FLUOROPHENYL DERIVATIVES OF ELEMENTS II–VI GROUPS
Phase transitions thermodynamics and growing films by CVD

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The enthalpies and temperatures of melting of RSi(CH3)3, R2Si, R3P, R3As, R3Sb, R3Bi, R2Te and R2Hg (R=C6F5) were obtained by scanning calorimetry measurements. The pressure of the saturated and unsaturated vapors of RSi(CH3)3, R2Si(CH3)2, R3Si, R3Ga, R3P, R3As, R3Sb, R3Bi, R2Te and R2Hg has been measured by the static method with a membrane-gauge manometer. It was established that all investigated substances proceed to vapor as monomers. Equations approximating the dependences of saturated vapor pressures on temperature and the enthalpies and entropies of vaporization were obtained. Graﬁte films with silicon intercalated up to 25 at.% were grown by CVD using R3Si as a precursor. These ﬁlms showed semiconductor properties in the temperature interval 80–300 K.

Keywords: CVD, enthalpy, entropy, fluorophenyl derivatives, scanning calorimetry, static method with a membrane-gauge manometer

Introduction

The data on thermodynamic properties of halogen-organic derivatives of elements II–VI groups are necessary for modeling precipitation processes from gas phase Si and SiC and also for obtaining complex semiconductor compounds A(III)–B(V) and A(II)–B(VI). At present silane and its chlorinated organic derivatives of the general formula RxSiHyClz,w where R is a hydrocarbon and x+y+z=4, have found a use for growing silicon carbide crystals, epitaxial films, and polycrystalline silicon [1–3]. The general disadvantage of all these compounds from the point of view of their application in technology is their high hydrolytic activity. In practice, this disturbs the operation of vacuum and gas valves, systems for controlling gas ﬂows, and other construction units. In this connection works on synthesizing new organic derivatives are continuously performing. For use these compounds in effective processes of gas phase deposition, several other requirements in addition to stability toward hydrolysis should be performed. These are a low temperature (lower than the pyrolysis temperature of organic radicals) of Si (SiC) deposition, the stability of gaseous compounds formed and the presence of organic derivatives as monomers in the vapor phase.

Among such compounds, ﬂuoroorganic derivatives appear to offer promise.

The aim of this study is to obtain the reliable information on thermodynamic of sublimation, melting and evaporation processes of fluorophenyl derivatives of Hg, Ga, Si, P, As, Sb, Bi, Te and to use some investigated substances as precursors at growing films by CVD.

Experimental

Materials

The samples of investigated compounds (RSi(CH3)3, R2Si(CH3)2, R3Si, R3Ga, R3P, R3As, R3Sb, R3Bi, R2Te, R2Hg, where R=C6F5) were synthesized and identiﬁed at the Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Branch of Russian Academy of Sciences. The syntheses were performed as described in [4]; this technique guaranteed the content of impurities in the samples to be 0.5 at.% or less.

The substances were loaded in glass calorimetric ampoules in a dry box ﬁlled with argon; phosphorus pentoxide was used as a desiccant. Sample masses were 40–140 mg. After weighing, the ampoules were evacuated and sealed. The membrane-gauge manometers were ﬁlled using special reactors that excluded contact between the samples to be studied and air. Sample masses amounted to 40–300 mg.

Methods

Scanning calorimetry

Calorimetric measurements were performed on a Setaram DSC 111 scanning calorimeter at heating and cooling rates of 0.5–0.3 K min–1. The errors in the heat effect measurements estimated from calibration experiments (C6H5COOH, In, Sn) were less than 1.5%. Two–three calorimetric experiments were performed for each investigated compounds.

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Static method
The pressure of the saturated and unsaturated vapors was measured by the static method using a quartz membrane zero manometer from Novikov–Suvorov [5]. The principal characteristics of the unit described in detail in [6] were: the pressure measurement error did not exceed 40 Pa; the temperature measurement error estimated from calibration against mercury, naphthalene, and argon did not exceed 0.3 K; the accuracy of maintaining constant temperature was ±0.1 K; and the radial and linear gradient of the temperature in the working cell of manometer did not exceed 0.5 K. The loading of membrane zero manometers included preliminarily heating them in a high vacuum at maximum temperature of measurement for 4 h; we also used special devices to exclude contact between the substance to be studied and air during loading. This procedure allowed us to minimize residual pressure, mainly caused by the interaction between substances and gases adsorbed on quartz, in most of the experiments.

