporation temperature) $>T_4$ (condensation temperature), the sample is transported to the measuring cell. The evaporation and condensation temperatures have to be

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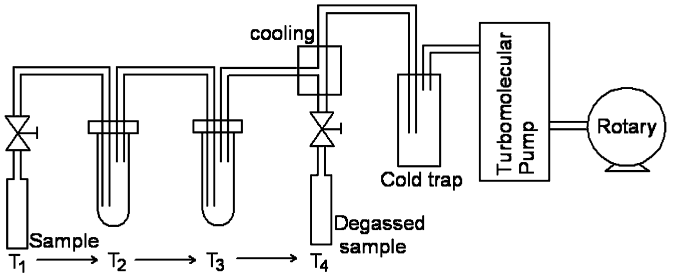

Fig. 1. Distillation apparatus for sample degassing. The material is evaporated from the cell placed at higher temperature (T_1, evaporation temperature) and transported to the cell placed at lower temperature (T_2, condensation temperature) at which the sample condenses and non-condensable gases are pumped out. In two subsequent steps, during which T_2 (evaporation temperature) $>T_3$ (condensation temperature) and T_3 (evaporation temperature) $>T_4$ (condensation temperature), the sample is transported to the measuring cell.

properly selected in order to achieve the greatest efficiency of degassing. $Ge(OCH_3)_4$ was distilled from the temperature of 248 K to 223 K for 4 days giving approximately 2.5 g of the degassed material. After degassing by multistep vacuum distillation the measured pressure decreased by 40% as compared with the value obtained when degassing using LNT was used. $Ge(OC_2H_5)_4$ was distilled from the temperature of 281 K to 223 K for 1 day yielding about 3.5 g of the degassed material. The measured pressure decreased by 20% but was still slightly decreasing during the vapor pressure measurement. Therefore, the sample of $Ge(OC_2H_5)_4$ was distilled once again for 2 days from the temperature of 273 K to 223 K giving about 3 g of the degassed material. The decrease of the measured pressure was 10% as compared to the value obtained after the first cycle of multistep vacuum distillation. During the vapor pressure measurement the measured pressure at constant temperature did not change with the number of measuring cycles indicating that the sample was sufficiently degassed. Mass spectra show that the samples of $Ge(OCH_3)_4$ and $Ge(OC_2H_5)_4$ were also purified during vacuum distillation (see Figs. 3 and 4).

Vapor pressure measurements were performed using the static method with a newly built apparatus (internally denoted as STAT7) shown in Fig. 2 which was designed to be capable of measuring toxic materials. The apparatus is constructed of stainless-steel internally electrochemically polished tubing of internal diameter of 4.4 mm with VCR fittings and NUPRO SS-BNV51-2C valves (Swagelok Co., USA). The pressure is measured by a capacitance diaphragm absolute gage MKS Baratron 631A12TBEM (MKS Instruments Inc., USA). Its measuring upper limit is 13,332 Pa, and the uncertainty is 0.25% of the reading as stated by the manufacturer. The temperature of the pressure sensor is kept at $T=398$ K by the self-controlling temperature system. The pressure gage was calibrated at 398 K by the manufacturer at seven equally spaced pressures from 0 to 13,332 Pa. Additional calibration focusing on the beginning of a pressure span was performed in the Czech Metrology Institute. The MKS Baratron is connected to the container with the measured material placed in a Lauda RE 206 thermostat (Lauda, Germany) that allows adjustment of the sample temperature from 253 up to 473 K with stability of 0.01 K. The sample temperature is 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 standard platinum resistance thermometer (SPRT). This SPRT is calibrated to the ITS-90 and its calibration is traceable to the National Institute of Standards and Technology (NIST). The uncertainty of the temperature measurements is estimated to be less than 0.02 K. All temperatures reported here are based on the international temperature scale ITS-90. The tubing between the cell and the pressure gage is placed in an insulated metallic box thermostated at a temperature higher (in this work at 333 K) than that of the sample in order to avoid condensation of its vapor.

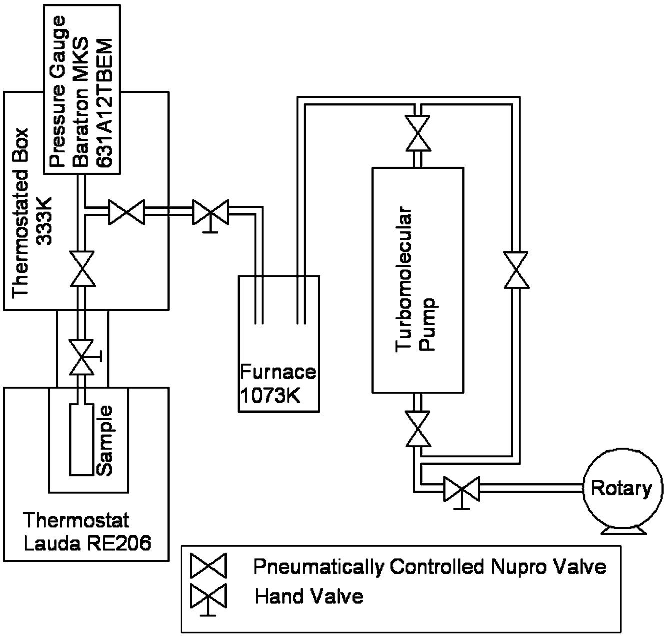

Fig. 2. Static apparatus for vapor pressure measurement.

The data acquisition system consists of a Keithley $6\frac{1}{2}$ digits 181 nanovoltmeter (Keithley Instruments Inc., USA), which monitors the analog output from the MKS Baratron, and a Keithley $6\frac{1}{2}$ digits 192 multimeter which monitors the analog output from the resistance thermometer. A program developed in Agilent VEE Pro records the pressure and the temperature of the sample and controls the measuring procedure using the computer-controlled valves and programmable thermostat LAUDA. The Keithley data loggers, the Lauda thermostatic bath and the valves are connected to a computer using a RS-232 C interface.

The vacuum pump used to evacuate the system between the measuring cycles is a turbomolecular pump Leybold Turbovac 150 CSV (Oerlikon Leybold Vacuum GmbH, Germany). The primary vacuum is assured by a rotary pump Leybold Trivac D4A. A furnace kept at 1073 K, at which all materials are decomposed, is placed between the measuring system and the turbomolecular pump.

Mass spectra were determined using a Balzers QuadStar 421 (Balzers Instruments AG, Liechtenstein) working in the maximum range of 200 amu from 0 to 300 amu.

3. Results and discussion

3.1. *Mass spectra*

In order to check how the slow vacuum distillation degasses the precursors, mass spectra of the studied Ge alkoxides were measured in the range between 13 and 213 amu. The total pressure of measured gas was held at the value of 2×10^{-3} Pa during all experiments. In all mass spectra beside Ge isotopes (70, 72, 73, 74, 76 amu), appropriate mono-, di- and tri-germanium alkoxide fragments GeR, GeR_2 and GeR_3, where $R=OCH_3$ or OC_2H_5, were detected. One can also observe $GeO(OR)_x$ fragments.