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Physics Procedia 46 (2013) 200 – 208

Physics Procedia

Nineteenth European Conference on Chemical Vapor Deposition, (EUROCVD 19)

Scandium(III) Beta-Diketonate Derivatives As Precursors For Oxide Film Deposition By CVD

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Abstract

Complexes with acetylacetone Sc(acac)$_3$, dipivaloylmethane Sc(thd)$_3$, 2,2,6,6–tetramethyl-4-fluoro-3,5-heptanedione Sc(tfhd)$_3$, pivaloyltrifluoroacetone Sc(ptac)$_3$, trifluoroacetylacetone Sc(tfac)$_3$, and hexafluoroacetylacetone Sc(hfac)$_3$ were synthesized, purified and identified by elemental analysis, m.p., IR and NMR spectroscopy, and mass spectrometry. The thermal behaviour of the synthesized compounds in the solid state was investigated by the method of difference-scanning calorimetry in vacuum. As a result the thermodynamic characteristics of the melting processes were determined. The temperature dependences of saturated and unsaturated vapour pressure of complexes under study were measured by static method with membrane-gauge manometers. The average molecular weight of gas calculated from the experimental data on unsaturated vapours using ideal gas law was close to the molecular weight of monomer for all investigated compounds. Decomposition temperatures of compounds under study were defined as the temperature above that pressure changes became irreversible. The information about melting and decomposition processes were taken into account at measuring saturated vapour pressure of complexes. The row of volatility Sc(hfac)$_3$ > Sc(ptac)$_3$ > Sc(tfac)$_3$ > Sc(thd)$_3$ ≥ Sc(tfhd)$_3$ > Sc(acac)$_3$) was determined from the p–T dependences obtained. Above information about thermal behaviour of complexes enabled one to use it as a guide for CVD experiments aimed at achieving oxide films with high optical properties. Precursor chosen for film deposition was Sc(thd)$_3$. The Sc$_2$O$_3$ film deposition conditions were following: the gas-carrier rate 1 l/h, He gas-reagent rate 10 l/h, total pressure 10 Torr, evaporator temperature 105-110°C, substrate temperature 450-650°C, substrate Si(100). Ellipsometry was applied to characterize the film thickness and refractive index. The morphology and the composition of the films were determined with XPS and SEM.

Selection and peer-review under responsibility of Organizing Committee of EUROCVD 19.

Keywords: scandium beta-diketonates; DSC; vapour pressure; MOCVD; Sc$_2$O$_3$ films

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Selection and peer-review under responsibility of Organizing Committee of EUROCVD 19.
doi:10.1016/j.phpro.2013.07.068

1. Introduction

At the present time the functional coatings based on scandium oxide are widely used in different areas of material science and of interests related to perspective applications. So, Sc_2O_3 and its composites are promising materials for laser optical coatings (Xu, et al., 2001) in superluminescent light-emitting diodes (Ladany, et al., 1986), for damage-resistant antireflection multilayer coatings in high-power UV lasers (Tamura, et al., 1993), for scandia-doped dielectric layers in MIS structure (Rouffignac, et al., 2006), for scandia-stabilized ZrO_2 electrolyte layers in solid oxide fuel cells (Yamaguchi, 2009).

One of the methods widely applied for fabricating Sc_2O_3 films and coatings with assigned structure and functional properties is Metal-Organic Chemical Vapor Deposition (MOCVD). Being multiparameter complicated process, one of the important factors of successful MOCVD experiments is the usage of the precursors with certain physico-chemical properties agreeable to the following basic method requirements: high thermal stability and high vapor pressure at low temperatures. The above physico-chemical features of metal β-diketonates make these compounds very useful in the MOCVD process (Xu, et al., 2001; Fleeting, et al., 1999). This has lead to more research in synthesis of high purity precursors and reasonable systematic thermodynamic investigation especially in quantitative physico-chemical characteristic calculations, saturated vapor pressure and thermal stability study necessary for choosing optimal deposition conditions.

