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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 $RSi(CH_3)_3$, R_4Si, R_3P, R_3As, R_3Sb, R_3Bi, R_2Te and R_2Hg (R=C_6F_5) were obtained by scanning calorimetry measurements. The pressure of the saturated and unsaturated vapors of $RSi(CH_3)_3$, $R_2Si(CH_3)_2$, R_4Si, R_3Ga, R_3P, R_3As, R_3Sb, R_3Bi, R_2Te and R_2Hg has been measured by the static method with a membrane-gauge manometer. It was established that all investigated substances proceeded 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 R_4Si 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 $R_xSiH_yCl_z$, 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 ($RSi(CH_3)_3$, $R_2Si(CH_3)_2$, R_4Si, R_3Ga, R_3P, R_3As, R_3Sb, R_3Bi, R_2Te, R_2Hg, where R=C_6F_5) 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 (C_6H_5COOH, 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 R_4Si. 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 sitall were used as substrate.

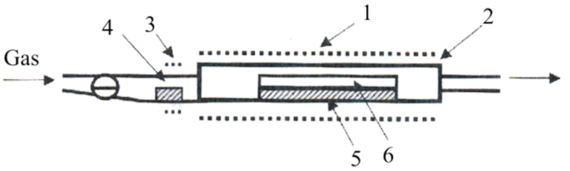

Fig. 1 The scheme of CVD apparatus: 1, 3 – heaters, 2 – reactor, 4 – solid R_4Si, 5 – substrate and 6 – film

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

The electrical resistivity measurement of films growing on sitall 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 $RSi(CH_3)_3$, R_4Si, R_3P, R_3As, R_3Sb, R_3Bi, R_2Te and R_2Hg. 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 $RSi(CH_3)_3$, $R_2Si(CH_3)_2$, R_4Si, R_3Ga, R_3P, R_3As, R_3Sb, R_3Bi, R_2Te and R_2Hg. 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 (T_m), enthalpies ($\Delta_m H^0_{T_m}$) and entropies ($\Delta_m S^0_{T_m}$) of melting fluorophenyl derivatives of Si, P, As, Sb, Bi, Te, Hg

Compound	T_m/K	$\Delta_m H^0_{T_m}$ /kJ mol^{-1}	$\Delta_m S^0_{T_m}$ /J mol^{-1} K^{-1}
$RSi(CH_3)_3$	223.0±0.5	8.4±0.2	37.7±0.5
R_4Si	518.0±0.5	46.9±0.9	90.5±1.0
R_3P	380.0±0.5	22.1±0.4	58.1±0.6
R_3As	380.1±0.5	26.5±0.5	69.7±0.7
R_3Sb	355.0±0.5	22.4±0.4	63.1±0.6
R_3Bi	370.2±0.5	28.9±0.6	78.1±0.8
R_2Te	322.3±0.5	16.3±0.3	50.6±0.6
R_2Hg	402.6±0.5	27.8±0.5	69.1±0.7

Table 2 Molecular masses (g mol^{-1}) of compounds in the gas phase calculated from experimental data (M_2) and molecular masses of monomers (M_1)

Compound	M_1	M_2
$RSi(CH_3)_3$	240.25	235±6
$R_2Si(CH_3)_2$	392.27	398±7
R_4Si	696.32	710±15
R_3Ga	570.7	582±13
R_3P	532.148	535±4
R_3As	576.92	583±7
R_3Sb	622.88	629±7
R_3Bi	710.98	713±4
R_2Te	461.72	464±3
R_2Hg	534.71	526±9

of the absence of other molecular forms in the gas phase to within the accuracy specified above.

This circumstance allowed to be processed data on saturated vapors of all the compounds studied using the simplest physicochemical model of vaporization,

$$A(s)=B(g) \tag{1}$$

$$A(l)=B(g) \tag{2}$$

In that case the temperature dependence of saturated vapor pressure may described by the Clapeyron–Clausius equation:

$$p_{\mathrm{calc}}=p^0\exp(-\Delta_{\mathrm{vap}}H^0/RT+\Delta_{\mathrm{vap}}S^0/R) \tag{3}$$

where $\Delta_{\mathrm{vap}}H^0$ and $\Delta_{\mathrm{vap}}S^0$ are the enthalpy and entropy of vaporization at temperature T, p^0 is 101325 Pa and R is the gas constant.

