Tin(II) hexafluoroacetylacetonate as a precursor in atmospheric pressure chemical vapour deposition: synthesis, structure and properties

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A new method for the synthesis of volatile tin(II) hexafluoroacetylacetonate [Sn(C$_5$HO$_2$F$_6$)$_2$] was suggested, the compound was characterized by elemental analysis, IR spectroscopy, and DTA/TGA; the crystal structure was established by X-ray diffraction; the morphology and composition of the coating deposited by atmospheric pressure chemical vapour deposition were studied by SEM-EDX and XRD.

Volatile tin compounds, passing into the gas phase at moderate temperatures without thermal decomposition, are promising for the synthesis of thin tin oxide films using gas-phase processes.[1,2]

The synthesis of layers and nanostructures with desired properties (crystallite size, coating thickness, its structure and morphology) depends on not only the chemical vapour deposition (CVD) process parameters, but also the properties of precursors, including their structure.[3–5] Therefore, the development of methods for the synthesis and study of coordination compounds – promising precursors for CVD of nanostructured thin films – is practically important problem.[6,7]

Due to the most recognized and sought after sensitive material for semiconductor gas sensors, CVD of the thin tin oxide films has attracted much attention.[8–11]

β-Diketonates are the most widely used precursors for the preparation of thin films by metalorganic chemical vapour deposition.[12] Kai-Ming *et. al.*[13] attempted to synthesize and characterize tin(II) hexafluoroacetylacetonate by the interaction of tin dichloride with sodium hexafluoroacetylacetonate in THF in an inert atmosphere of nitrogen. They noted an obvious practical difficulty of the experiment: the process should be carried out in an inert atmosphere, careful preparation (dehydration) of the starting reagents and solvents are needed.

From our point of view, since hexafluoroacetylacetone is a sufficiently strong acid[14] (pK_a = 4.35), the simplest and most effective preparation method is the direct interaction of tin powder with β-diketone (hexafluoroacetylacetone) with further separation and identification of the volatile product, [Sn(C$_5$HO$_2$F$_6$)$_2$].†

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† Tin powder (99.9%, Khimreaktiv) was used without further purification; 1,1,1,5,5,5-hexafluoropentane-2,4-dione (98%, P&M-Invest) was distilled to remove impurities.

Elemental CH analysis was made on an EA1100 CHNS-0 elemental analyzer from Carlo Erba Instruments.

The IR spectra were recorded on an Infralum FT-08 FTIR spectrophotometer (Lumex, Russia) on Nujol mull in KBr pellets.

XRD data were collected on a DRON-2 diffractometer with germanium monochromated CuKα radiation, Huber camera and an Imaging Plate detector (LOMO, USSR).

DTA/TGA analysis was made on an SDT Q600 (TA Instruments, USA) in aluminum crucibles; heating rate, 5 K min^{-1}, argon carrier gas flow rate, 20 ml min^{-1}.

The atmospheric pressure chemical vapour deposition (APCVD) experiments were carried out in a furnace-heating hot-wall reactor with a carrier gas Ar (flow rate, 50 ml min^{-1}). The temperatures in the evaporation and deposition zones were 75±5 and 517±5 °C, respectively.
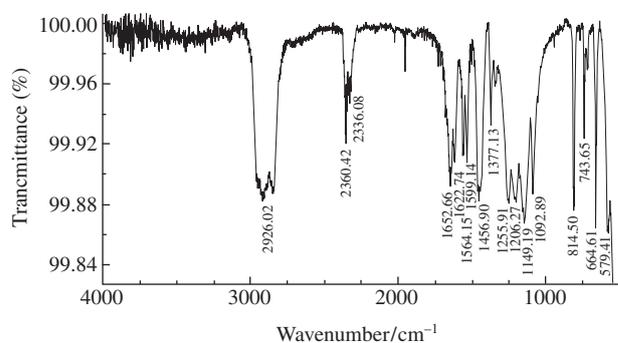

Figure 1 IR spectrum of [Sn(C$_5$HO$_2$F$_6$)$_2$].

A high intensity band ν$_{CO}$ in the IR spectra of tin(II) hexafluoroacetylacetonate (Figure 1) is shifted from 1690 cm^{-1} in the free ligand to 1652 cm^{-1}, confirming the coordination of hexafluoroacetylacetonato groups. The absence of absorption bands due to the OH group stretch in the range of 3000–3400 cm^{-1} evidenced that the synthesized compound is anhydrous.