The goal of the present work is the systematic investigation of the vaporization processes together with studying the thermal behaviour in condensed phase for six volatile scandium(III) complexes with acetylacetone $Sc(acac)_3$, dipivaloylmethane $Sc(thd)_3$, 2,2,6,6–tetramethyl-4-fluoro-3,5-heptanedione $Sc(tfhd)_3$, pivaloyltrifluoroacetone $Sc(ptac)_3$, trifluoroacetylacetone $Sc(tfac)_3$, and hexafluoroacetylacetone $Sc(hfac)_3$ and the demonstration how the complex investigation of thermal properties can underlie both choosing precursor and defining CVD regime intervals by an example of Sc_2O_3 deposition.

2. Experimental

2.1. Synthesis

The synthesis of scandium(III) beta-diketonate derivatives was carried out according to procedures descried by Eisentrout and Sievers, 1968 ($Sc(acac)_3$, $Sc(ptac)_3$, $Sc(thd)_3$ and $Sc(tfhd)_3$) and Smolentsev, et al., 2011 ($Sc(tfac)_3$, $Sc(hfac)_3$). The compounds were purified by fractional sublimation at p = 0.1 Pa and temperature range 323–453 K depending on nature of ligand. Yields varied 50-90% depending on the ligand nature. The complexes were identified by elemental analysis, m.p., IR and NMR spectroscopy, mass spectrometry, and X-ray structural diffraction analysis.

2.2. DSC

The investigation of the compound thermal behaviors in the solid state and the definition of thermodynamic characteristics ($m.p.$, $\Delta_{\text{melt}}H_{m.p.}$, $\Delta_{\text{melt}}S^\circ_{m.p.}$) was performed by difference-scanning calorimetry (DSC) in vacuum using Setaram DSC 111 (heating rate 0.5–1.0 $K{\cdot}min^{-1}$, sample weights 13-30 mg). Three-six calorimetric experiments were performed for each investigated compounds. The maximum error in determining the thermal effect was 1% of the value determined, as was estimated from calibrations.

2.3. Vapour pressure

The vapor pressure of the compounds was measured by a static method with a membrane zero-manometer (Suvorov, 1970). The scheme and the main parameters of the experimental set-up were described in detail by

Zelenina, et al., 2003. Two-three series of experiments with samples of 5-25 mg were performed to measure the saturated vapor pressure. The error in pressure measurement was 40 Pa. The error in temperature measurement estimated from calibration against mercury, naphthalene and argon did not exceed 0.5 K.

2.4. CVD experiments

Sc_2O_3 films on silicon substrates (100) were obtained using $Sc(thd)_3$ as a precursor in a vertical-type reactor described by Igumenov, et al., 2001. The growth conditions of films were as follows: the gas-carrier flow rate (Ar) was 1 l/h, gas reagent flow rate (O_2) 10 l/h, the operating pressure was 1330 Pa, the evaporator temperature was 105–110°C, and the substrate temperature was varied on 400–650°C.

2.5. Film investigations

The morphology of the films was studied by scanning electron microscopy (SEM) using an electron microscope JEOL-JSM 6700F connected with EDX-analyzer EX-23000 BU.

Monochromatic laser null ellipsometry was applied to characterize the film thickness and refractive index using different models of the optical structure of the sample. The models of single- and two-layer films were applied to solve the inverse problem. The errors in determination of thickness and refractive index were not above 5 nm and 0.05 respectively. The used setup, details of measurements and calculations methodology of searching of initial estimations for unknown parameters and solution of ellipsometry inverse problem was described by Lebedev, et al., 2009 and Ayupov, et al., 2009. The optical measurements were performed with a single wavelength LEF-3M ellipsometer equipped with a He-Ne laser ($\lambda = 632.8$ nm).

Chemical composition of the coatings (surface and depth) was studied by means of X-ray photoelectron spectroscopy (XPS) with electron spectrometer SPECS (Germany) using the characteristic radiation Al K_α (1486.6 eV), the source power was 200 W, X-ray beam diameter – 1 mm. Calibration of the binding energy was performed by the method of internal standard on carbon binding energy in adsorbed hydrocarbonates C1s 285.0 eV (Handbooks of Monochromatic XPS spectra, 2005). Spectra obtained were processed by specialized software «CASA» delivered with the spectrometer. In order to carry out the layer-by-layer analysis of the chemical composition by mean of XPS, the films were etched with argon ions.