Experimental data processing was performed by the method of least squares using the objective function recommended in [7, 8]. The sought values were the enthalpies and entropies of vaporization at the mean temperature, because the heat capacity data on the substances under consideration were lacking. The temperature dependences of pressure for sublimation and evaporation are summarized in Table 3.

The deviations of the experimental pressures from those calculated by the equations given in Table 3 did not exceed admissible errors calculated from the errors in temperature and pressure measurements. They were random in character and it was evidence of the absence of significant systematic errors in our results. As an ex-

Table 3 Temperature dependences of pressure for sublimation and evaporation fluorophenyl derivatives of Si, Ga, P, As, Sb, Bi, Te, Hg

Compound	$\ln(p/p^0)=f(T)$	ΔT/K
$RSi(CH_3)_3(l)$	$10.77-4882.3/T\pm2\sigma;\ \sigma^2=1269/T^2-6.50/T+8.38\cdot10^{-3}$	273–440
$RSi(CH_3)_3(s)^1$	$15.27-5893.5/T$	–
$R_2Si(CH_3)_2(l)$	$12.857-6656/T\pm2\sigma;\ \sigma^2=1376/T^2-6.44/T+7.5\cdot10^{-2}$	366–463
$R_2Si(CH_3)_2(s)^2$	$19-9021/T$	–
$R_3SiCH_3(l)^2$	$14-8179/T$	–
$R_3SiCH_3(s)^2$	$23-12208/T$	–
$R_4Si(l)$	$15.728-9694.6/T\pm2\sigma;\ \sigma^2=526/T^2-1.97/T+1.84\cdot10^{-3}$	463–565
$R_4Si(s)$	$26.805-15429/T\pm2\sigma;\ \sigma^2=4834/T^2-19.14/T+1.9\cdot10^{-2}$	433–517
$R_3Ga(l)$	$15.45-9978.4/T\pm2\sigma;\ \sigma^2=18484/T^2-69.6/T+0.065$	423–550
$R_3P(l)$	$14.3-8354.7/T\pm2\sigma;\ \sigma^2=3804.7/T^2-55.88/T+0.015$	383–547
$R_3P(s)^1$	$21.3-11017/T$	–
$R_3As(l)$	$14.6-8605.2/T\pm2\sigma;\ \sigma^2=4489.4/T^2-18.04/T+0.02$	383–536
$R_3As(s)^1$	$23.0-11787/T$	–
$R_3Sb(l)$	$14.6-8822/T\pm2\sigma;\ \sigma^2=2087/T^2-8.36/T+0.08$	379–536
$R_3Sb(s)^1$	$22.19-11515/T$	–
$R_3Bi(l)$	$14.9-9323/T\pm2\sigma;\ \sigma^2=10416/T^2-39.1/T+0.037$	386–598
$R_3Bi(s)^1$	$24.42-12745/T$	–
$R_2Te(l)$	$12.05-6827/T\pm2\sigma;\ \sigma^2=346.12/T^2-1.36/T+0.0013$	394–560
$R_2Te(s)^1$	$18.14-8792/T$	–
$R_2Hg(l)$	$13.16-7637.6/T\pm2\sigma;\ \sigma^2=2702.5/T^2-10.9/T+0.011$	403–533
$R_2Hg(s)^1$	$21.5-10981.5/T$	–

[1] Our calculations from the thermodynamic data on evaporation and melting of the corresponding compounds; [2] Our estimate from the dependence of the thermodynamic characteristics of vaporization on the molecular masses of compounds of the general formula $R_nSi(CH_3)_m$; the temperature interval given in parentheses corresponds to supercooled liquid

