SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Tin Trifluoroacetylacetonate $[Sn(C_5H_4O_2F_3)_2]$ as a Precursor of Tin Dioxide in APCVD Process

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Abstract—A new method of synthesis of volatile complex, tin trifluoroacetylacetonate $[Sn(C_5H_4O_2F_3)_2]$, was proposed. The prepared compound was identified by IR spectroscopy, CH analysis, X-ray powder diffraction, and DTA/TGA, the composition was confirmed by MALDI-TOF mass spectrometry, crystal structure was established. Thin films of tin dioxide on silicon were obtained by atmospheric pressure chemical vapor deposition using $[Sn(C_5H_4O_2F_3)_2]$ as a precursor. The morphology and composition of the films were studied by scanning electron microscopy, EDX elemental analysis, and X-ray powder diffraction. Surface resistance and light transmission in visible and near IR region were studied.

Keywords: precursor, SnO₂, CVD, thin films **DOI**: 10.1134/S003602361605017X

Tin dioxide, one of the most required semiconducting materials for gas sensors [1, 2] and solar cell technology, is widely used as a transparent conducting oxide layer [1, 3, 4]. The application of chemical vapor deposition approach to the synthesis of tin dioxide at atmospheric pressure requires a wide series of volatile stable precursors. As it was shown in a series of works [5–8], the morphology and properties of coatings based on tin dioxide produced under identical conditions are dependent on the nature of precursor compound.

Different metal β -diketonates are widely used as precursors for the preparation of metallic and oxide materials by CVD method [9–17], while the prediction of their volatility is very promising due to analysis and modeling of their structure [18]. The use of tin(II) hexafluoroacetylacetonate [Sn(C₅HO₂F₆)₂] [19] and dichloro-bis(2,4-pentadionato)tin(IV) [20–22] as precursors for the synthesis of tin dioxide by CVD method is reported in the literature.

It is practically important and urgent task to extend the scope of stable tin complexes capable of transferring to gas phase at atmospheric pressure. The analog of the above mentioned hexafluoroacetylacetonate, tin(II) trifluoroacetylacetonate, is one of promising compounds for preparing thin films of SnO_2 by atmospheric pressure chemical vapor deposition (APCVD). This compound was obtained in [23, 24] using a complicated procedure based on alkoxides and substituted cyclopentadienyl tins, which requires specially prepared solvents. Using this procedure, $[Sn(C_5H_4O_2F_3)_2]$ was synthesized in the work [25], which also reported on its use as a precursor for preparing SnO_2 in O_2 flow and crystal structure of this compound. However, there is no data in CCDC on the structural characteristics necessary for the valuable analysis of structural information, especially the character of packing in lattice. Therefore, the aim of this work is to develop a new simple method for the preparation and isolation of $[Sn(C_5H_4O_2F_3)_2]$ that requires no specially prepared solvents and moisture-sensitive initial tin compounds, to study certain physicochemical properties of $[Sn(C_5H_4O_2F_3)_2]$ and its approbation as a precursor for preparing thin, transparent, and electrically conducting SnO₂ films by APCVD method in comparison with the closest structural analog $[Sn(C_5HO_2F_6)_2]$.

EXPERIMENTAL

Chemicals used: granulated tin (99.9%, Khimreactiv) was used without additional purification, 1,1,1-trifluoro-2,4-pentanedione (trifluoroacetylacetone, 98%, P&M-Invest) was purified by distillation.

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Fig. 1. Schematic diagram of installation for the deposition of coatings by APCVD method. (1) Quartz reactor, (2) resistive furnace (evaporation furnace), (3) induction furnace (destruction furnace), (4) pyrometer, (5) thermocouple, (6) digital gauge of gas supply with PC interface, (7) cylinder with carrier gas, (8) support, (9) graphite holder and heater.

Synthesis. Tin (0.40 g, 3.36 mmol) as a metal powder was dissolved in excess of freshly distilled trifluoroacetylacetone (1 mL, 8.24 mmol). The synthesis was conducted in a flask equipped with a reflux condenser at ultrasound activation and heating to 50°C. After 1 day, tin metal dissolved and transparent crystals formed in reactor volume. It was found that the obtained compound exhibited marked volatility at atmospheric pressure and was stable in air.

