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Vapor Pressure of Di-*tert*-butylsilane

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The vapor pressure of di-*tert*-butylsilane [CAS Registry No. 30736-07-3] to be used in metalorganic vapor phase epitaxy (MOVPE) was measured by a static method in the technologically important temperature range from (241 to 288) K. The experimental data were fitted by the Antoine equation. To the best of our knowledge, this is the first time that the vapor pressure measurements of di-*tert*-butylsilane are reported.

Introduction

The extensive use of metalorganic vapor phase epitaxy (MOVPE) technology for the rapidly increasing production of sophisticated optoelectronic and UHF electronic components based on type III−V semiconductors is now starting to cover also the production of advanced silicon-based heterostructures and other important materials. The wide variety of technological processes needs a wide range of different precursors, offering full range of decomposition temperatures, vapor pressures, and chemical behavior during growth. Therefore the range of available precursors must follow the demand for new high-purity materials with well-defined chemical and physical properties for both research and production. Our laboratory is involved in a systematic measurement of vapor pressure of new as well as recently available high-quality precursors for MOVPE[1−3] for which the data on vapor pressure are missing and/or the data have been measured a long time ago and reflect the state of purity and measuring techniques available then.

The currently used gases silane and disilane show high toxicity and are known to be highly pyrophoric. Di-*tert*-butylsilane instead is a non-toxic and non-pyrophoric liquid that enables a safer MOVPE growth technology and better process control as it can be used in standard bubble through configuration. Leu et al.[4] have studied the doping behavior and the decomposition of di-*tert*-butylsilane in detail; they also compared di-*tert*-butylsilane with other possible organosilicon compounds that have been discussed as possible alternatives to gas sources.

Di-*tert*-butylsilane has been especially refined to meet the purity demands of the semiconductor industry. This non-pyrophoric compound has a normal boiling temperature of about 401 K[5] and a melting temperature of 235.15 K.[6] To the best of our knowledge, the data obtained in this paper are the first experimental vapor pressure data reported for this material measured in a temperature range utilizable for MOVPE process. The data obtained cover both low vapor pressure region for use of di-*tert*-butylsilane at very low temperatures as dopant in type III−V semiconductors as well as sufficiently high vapor pressure region for the growth of Si-containing materials with the temperature of the bubbler still below room temperature, which simplifies greatly the construction of the necessary MOVPE system. Di-*tert*-butylsilane is used as Si dopant for the growth of GaAs- and InP-based devices[7] as well as GaN-based devices and hence has attracted increasing interest in the deposition of Si layers and compounds. Vapor pressure data are essential for MOVPE users and are also important in thermodynamic calculations.[8−10]

Experimental Section

Chemicals. Di-*tert*-butylsilane of “Epi-proof” quality was supplied by Akzo Nobel in a container with VCR fittings, allowing direct connection to the apparatus for vapor pressure measurement as well as to the apparatus for degassing of samples. This avoided possible contamination of the material during handling.

Prior to measurement of vapor pressure, the sample was carefully degassed in a separate apparatus using a turbomolecular pump connected to the sample cell. To minimize the loss of the sample material, a poly(dimethylsiloxane) membrane[2] was placed between the sample cell and the pump. This membrane is permeable for low molecular weight gases (oxygen, nitrogen, etc.) but not for the sample molecules. This method has proved to be highly efficient.

Apparatus and Procedure. The vapor pressure was measured by a static method using an apparatus shown in Figure 1 and described in more details in ref 3. The pressure is measured by a capacitance diaphragm absolute gauge MKS Baratron type 690A11TRA (measuring range up to 1333 Pa, accuracy stated by the manufacturer 0.05 % of reading). The gauge temperature was kept at 318 K; its calibration at 318 K performed by the manufacturer at 11 equally spaced pressures from 0 to 1300 Pa with a maximum deviation of 0.03 %, is traceable to the National Institute of Standards and Technology. Sample temperature was measured by a platinum resistance thermometer Burns Engineering 12001-A-12-6-2-A in a four-wire connection calibrated by comparison to standard platinum resistance thermometer (SPRT). This SPRT was calibrated