3. Results and discussion

Thermal properties of scandium(III) β-diketonates seem to be thoroughly represented in literature: the thermal behaviour of scandium acetylacetonate $Sc(acac)_3$ (Melia and Merrifield, 1970; Fahlman and Barron, 2000; Komissarova, et al., 1979), dipivaloylmethanate $Sc(thd)_3$ (Fahlman and Barron, 2000; Mészáros-Szécsényi, et al., 2002), pivaloyltrifluoroacetonate $Sc(ptac)_3$ (T. Shigematsu, et al., 1968), trifluoroacetylacetonate $Sc(tfac)_3$ (Komissarova, et al., 1979; Matsubaru and Kuwamoto, 1985; Igumenov, et al., 1982) and hexafluoroacetylacetonate $Sc(hfac)_3$ (Komissarova, et al., 1979; Fahlman and Barron, 2000) in the condensed phase was investigated, saturated vapour pressure of $Sc(acac)_3$ (Melia and Merrifield, 1970; Fahlman and Barron, 2000; Komissarova, et al., 1979; Semyannikov, et al., 2001), $Sc(tfac)_3$ (Matsubaru and Kuwamoto, 1985; Fahlman and Barron, 2000; Komissarova, et al., 1979), $Sc(hfac)_3$ (Fahlman and Barron, 2000; Komissarova, et al., 1979), $Sc(thd)_3$ (Fahlman and Barron, 2000; Konstantinov, et al., 1985) was studied using different methods. However, the data reported in those works differ from each other substantially, both in melting points and in the obtained thermodynamic characteristics of the sublimation and evaporation processes which sometimes have values nonreal for metal β-diketonates (for example for $Sc(tfac)_3$ $\Delta_{subl}H_{T\mathrm{ave.}} = 28.6\pm1.3$ kJ·mol^{-1}, $\Delta_{subl}S°_{T\mathrm{ave.}} = 75.8$ ±J·mol^{-1}·K^{-1} obtained by Komissarova, et al., 1979).

Due to great importance of valid data for optimizing the MOCVD parameters of oxide coating deposition the further investigations aimed at obtaining more precise data about the thermal behaviour of the complexes in the condensed and gas phase, temperature dependences of the saturated vapour pressure for the complexes is needed.

3.1. DSC

The compounds seem to be thermally stable and exhibit only one phase transition - melting over the temperature range studied (300 – 473 K). Results are listed in Table 1.

Table 1. Melting points (*m.p.*), enthalpies ($\Delta_{melt}H_{m.p.}$) and entropy ($\Delta_{melt}S^{o}_{m.p.}$) for the compounds under study.

Compounds	*m.p.*, °C	$\Delta_{melt}H_{m.p.}$, kJ mol^{-1}	$\Delta_{melt}S_{m.p.}$, J mol^{-1} K^{-1}
Sc(acac)$_3$	188.0±0.2	25.3±0.7	54.8±1.3
Sc(thd)$_3$	152.4±0.6	26.7±0.3	62.8±0.8
Sc(tfhd)$_3$	149.8±0.3	21.6±1.3	51.1±1.3
Sc(tfac)$_3$	106.5±1.0	30.1±1.0	79.3±1.1
Sc(ptac)$_3$	58.6±0.8	25.4±1.2	76.6±1.4
Sc(hfac)$_3$	96.9±0.8	29.7±0.5	80.4±1.0

3.2. Vapour pressure

The measurements on vapour pressure were carried out by static method in a wide temperature interval. The average molecular weight of gas calculated from the experimental data on unsaturated vapours using ideal gas law was close to the molecular weight of monomer for all investigated compounds. Decomposition temperatures of compounds under study were defined as the temperature above that pressure changes became irreversible. The information about melting and decomposition processes were taken into account at measuring saturated vapour pressure of complexes. All data on *p–T* are shown in Fig.1. In some cases calorimetric data was also involved to predict vapour pressure over solid or liquid compound.