The obtained compound was purified by sublimation at 30–40°C under reduced pressure ($P = 10 \pm 1 \text{ kPa}$) to give transparent crystals of [Sn(C₅H₄O₂F₃)₂] in the cold reactor zone.

Chemical vapor deposition of coatings on laboratory installation (Fig. 1) at atmospheric pressure (APCVD) was carried out in argon flow (80 mL/min). The temperature in evaporation zone was $75 \pm 5^{\circ}$ C, decomposition zone temperature was $517 \pm 5^{\circ}$ C. The subsequent annealing of coatings was conducted in air at 700°C for 2 h.

CH analysis was carried out on a Carlo Erba Instruments EA1100 CHNS-0 elemental analyzer.

IR spectra were recorded on a Lyumeks Infralyum FT-08 Fourier-transform IR spectrometer (Russia) (Nujol mull, KBr windows).

X-ray powder diffraction of the precursors was performed on a LOMO DRON-2 device (Huber chamber, Imaging Plate detector, germanium microchromator, Cu K_{α} radiation) (USSR).

Mass spectrometry. MALDI-TOF mass spectra were obtained on a Bruker Daltonics Ultraflex spectrometer in positive ions mode using reflecto mode with voltage on target of 20 mV.

X-ray diffraction study. Experimental data were collected on a Bruker SMART APEX II automated

diffractometer (Mo K_{α} radiation, $\lambda = 0.71073$ A, graphite monochromator) in ω -scan mode at 130 K. Absorption corrections were made by measuring intensities of equivalent reflections. The crystals of $C_{10}H_8O_4F_6Sn$ are triclinic, FW = 424.85, a = 8.5878(4) Å, b = 10.8501(5) Å, c = 15.6157(7) Å, $\alpha = 71.927(1)^\circ$, $\beta = 82.026(1)^\circ$, $\gamma = 80.914(1)^\circ$, V = 1359.65(11) Å³, space group $\overline{P}1$, Z = 4, $\rho_{calcd} = 2.076$ g/cm³, F(000) = 816, $\mu(MoK_{\alpha}) = 1.962$ mm⁻¹, colorless cubic crystals with dimensions $0.20 \times 0.15 \times 0.15$ mm. For $C_{10}H_8F_6O_4Sn$, 10263 reflections were measured (4973 independent reflections, $R_{int} = 0.0269$).

The structure was solved by direct methods and refined by full-matrix anisotropic least squares on F^2 for all non-hydrogen atoms (SHELXTL-Plus [26]). Hydrogen atoms were added in ideal positions using the Riding model.

The final values $R_1 = 0.0263$, $wR_2 = 0.0680$ for 4145 observed reflections with $I > 2\sigma(I)$; $wR_2 = 0.0680$ for all reflections, GOOF = 1.054; 383 refined parameters; $\Delta \rho_{max/min} = 1.116/-0.565$ e/Å³.

The crystallographic information was deposited in the Cambridge Crystallographic Data Center: CCDC 950598 www.ccdc.cam.ac.uk/data_request/cif.

DTA/TGA was performed on a TA Instruments SDT Q600 thermal analyzer (USA) in aluminum crucibles (heating rate 5 K/min, argon carrier gas flow rate 100 mL/min).

Scanning electron microscopy (SEM) was accomplished on a Carl Zeiss NVision 40 three-beam workstation, elemental composition was determined using an EDX Oxford Instruments add-on unit for energydispersive analysis.



Fig. 2. IR spectrum of $[Sn(C_5H_4O_2F_3)_2]$.

RESULTS AND DISCUSSION

Study of Prepared Precursor $[Sn(C_5H_4O_2F_3)_2]$

For C₁₀H₈O₄F₆Sn (*FW* 426.81) anal. calcd. (%): C, 28.14; H, 1.87. Found (%): C, 27.22; H, 2.01.