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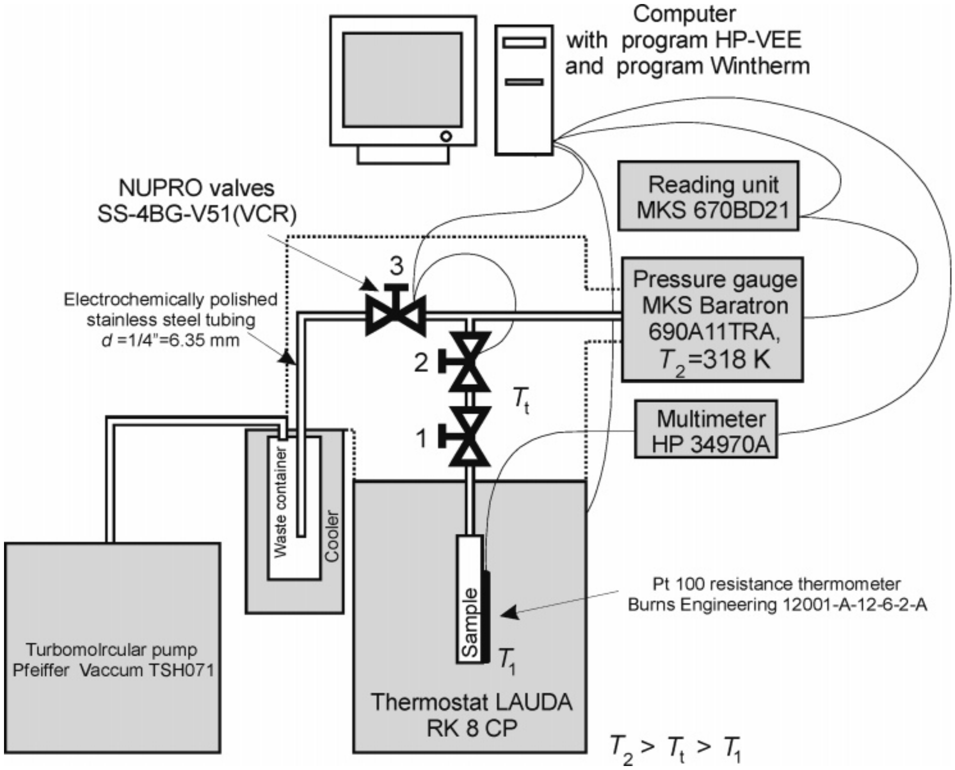

Figure 1. Static apparatus for the measurement of vapor pressure. Valve 1 is the container valve. Valves 2 and 3 are computer controlled.

Table 1. Experimental Values of Vapor Pressure of Di-*tert*-butylsilane $p_{\mathrm{sat}}^{\mathrm{exp}}$ [a]

T/K	$p_{\mathrm{sat}}^{\mathrm{exp}}$/Pa	Δp/Pa	T/K	$p_{\mathrm{sat}}^{\mathrm{exp}}$/Pa	Δp/Pa	T/K	$p_{\mathrm{sat}}^{\mathrm{exp}}$/Pa	Δp/Pa	T/K	$p_{\mathrm{sat}}^{\mathrm{exp}}$/Pa	Δp/Pa
241.49	46.24	0.35	253.49	124.45	0.57	268.48	366.36	−1.86	280.99	821.99	0.70
241.49	46.15	0.26	253.49	124.44	0.56	268.48	366.33	−1.89	280.99	822.09	0.80
241.49	46.21	0.32	258.49	181.65	0.40	273.49	512.11	−1.05	280.99	822.19	0.90
241.49	46.22	0.33	258.49	181.65	0.40	273.49	512.00	−1.16	280.99	822.08	0.79
242.49	50.20	0.12	258.49	181.65	0.40	273.49	511.96	−1.20	283.49	955.06	0.73
242.49	50.31	0.23	258.49	181.65	0.40	273.49	511.83	−1.33	283.49	955.11	0.78
242.49	50.34	0.26	258.49	181.64	0.39	273.49	511.88	−1.28	283.49	954.93	0.60
243.49	54.86	0.26	263.49	260.61	0.06	275.99	603.29	0.98	283.49	954.71	0.38
243.49	54.86	0.26	263.49	260.57	0.02	275.99	603.20	0.89	285.99	1105.2	−0.24
243.49	54.84	0.24	263.49	260.54	−0.01	275.99	603.19	0.88	285.99	1104.6	−0.84
248.49	83.08	−0.01	263.49	260.59	0.04	275.99	603.12	0.81	285.99	1104.5	−0.94
248.49	83.08	−0.01	263.49	260.59	0.04	278.49	705.70	1.19	288.19	1254.7	−0.22
248.49	83.09	0.00	268.48	366.48	−1.74	278.49	705.65	1.14	288.19	1254.6	−0.32
253.49	124.44	0.56	268.48	366.41	−1.81	278.49	705.60	1.09	288.19	1254.5	−0.42
253.49	124.45	0.57	268.48	366.44	−1.78	278.49	705.60	1.09	288.19	1253.9	−1.02
253.49	124.44	0.56									

[a] $\Delta p = p_{\mathrm{sat}}^{\mathrm{exp}} - p_{\mathrm{sat}}^{\mathrm{calc}}$, where $p_{\mathrm{sat}}^{\mathrm{calc}}$ is calculated from the Antoine eq 1 using parameters from Table 2.

to the ITS-90, and its calibration was traceable to NIST. The uncertainty of the measurement of sample temperature is estimated to be 0.02 K. The temperature is based on the international temperature scale ITS-90.