As you can see from this figure the fluorinated complexes are more volatile than the non-fluorinated ones: the higher the fluorination into the beta-diketonate ligand (i.e., hfac *versus* tfac *versus* acac or ptac *versus* thd), the greater the volatility of compounds is. Substitution of ^{t}Bu-group for CH$_3$-one (i.e., thd *versus* acac) also results the increase in vapor pressure by 2-3 order of magnitude. It should be noted that the introduction of fluorine atom into the γ-position of 2,2,6,6-tetramethyl-3,5-heptanedione has not substantial effect on the volatility of the compound; these two compounds are also close to each other in thermodynamic parameters. These facts are in agreement with those observed earlier by us for the beta-diketonates of other metals (Morozova, et al., 2009; Zherikova, et al., 2008).

The following row of volatility was obtained for beta-diketonaet derivatives of scandium(III) on the basis of *p–T* dependencies (for $\ln(p/p_0) = -8$): Sc(hfac)$_3$ > Sc(ptac)$_3$ > Sc(tfac)$_3$ > Sc(tfhd)$_3$ ≈ Sc(thd)$_3$ > Sc(acac)$_3$. (p_0 = 1 atm = 101325 Pa).

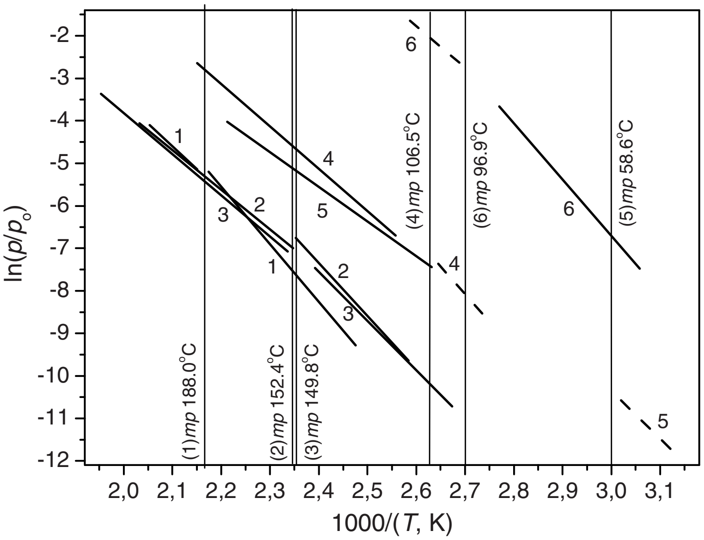

Fig. 1. Dependencies of logarithm of saturated vapor pressure on reciprocal temperature for the complexes Sc(acac)$_3$ – 1, Sc(thd)$_3$ – 2, Sc(tfhd)$_3$ – 3, Sc(tfac)$_3$ – 4, Sc(ptac)$_3$ – 5, Sc(hfac)$_3$ – 6 obtained by static method and calculated from the vapour pressure measurements and calorimetric data (they are marked out with dash line)

3.3. CVD experiments

Sc(thd)$_3$ has been used as precursor for the oxide film formation by MOCVD. The film decomposition conditions were chosen on the base of information about thermal behavior of the complex.

The investigation of film growth rate indicates that at constant other CVD parameters it strongly depends on the substrate temperature and the source temperature (Table 2, Fig. 2). The growth rate increases with the raise of substrate temperature reaching the maximum value (80 nm/h) at $T_{sub.}$ = 550°C and is most likely to decrease after 600°C (Fig. 2). As the source temperature increases only by five degrees (from 105°C to 110°C) the growth rate raises from 17 to 22 nm/h (Table 2).

The procedure of laser null ellipsometry (Lebedev, et. al., 2009) allows the study of the character of changes of the refractive index across the film thickness by measuring polarization parameters ψ and Δ, then solving the inverse problem of ellipsometry involving the multilayer models. The results are listed in table 2. The films were found to consist of Sc_2O_3 with the value of refractive index varied in 1.9-2.1 range. SiO_2 layer with thickness of 3-5 nm was also found between target film and substrate.