Comparison of the powder diffraction data for fresh-sublimated product [Figure 2(*a*)] with those from the International Centre for Diffraction Data and Cambridge Structural Database did not reveal coincidences that confirm the formation of a new phase.

The beginning of the sublimation process was observed at 30±5 °C (0.1 Torr). The melting temperature of [Sn(C$_5$HO$_2$F$_6$)$_2$] determined by capillary method is 65±1 °C. According to the DTA data, decomposition of the compound did not occur up to 90±5 °C.

The molecular structure of [Sn(C$_5$HO$_2$F$_6$)$_2$] contains two crystallographically independent molecules with very close geometric parameters (Figure 3).‡ The coordination polyhedron of tin(II)

Deposited films were characterized by scanning electron microscopy (SEM) using an NVision 40 instrument with EDX elemental analysis (Carl Zeiss, Germany).

Tin powder (0.35 g, 2.94 mmol) was dissolved in an excess of freshly distilled hexafluoroacetylacetone (1 ml, 7.07 mmol). The synthesis was carried out in a reflux system with ultrasonic activation and heating up to 80 °C. Powder tin dissolution and white crystals formation were observed in the volume of the reactor after one-day expiration.

The purification of the crude product by sublimation at 30–70 °C under reduced pressure (0.1 Torr) resulted in the formation of white crystalline [Sn(C$_5$HO$_2$F$_6$)$_2$] (1.45 g, 93% yield) at the cold reactor zone. Found (%): C, 21.84; H, 0.47. Calc. for C$_{10}$H$_2$O$_4$F$_{12}$Sn (%): C, 22.51; H, 0.38.
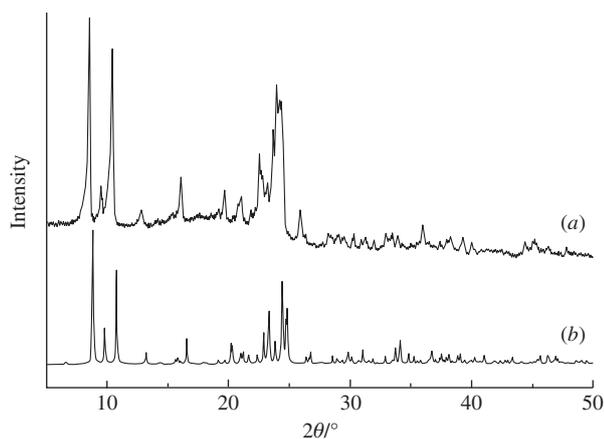
Figure 2 (*a*) Powder diffraction data and (*b*) simulated diffraction data based on the structure of [Sn(C$_5$HO$_2$F$_6$)$_2$].

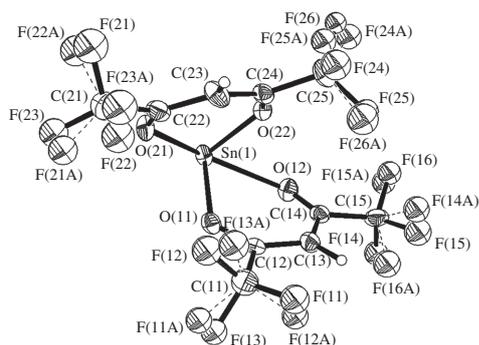**Figure 3** Molecular structure of [Sn(C$_5$HO$_2$F$_6$)$_2$]. Ellipsoids are shown at 50% probability level. For minor components of disorder, C–F bonds are drawn as dashed lines. Selected bond lengths (Å) and angles (°): Sn–O$_{ax}$ 2.327(6)–2.348(6), Sn–O$_{eq}$ 2.167(6)–2.196(6), C–O$_{ax}$ 1.210(14)–1.229(11), C–O$_{eq}$ 1.258(11)–1.280(11); O$_{ax}$–Sn–O$_{ax}$ 141.4(3), 141.5(2), O$_{eq}$–Sn–O$_{eq}$ 86.2(2), 86.4(2).