The pressures measured from low to high temperatures and backwards were identical at the same temperature. The equilibrium was considered to attain when the pressures measured on approaching the specified temperature from above and from below were being equal to within the experimental accuracy. The time required for reaching equilibrium for all studied compounds was 15–30 min.

CVD method
The substances considered are precursors for low-temperature chemical vapor deposition of elemental or binary semiconductors as well as solid solutions and solid phase mixtures. The possibility of growing films by CVD was tested on R₄Si. The scheme of CVD apparatus is represented on Fig. 1. Argon and hydrogen were used as carrier gas. The polished plates of monocrystalline germanium or polycrystalline siall were used as substrate.

![Fig. 1 The scheme of CVD apparatus: 1, 3 – heaters, 2 – reactor, 4 – solid R₄Si, 5 – substrate and 6 – film](image)

The films growing on germanium substrate were analysed on the microprobe analyzer LEO 430.

The electrical resistivity measurement of films growing on siall substrate was performed by a DC four-probe technique. Voltage drop was measured with accuracy 0.1%. Measuring current was 0.01–0.1 mA.

Results and discussion
Calorimetric measurements were performed for R₃Si(CH₃)₃, R₅Si, R₃P, R₃As, R₃Sb, R₃Bi, R₃Te and R₂Hg. The samples exhibited an only phase transition (melting) over the temperature range studied (190–520 K). It follows that the samples were individual phases to within the sensitivity of measurements. The enthalpies of melting obtained in heating and cooling coincided to within 1–2%. The thermodynamic characteristics of melting are listed in Table 1.

Static method experiments were performed for all the compounds studied, that is, for R₃Si(CH₃)₃, R₅Si(CH₃)₂, R₅Si, R₃Ga, R₃P, R₃As, R₃Sb, R₃Bi, R₃Te and R₂Hg. For each of them two-three series of measurements were realized (one series was a static experiment with one substance load) over the temperature range whose lower boundary was as a rule determined by the sensitivity of membrane zero manometers (6 Pa) and the upper boundary by the temperature above that pressure changes became irreversible.

The average molecular mass of gas calculated from the experimental data on unsaturated vapors using ideal gas law was close to the molecular mass of monomer for all investigated compounds (Table 2), that was evidence

### Table 1 Temperatures (Tₘ), enthalpies (ΔₙHₘ⁰) and entropies (ΔₙSₘ₀) of melting fluorophenyl derivatives of Si, P, As, Sb, Bi, Te, Hg

<table>
<thead>
<tr>
<th>Compound</th>
<th>Tₘ/K</th>
<th>ΔₙHₘ⁰ /kJ mol⁻¹</th>
<th>ΔₙSₘ₀ /J mol⁻¹ K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>R₃Si(CH₃)₃</td>
<td>223.0±0.5</td>
<td>8.4±0.2</td>
<td>37.7±0.5</td>
</tr>
<tr>
<td>R₅Si</td>
<td>518.0±0.5</td>
<td>46.9±0.9</td>
<td>90.5±1.0</td>
</tr>
<tr>
<td>R₃P</td>
<td>380.0±0.5</td>
<td>22.1±0.4</td>
<td>58.1±0.6</td>
</tr>
<tr>
<td>R₃As</td>
<td>380.1±0.5</td>
<td>26.5±0.5</td>
<td>69.7±0.7</td>
</tr>
<tr>
<td>R₃Sb</td>
<td>355.0±0.5</td>
<td>22.4±0.4</td>
<td>63.1±0.6</td>
</tr>
<tr>
<td>R₃Bi</td>
<td>370.2±0.5</td>
<td>28.9±0.6</td>
<td>78.1±0.8</td>
</tr>
<tr>
<td>R₃Te</td>
<td>322.3±0.5</td>
<td>16.3±0.3</td>
<td>50.6±0.6</td>
</tr>
<tr>
<td>R₂Hg</td>
<td>402.6±0.5</td>
<td>27.8±0.5</td>
<td>69.1±0.7</td>
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</tbody>
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