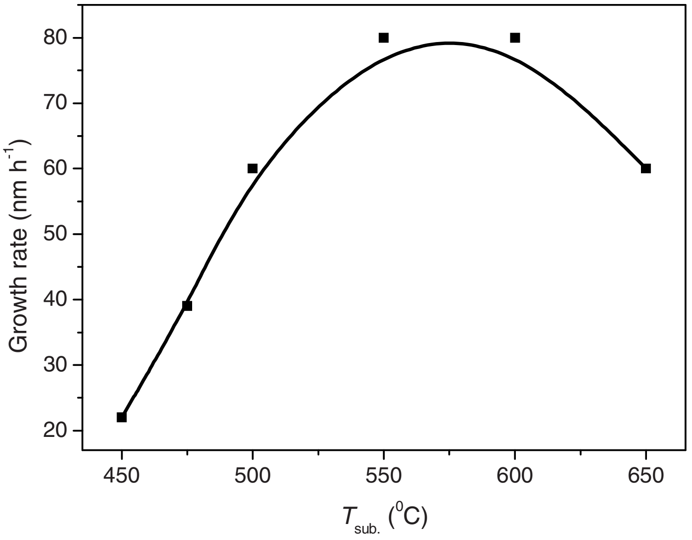

Fig. 2. Effect of the substrate temperature ($T_{sub.}$) on the film growth rate.

Table 2. The thickness, refractive index of Sc_2O_3 films deposited at different source and substrate temperatures according to ellipsometry and SEM data.

Sample number	1	2	3	4	5	6	7
T_{source},°C	105	110	110	110	110	110	110
$T_{sub.}$,°C	450	450	475	500	550	600	650
Thickness, nm	25	44	76	120	160	160	124
Refractive index	1.95	1.96	1.86	2.05	1.99	1.92	2.11
Thickness, nm (SEM)			70-80	115-130	160-170	150-160	

According to SEM investigation (Fig. 3) the films consist of sharply defined crystallites whose size increases (from 15 to 60 nm) with the growth of substrate temperature.