The IR spectrum of prepared tin trifluoroacetylacetonate (Fig. 2) shows a shift of strong absorption band v(CO) to higher wave numbers up to 1620 cm⁻¹ ($\Delta =$ 17 cm⁻¹) as compared with the initial ligand, which indicates the coordination of trifluoroacetylacetonato groups. The lack of absorption bands in the region 3000–3400 cm⁻¹ corresponding to the stretching vibrations of OH group implies that anhydrous compound was obtained. Similar behavior was observed for [Sn(C₅HO₂F₆)₂] [19].

The preparative sublimation was found to begin at $30 \pm 5^{\circ}$ C at 10 ± 1 kPa. Melting point determined in capillary tube was found to be $40 \pm 1^{\circ}$ C. According to DTA data, melting with decomposition is observed at $48 \pm 5^{\circ}$ C (Fig. 3). DSC experiment revealed melting enthalpy for the obtained coordination compound to be 35.35 ± 1.06 kJ/mol, which is higher than that for $[Sn(C_5HO_2F_6)_2]$ (25.29 ± 0.76 kJ/mol).

The comparison of X-ray powder diffraction data for the product immediately after sublimation (Fig. 4) displays no coincidence with ICCD and CSD data, which confirms the formation of new rather than previously described phase.

We used MALDI-TOF (Matrix-assisted, laser desorption/ionization time-of-flight) mass spectrometry to identify the compound, one of the most important advance of the method is a "mild" ionization that allows one to identify molecular ion without its further defragmentation. The revealed ions were identified using their isotope distribution. To identify unknown peak, a group of peaks was selected that reflects the corresponding isotope distribution. The theoretical calculation of isotope pattern for ion supposedly corresponding to experimental isotope distribution was conducted with the use of the IsoPro free software. Table 1 shows the main experimental and calculated signals. It is seen that the results of MALDI-TOF agree well with theoretical calculations, which also confirms the composition of the obtained compound, [Sn(C₅H₄O₂F₃)₂].

Colorless crystals of $[Sn(C_5H_4O_2F_3)_2]$ obtained by sublimation at 30°C under reduced pressure $(10 \pm 1 \text{ kPa})$ were selected for X-ray diffraction study. Molecular structure of the compound includes two independent molecules with very close geometrical parameters (Fig. 5). Coordination polyhedron of tin(II) atom is a distorted trigonal bipyramid with stereoactive unshared electron pair located as usual in the equatorial position. Both trifluoroacetylacetonate chelating ligands occupy one axial and one equatorial position

Table 1. The main signals of MALDI-TOF mass spectrum of $[Sn(C_5H_4O_2F_3)_2]$

Fragment	Calculated m/z value	Experimental m/z value		
$[C_5H_4O_2F_3]^+$	153.1	153.1		
$[Sn(C_5H_4O_2F_3)_2]^+$	423.9	423.0		



Fig. 3. DSC/TGA for $[Sn(C_5H_4O_2F_3)_2]$ and $[Sn(C_5HO_2F_6)_2]$.



Fig. 4. X-ray diffraction pattern of $[Sn(C_5H_4O_2F_3)_2]$ after sublimation.

each. The angles at the tin atom between the axial oxygen atoms are ~150°, whereas the angles between the equatorial substituents are close to 87° (Table 2). As should be expected, the bonds of the central atom with the axial atoms are about 0.2 Å longer than with the equatorial ones. It is interesting to note that the partially double bonds of axial oxygen atoms with endocyclic carbon atoms are ~0.04 Å shorter than similar bonds of equatorial oxygen atoms. In both independent molecules, trifluoroacetylacetonate ligands are flat within 0.14 Å. Tin atoms are ~0.5 Å out of rootmean-square planes of the ligands. All four CF₃ groups are located in proximity to the equatorial plane of the central tin atom. As a whole, the geometry of the