represents a distorted trigonal bypyramid. As usual, a stereo-active lone electron pair occupies an equatorial position. Both chelating ligands engage one equatorial and one axial sites. The angles between axial oxygen atoms are approximately 150°, while the angles between equatorial O atoms are close to 87°. As expected, the Sn–O bonds formed by the central tin atom with axial oxygen atoms are ~0.2 Å longer than those formed by equatorial O atoms. Of interest, partially double C–O$_{ax}$ bonds with endocyclic carbon atoms are approximately 0.05 Å shorter than the same C–O$_{eq}$ bonds. For both independent molecules, hexafluoro ligands are planar within 0.135(2) Å. The displacements of the tin atoms from least-squares planes of the ligands are
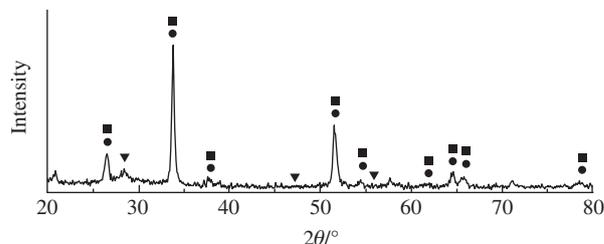
Figure 4 XRD profiles of (■) cassiterite tin dioxide film (ICDD 14-1445), (▼) silicon substrate and (●) tin dioxide film deposited from [Sn(C$_5$HO$_2$F$_6$)$_2$].

approximetely 0.5 Å. In general, the geometry of [Sn(C$_5$HO$_2$F$_6$)$_2$] is close to that previously found for the related complex Sn[Ph–C(O)–CH–C(O)–Me]$_2$.[17]

Comparing simulated diffraction pattern of [Sn(C$_5$HO$_2$F$_6$)$_2$] based on structure data [Figure 2(*b*)] calculated by means of the program complex Mercury CSD 2.3 with experimentally obtained by XRD for sublimated powder [Figure 2(*a*)] confirm that taken crystal belongs to the base phase [Sn(C$_5$HO$_2$F$_6$)$_2$].

The volatile compound [Sn(C$_5$HO$_2$F$_6$)$_2$] was used as a precursor for the deposition of thin polycrystalline tin-containing films on a polished silicon substrate by CVD. The parameters of the APCVD process were selected according to obtained thermo-chemical properties of the compound: the temperatures in the evaporation zone of 75±5 °C and in the deposition zone of 517±5 °C.

X-ray analysis of the tin containing layer indicates the forma-tion of tin dioxide in the cassiterite phase (Figure 4).

The microstructure of the coatings, obtained by SEM, is pre-sented in Figure 5. The polycrystalline coating is a homogeneous solid with no significant defects. Particle size distribution was made using SEM data. The average grain size is 55±15 nm.

The results of the EDX analysis indicate involving of signi-ficant fluorine impurities in coating (Sn : F = 2.89 : 1), that affect the semiconductor properties of the films.[18,19]

In conclusion, the new, one-step, easy to implement method, which does not require careful preparation of reagents and solvents, was developed for the synthesis of tin(II) hexafluoroacetylacetonate [Sn(C$_5$HO$_2$F$_6$)$_2$]. The compound was identified by IR spectroscopy, elemental analysis and XRD; the crystal structure was established for the first time. According to experimentally derived thermochemi-cal data (sublimation, melting and decomposition temperatures), this highly volatile complex can be recommended as a precursor of the nanostructured tin oxide films in gas-phase processes, that was confirmed by the APCVD experiments.
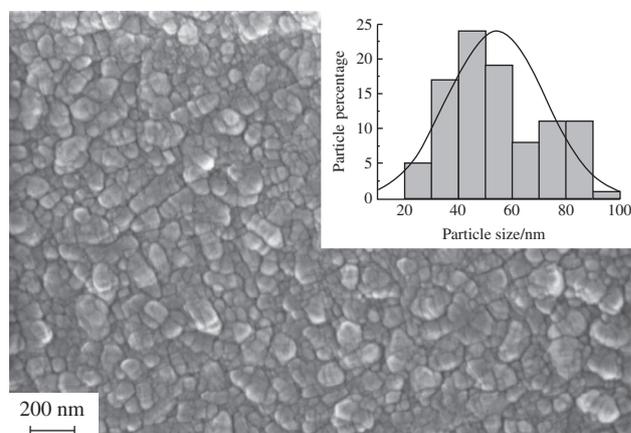
Figure 5 Scanning electron micrographs and particle size distribution of the tin dioxide film deposited from [Sn(C$_5$HO$_2$F$_6$)$_2$].

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