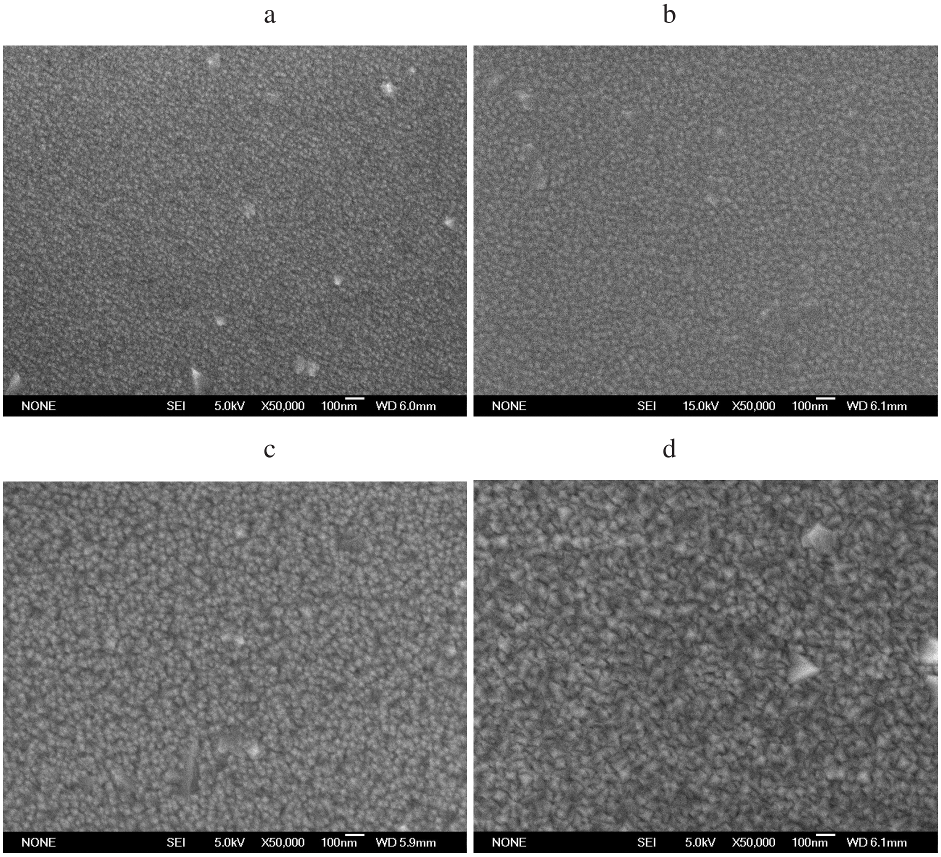

Fig. 3. SEM images of the samples deposited at 450°C (a), 475°C (b), 500°C (c), 550°C (d).

The films were characterized by XPS depth profiling. The results indicate that Sc(thd)$_3$ give rise to pure Sc$_2$O$_3$ in the bulk of the film, with carbon impurity is less then 2% (Fig. 4a). Scandium line spectrum (Fig. 4b) is splitted into two components with binding energies Sc 2p3/2 = 401.76 eV and Sc 2p1/2 = 406.23 eV. This completely corresponds to scandium oxide for which Sc 2p3/2 = 401.8 eV and Sc 2p1/2 = 406.2 eV (Moulder, et. al., p. 71). Lines corresponding to other scandium compounds were not found.

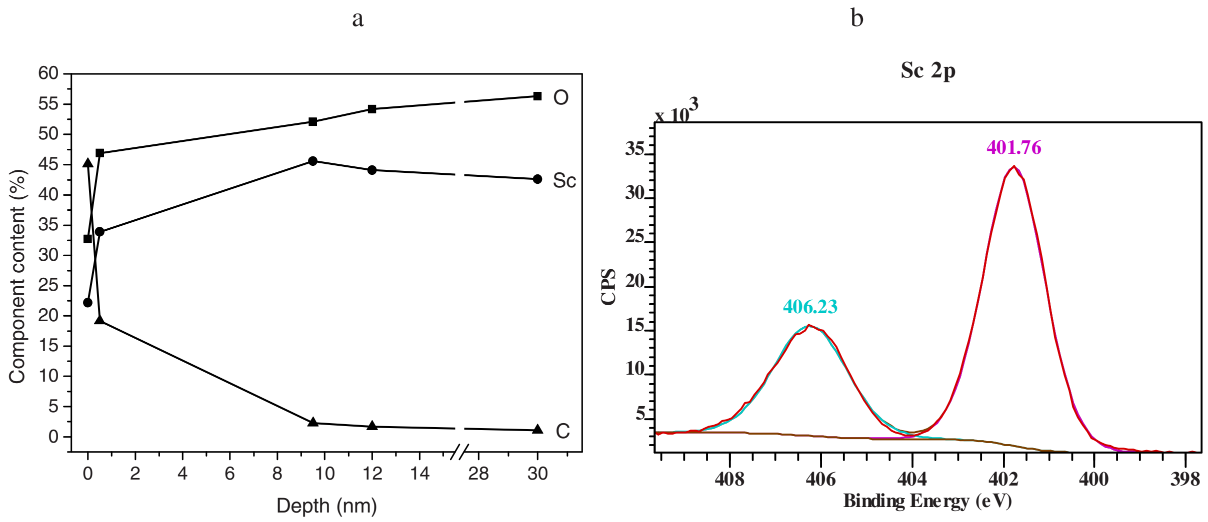

Fig. 4. XPS depth profiling (a) and scandium spectrum at the etching depth of 6.3 nm (b) (sample 1).

In conclusion, this investigation was undertaken to show how the complex study of thermal properties could underlie both choosing precursor and defining regime intervals for film deposition by CVD. Realizing this approach, six scandium beta-diketonates were obtained and thermally characterized in the solid and gaseous states. The information obtained about thermal behaviour of the complexes enabled us to use it as a guide for CVD experiments aimed at achieving oxide films with high optical properties.

Acknowledgements

The work was supported by the Russian Foundation for Basic Research (grant №12-03-01039-a).

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