Molecule A		Mo	Molecule B		
Sn(1)–O(11)	2.140(2)	Sn(2)–O(31)	2.144(2)		
Sn(1)–O(21)	2.147(2)	Sn(2)–O(41)	2.146(2)		
Sn(1)–O(12)	2.326(2)	Sn(2)–O(42)	2.330(2)		
Sn(1)–O(22)	2.330(2)	Sn(2)–O(32)	2.331(2)		
O(11)–C(12)	1.300(4)	O(31)-C(32)	1.299(3)		
O(21)-C(22)	1.297(4)	O(41)-C(42)	1.292(4)		
O(12)-C(14)	1.249(4)	O(32)–C(34)	1.255(4)		
O(22)-C(24)	1.250(4)	O(42)-C(44)	1.252(4)		
O(11)Sn(1)O(21)	86.93(8)	O(31)Sn(2)O(41)	86.74(8)		
O(11)Sn(1)O(12)	79.27(8)	O(31)Sn(2)O(42)	78.93(8)		
O(21)Sn(1)O(12)	78.73(8)	O(41)Sn(2)O(42)	79.53(8)		
O(11)Sn(1)O(22)	79.69(8)	O(31)Sn(2)O(32)	79.08(8)		
O(21)Sn(1)O(22)	79.08(8)	O(41)Sn(2)O(32)	79.44(8)		
O(12)Sn(1)O(22)	150.04(8)	O(42)Sn(2)O(32)	150.24(8)		

Fable 2. Certain bond distances (Å)	and angles	(deg)	in	$[Sn(C_5H_4O_2F_3)_2]$
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compound is close to that previously found for complexes $Sn[F_3C-C(O)-CH-C(O)-CF_3]_2$ [19] and $Sn[Ph-C(O)-CH-C(O)-Me]_2$ [27]. Basically, our results extend previous data [25] with information on molecular packing in the crystal.

Tin atoms in the crystal are involved into weak intermolecular interactions with oxygen atoms of neighboring molecules (Fig. 6). The Sn…O distances vary within 3.245–3.310 Å. For comparison, the sum

of the van der Waals radii of tin and oxygen may be assessed as 2.2 + 1.5 = 3.7 Å [28]. Thus, the coordination state of the tin atom can be described as 4 + 2. Taking into consideration the location of unshared electron pair, the coordination polyhedron can be considered as a distorted pentagonal pyramid. As should be expected, weak Sn···O interactions result from slightly shortened Sn···Sn intermolecular distances (4.290 and 4.299 Å). It should be noted that Sn···O intermolecular interactions unite neighboring



Fig. 5. Molecular structure of $[Sn(C_5H_4O_2F_3)_2]$. Only one crystallographically independent molecule is shown. The arrangement of disordered trifluoromethyl groups (ellipsoids) is given at the 50% probability level.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY Vol. 61 No. 5 2016



Fig. 6. Intermolecular Sn...O interactions of neighboring molecules (shown by dashed lines).

molecules into chains along the *a* crystallographic axis (Fig. 6). As a result, the same structure is observed in this case (Fig. 7) as was previously noted for $[Sn(C_5HO_2F_6)_2]$. In our opinion, this structure can provide the formation of dimers, including those existing in gas phase, which can lead to decrease of sublimation temperature.

Chemical Vapor Deposition of SnO₂ Coatings

The obtained volatile coordination compound $[Sn(C_5H_4O_2F_3)_2]$, like $[Sn(C_5HO_2F_6)_2]$, was used as a precursor for the deposition of thin polycrystalline SnO_2 coatings on a polished support using APCVD procedure in an argon flow. The parameters of APCVD process were selected in accordance with the obtained data on the thermochemical properties of the compound: evaporation zone temperature was $75 \pm 5^{\circ}$ C,

deposition zone temperature was 517 \pm 5°C, deposition time was 5 min.

X-ray powder diffraction showed that tetragonal SnO₂ phase forms, space group *P4/mnm* (ICDD card 041-1445, cassiterite) (Fig. 8). Crystallite dimensions assessed by the Sherer formula for thin SnO₂ film of deposited using [Sn(C₅H₄O₂F₃)₂] and [Sn(C₅HO₂F₆)₂] were found to be 15 and 18 nm, respectively. The available supplementary reflections refer to the supports of polished silicon that were coated. The authors [25] note that the deposition of thin films with the use of [Sn(C₅H₄O₂F₃)₂] as precursor in argon is accompanied by the formation of tin metal within films, however, the phase composition of coatings in our studies was only tin dioxide for both [Sn(C₅H₄O₂F₃)₂] and [Sn(C₅HO₂F₆)₂].