Prior to measurement of di-*tert*-butylsilane, the apparatus was checked for tightness by a MKS PICO vacuum leak detector. The apparatus was evacuated between individual measurement cycles by turbomolecular pump to a pressure of 10^{-5} Pa. A computer using HP-VEE program monitored the pressure and the temperature of the sample and controlled the measuring procedure. Experiments were carried out in the given temperature interval by varying the temperature at random in order to avoid systematic errors caused by possible decomposition or insufficient degassing of the sample. The whole experimental setup was checked by extensive measurements with solid naphthalene in the temperature range from 273 K to 313 K.[11]

Results and Discussion

Experimental results on vapor pressure listed in Table 1 were fitted by the Antoine equation

$$\ln(p_{\mathrm{sat}}/\mathrm{Pa}) = A - \frac{B}{T/\mathrm{K} + C} \qquad (1)$$

where p_{sat} is vapor pressure; T is temperature; and A, B, and C are parameters of the Antoine eq 1. These parameters are presented in Table 2, which also contains deviation of the fit σ and standard relative deviation σ_{r} defined as

$$\sigma = \left[\frac{\sum_{i=1}^{n}(p_{\mathrm{sat}}^{\mathrm{calc}} - p_{\mathrm{sat}}^{\mathrm{exp}})_i^2}{n-3}\right]^{1/2} \qquad (2)$$

Table 2. Parameters of the Antoine Eq 1, Standard Deviation of the Fit σ, and Relative Standard Deviation σ_r

A	B	C	T_{min}/K	T_{max}/K	σ/Pa	σ_r/%	$\Delta p_{max}{}^a$/Pa	$\Delta p_{r,max}{}^b$/%
20.90382	3318.901	−47.14840	241	288	0.85	0.32	1.89	0.77

[a] Δp_{max} is the maximum absolute difference between the experimental value p_{sat}^{exp} and value p_{sat}^{calc} obtained from Antoine eq 1 using parameters listed in this table. [b] $\Delta p_{r,max}$ is the maximum relative difference between experimental value p_{sat}^{exp} and the smoothed value p_{sat}^{calc}.

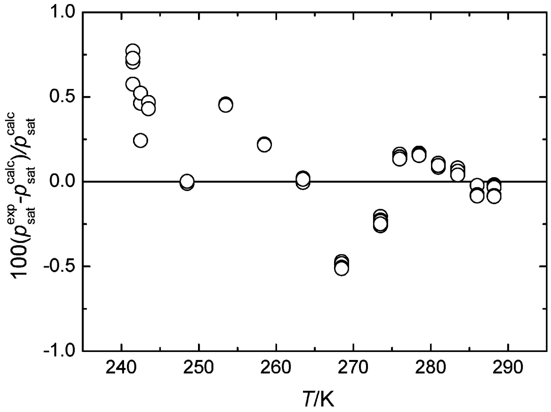

Figure 2. Deviation plot of vapor pressure of di-*tert*-butylsilane. p_{sat}^{calc} is calculated from the Antoine eq 1 using parameters from Table 2, p_{sat}^{exp} refers to experimental vapor pressure data obtained in this work.

and

$$\sigma_r = \left[\frac{\sum_{i=1}^{n}((p_{sat}^{calc} - p_{sat}^{exp})/p_{sat}^{exp})_i^2}{n-3}\right]^{1/2} \times 100 \qquad (3)$$

Here p_{sat}^{calc} is the vapor pressure calculated from the Antoine eq 1 at temperature T, p_{sat}^{exp} is the experimental value at the same temperature T, and n denotes the number of experimental points used in the fit. Experimental data are described by the Antoine eq 1 with parameters given in Table 2 within 0.8 % as can be seen from Figure 2.

Four papers related to vapor pressure of di-*tert*-butylsilane were found in the literature. Weidenbruch et al.[5] reported for di-*tert*-butylsilane a normal boiling temperature range of (400.15 to 402.15) K, Triplet and Curtis[12] reported a boiling temperature of 321.15 K at a reduced pressure of 6.0 kPa. Watanabe et al.[13] reported a normal boiling temperature of 401.15 K. Weidenbruch et al.,[5] Triplet and Curtis,[12] and Watanabe et al.[13] obtained the values of boiling temperature in a study devoted to synthesis of di-*tert*-butylsilane and of its derivatives. Grow et al.[14] reported normal boiling temperature of di-*tert*-butylsilane of 401.15 K and a boiling temperature of 293.15 K at a reduced pressure of 2730 Pa. It should be noted, however, that Grow et al.[14] neither determined the boiling temperatures they reported nor specified the source of these data.

Extrapolating the Antoine eq 1 far beyond the temperature for which its parameters apply should only be done with caution. Still, normal boiling temperature 401.05 K calculated from Antoine eq 1 with parameters from Table 2 is in good agreement with published values of normal boiling temperature.[5,14] One vapor pressure data point given by Grow et al.[14] is not consistent with our measurements (vapor pressure at 293.15 K calculated from our data equals 1657 Pa, differing significantly from their value 2730 Pa), and a value reported by Triplet and Curtis[12] is lower than our extrapolated value of vapor pressure at 321.15 K by 576 Pa (i.e., by 8.8 %).

Conclusions

The vapor pressure data of di-*tert*-butylsilane were obtained in the temperature range from 241 K to 288 K by a static method. Results on vapor pressure are reported as raw experimental data as well as in the terms of parameters of the Antoine equation. Obtained vapor pressure data are consistent with reported normal boiling point of di-*tert*-butylsilane.

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