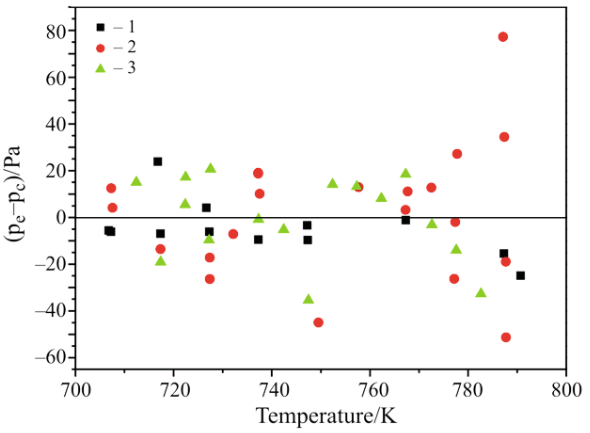

Fig. 2 Difference between the experimental pressures (p_e) and calculated ones (p_c) by the corresponding equation in Table 3 for the sublimation of tetrafluorophenylsilicon (R_4Si) in three series of experiments

ample such deviations are shown in Fig. 2 for sublimation of tetrafluorophenylsilicon (R_4Si).

The thermodynamic characteristics of vaporization are presented in Table 4.

Note that the temperature and enthalpy of melting of tetrafluorophenylsilicon (R_4Si) were determined by two independent methods, calorimetrically (T_m=518 K and $\Delta_m H^0_{518}$=46.9±0.2 kJ mol^{-1}) and by static method (T_m=518 K and $\Delta_m H^0_{518}$=47.4±1.3 kJ mol^{-1}). The results closely agreed with each other.

The data obtained for the evaporation and melting were used to calculate the enthalpies and entropies of sublimation (Table 4) and the temperature dependence of pressure for sublimation (Table 3).

The vaporization enthalpies and entropies of R_3SiCH_3 and $R_2Si(CH_3)_2$ were estimated by using the molecular mass dependences of the thermodynamic properties of compounds of the general formula $R_nSi(CH_3)_m$ ($n+m$=4). As an example such estimation is shown in Fig. 3 for the enthalpies of sublimation. These results are also given in Tables 3 and 4. All the experiments were performed for the first time.

On the base of presented thermodynamic information CVD-experiments were performed using R_4Si as precursor.

The experiments on growing films were realized in quartz reactor (Fig. 1). The precursor temperature

Table 4 Enthalpies (ΔH^0_T) and entropies (ΔS^0_T) of vaporization fluorophenyl derivatives of Si, Ga, P, As, Sb, Bi, Te, Hg corresponding to the mean temperature (T_{mean}) of the intervals studied

Process	T_{mean}/K	ΔH^0_T/kJ mol^{-1}	ΔS^0_T/J mol^{-1} K^{-1}
$RSi(CH_3)_3(l)=RSi(CH_3)_3(g)$	356.5	40.6±0.3	89.6±0.8
$RSi(CH_3)_3(s)=RSi(CH_3)_3(g)$[1]	–	49	127
$R_2Si(CH_3)_2(l)=R_2Si(CH_3)_2(g)$	414.5	55.3±0.6	106.9±1.4
$R_2Si(CH_3)_2(s)=R_2Si(CH_3)_2(g)$[2]	–	75	160
$R_3SiCH_3(l)=R_3SiCH_3(g)$[2]	–	68	119
$R_3SiCH_3(s)=R_3SiCH_3(g)$[2]	–	101.5	192
$R_4Si(l)=R_4Si(g)$	514	80.6±0.4	130.8±0.2
$R_4Si(s)=R_4Si(g)$	475	128.0±1.2	224.1±2.3
$R_3Sb(s)=R_3Sb(g)$[1]	–	96	184
$R_3Sb(l)=R_3Sb(g)$	458	73.3±0.8	121.4±1.5
$R_3As(l)=R_3As(g)$	460	71.5±1.1	121.5±2.6
$R_3As(s)=R_3As(g)$[1]	–	98	191
$R_2Hg(l)=R_2Hg(g)$	468	63.5±0.9	109.4±1.8
$R_2Hg(s)=R_2Hg(g)$[1]	–	91	179
$R_3Ga(l)=R_3Ga(g)$	486	83.0±2.3	128.4±4.3
$R_3Bi(s)=R_3Bi(g)$[1]	–	107	203
$R_3Bi(l)=R_3Bi(g)$	492	78.1±1.7	124.9±3.2
$R_2Te(l)=R_2Te(g)$	471	56.8±0.3	100.2±0.6
$R_2Te(s)=R_2Te(g)$[1]	–	73	151
$R_3P(l)=R_3P(g)$	465	69.5±1.0	118.9±2.1
$R_3P(s)=R_3P(g)$[1]	–	92	177