Table 3. Properties of coatings formed on glass

Precursor	Resistance, kOhm/□	Transmittance at 550 nm, %	Atom ratio Sn : F
$[\mathrm{Sn}(\mathrm{C}_{5}\mathrm{H}_{4}\mathrm{O}_{2}\mathrm{F}_{3})_{2}]$	57	44.0	1:0.02
$[Sn(C_5HO_2F_6)_2]$	63	74.8	1:0.09

SEM data indicate that an ierarchcal two-layer microstructure forms on silicon surface for the thin films of SnO₂ obtained by the gas-phase thermal destruction of obtained compound [Sn(C₅H₄O₂F₃)₂]: the coating consists of rather large (120–150 nm) aggregates of globular shape made of small particles of 20–30 nm in diameter (Fig. 9a). In comparison with coatings obtained from [Sn(C₅H₀2F₆)₂] (Fig. 9b), the aggregates prepared from [Sn(C₅H₄O₂F₃)₂] are more porous, while particle size is about half the size.

The rsults of elemental energodispersive analysis of coatings after annealing in air (EDX) (Table 3) indicate rather high content of fluorine in coating obtained from $[Sn(C_5H_4O_2F_3)_2]$ (Sn : F = 1 : 0.02 at.), which, nonetheless, is lower than it was noted in the



Fig. 7. Packing in $[Sn(C_5H_4O_2F_3)_2]$ crystal: (a) along the

column axis, (b) across the column axis (with slight shift

for clarity).

similar experiment with $[Sn(C_5HO_2F_6)_2]$ (Sn : F = 1 : 0.09 at.).

The obtained coatings are transparent in wavelength range 400–1100 nm (Fig. 10). For glass with coating obtained from $[Sn(C_5H_4O_2F_3)_2]$, the largest transmittance (51%) is observed in the long wavelength region (1100 nm). For the glass with coating obtained from $[Sn(C_5HO_2F_6)_2]$, the largest transmittance (77%) is observed at 610 nm. The transmittance of the coatings at 550 nm is presented in Table 3.

The surface resistance of the coatings on glass after annealing is shown in Table 3. It is seen that the obtained values for different precursors are close: 57 and 63 kOhm/ \Box for tin(II) trifluoro- and hexafluoro-acetylacetonates, respectively.

Thus, we proposed the new method of synthesis of volatile complex tin(II) trifluoroacetylacetonate $[Sn(C_5H_4O_2F_3)_2]$. The compound was characterized by IR spectroscopy, elemental and X-ray powder diffraction analysis, its thermal behavior was studied, the composition was confirmed by MALDI-TOF mass spectrometry, the crystal structure was established by X-ray diffraction study.

The experimental thermochemical data (temperatures of preparative sublimation, melting, thermal destruction) allow one to recommend this readily vol-



Fig. 8. X-ray diffraction pattern of tin dioxide obtained by decomposition of $[Sn(C_5H_4O_2F_3)_2]$ and $[Sn(C_5HO_2F_6)_2]$. Tin dioxide reflections with cassiterite structure (ICDD 14-1445) and silicon support.

551

(a) 200 nm (b) 200 nm

Fig. 9. SEM of tin dioxide coatings. Precursors: (a) $[Sn(C_5H_4O_2F_3)_2]$, (b) $[Sn(C_5HO_2F_6)_2]$.

atile complex as s precursor for the deposition of nanostructured oxide tin-containing films by gas-phase methods.

The application of coordination compound $[Sn(C_5H_4O_2F_3)_2]$ and its closest analog $[Sn(C_5HO_2F_6)_2]$ as precursors in APCVD process in inert atmosphere (argon) was shown to result in formation of thin films of tin dioxide with cassiterite crystal lattice doped with fluorine. It was found that morphology, dispersity, fluorine content, and light transmittance differ considerably for coatings obtained under the same conditions but using different precursors.



Fig. 10. Light transmittance of tin dioxide coatings obtained on glass.

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