[1] Our calculations from the thermodynamic data on evaporation and melting of the corresponding compounds; [2] Our estimate from the dependence of the thermodynamic characteristics of vaporization on the molecular masses of compounds of the general formula $R_nSi(CH_3)_m$; the temperature interval given in parentheses corresponds to supercooled liquid

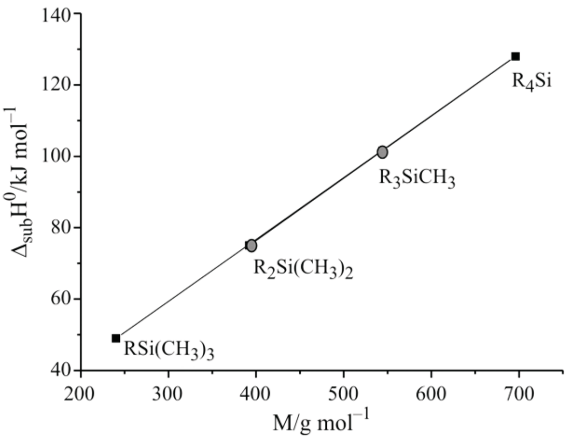

Fig. 3 Molecular mass dependence of the enthalpy of sublimation of fluorophenylsilicons (the values for R_3SiCH_3 and $R_2Si(CH_3)_2$ were obtained by interpolation)

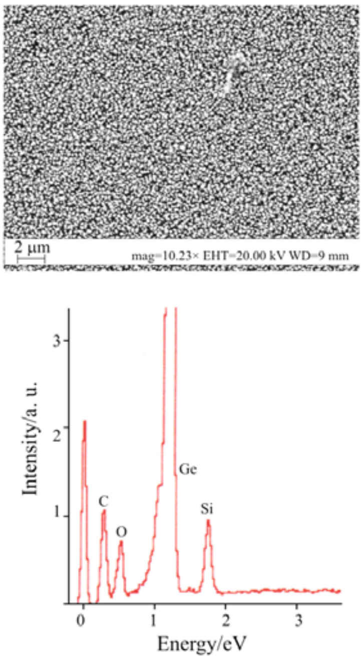

Fig. 4 SEM photograph and microprobe analysis result of graphite film intercalated by silicon

was chosen in accordance with pressure presented in Table 3: the R_4Si partial pressure was 300 Pa at 473 K. The carrier gas flow was 1.8 L h^{-1}. A substrate was located in a reactor region with controlled temperature of 773–1073 K. There is no a noticeable film deposition at temperature lower then 773 K. The process resulted in black deposits a few microns in thickness.

Microprobe analysis of obtained films has shown a significant Si content in carbon matrix: up to 17 at.% in films growing in Ar-atmosphere and up to 25 at.% in films growing in H_2-atmosphere (Fig. 4).

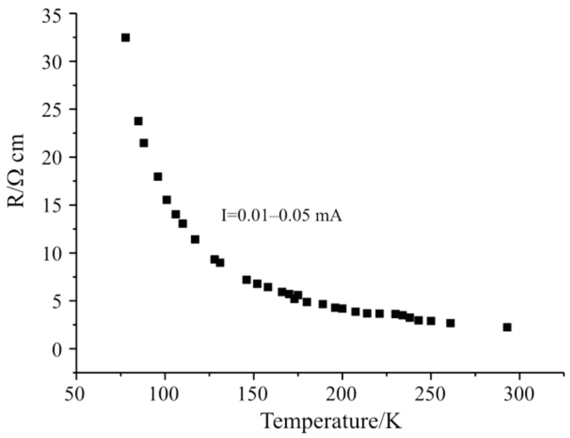

Fig. 5 Temperature dependence of the electrical resistivity of film

The electrical resistivity of films has increased at decreasing temperature (Fig. 5) i.e. they have demonstrated semiconductor dependence types.

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