Obtaining the Films of ZrO_2, HfO_2, SnO_2 from the Solutions of Complex Compounds

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Abstract

The films based on the oxides of zirconium (IV), hafnium (IV) and tin (IV) were obtained from the film-forming solutions of complex compounds of these metals with acetylacetone. Their properties are investigated. Optimal obtaining conditions were established using the results of thermal and X-ray phase analysis.

INTRODUCTION

Promising initial film-forming compounds for the development of thin-film materials based on the oxides of metals of the IV group of the Periodic Table are β-diketonates. These compounds are mainly formed by film deposition from the gas phase [1]. This method requires high energy consumption and is labour-intensive in comparison with the method of film obtaining from solution.

The present work deals with the investigation of the possibility to use acetylacetonates of zirconium (IV), hafnium (IV) and tin (IV) for obtaining thin films of ZrO_2, HfO_2, SnO_2 from alcohol solutions.

EXPERIMENTAL

Ethanol is most common solvent for obtaining films since it meets all the requirements to solvents in film-forming solutions (FFS) [2].

The film-forming solutions were prepared using 96 % ethanol as a solvent; acetylacetone (Hacac) was used as a ligand, and complex-forming metals were those of the IV group (oxychlorides of zirconium and hafnium, tin (II) chloride), with metal to ligand ratio Zr^{4+} (Hf^{4+}) : Hacac = 1 : 4, Sn^{2+} : Hacac = 1 : 2. We discovered that the complex of tin (II) with acetylacetone exists dissolved in ethanol only in the presence of hydrochloric acid not less than 0.4 mol/l.

The behaviour of acetylacetone in solution in 96 % ethanol and the structure of complex particles in FFS are described in [3–5]. Zirconium (IV) and hafnium (IV) give complexes with the dissociated enolic form of acetylacetone, while tin (II) gives complex with the enolic non-dissociated form and ketone form.

Viscosity was measured with VPZh-2, VPZh-4 viscosimeters at room temperature.

RESULTS AND DISCUSSION

Changes in the viscosity (η) of FFS are important for practical purposes. The character of its changes with time in the solutions based on zirconium and hafnium acetylacetonates is similar (Fig. 1, *a*, *b*). Maximal η value is achieved at the 6th day and decreases to a constant value at the 15th day. An increase in η is likely to be connected with hydrolysis processes and with the possibility of the formation of polymer associates

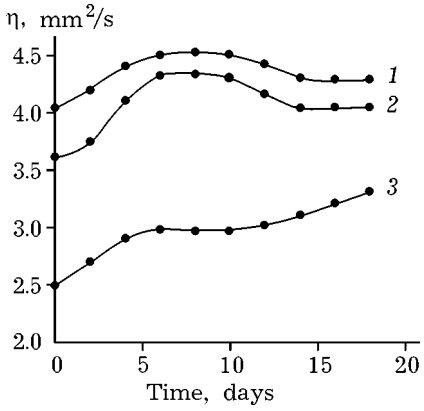

Fig. 1. Changes in the viscosity of FFS with time: *1* – $ZrOCl_2$ – Hacac – C_2H_5OH; *2* – $HfOCl_2$ – Hacac – C_2H_5OH; *3* – $SnCl_2 \cdot 2H_2O$ – Hacac – C_2H_5OH – HCl.

$$-M-O=\underset{\displaystyle CH_3}{\overset{|}{C}}-CH=\underset{\displaystyle CH_3}{\overset{|}{C}}-O-M-,\quad \text{where (M = Zr, Hf)}$$

because of the ability of acetylacetone to act as a bridging ligand. The destruction of associates (decrease in viscosity) may lead to the formation of coordination-saturated molecules of zirconium and hafnium acetylacetonates having chelate structure with the coordination number equal to 8 [5]. The character of changes in the viscosity of FFS based on tin (II) and acetylacetone (see Fig. 1, curve *3*) allowed us to conclude that the equilibrium is established in the solution at the 4th day and is characterized by constant viscosity during 6 days. An increase in viscosity at the 10th day is likely to be connected with the formation of polymer associates. The analysis of the η curves for the solutions showed that, in order to obtain uniform films, it is reasonable apply FFS based on $ZrOCl_2$ – Hacac – C_2H_5OH and $HfOCl_2$ – Hacac – C_2H_5OH at the 6–8th day, while the FFS based on $SnCl_2 \cdot 2H_2O$ – Hacac – C_2H_5OH are to be applied at the 4–10th day, when the h value becomes constant.

In order to establish temperature mode of the formation of zirconium, hafnium and tin oxides, both in the bulk state and as thin films, we carried out thermal analysis of the FFS dried at 333 K within temperature range 293–1073 K at heating rate of 10 °C/min with Q-1500 derivatograph of Paulic-Paulic-Erday system. The X-ray phase analysis (XPA) of the final products of the decomposition of dried FFS was carried out with DRON-3M diffractometer, CuK_α radiation (λ = 1.5418 Å), Ni filter. Heating rate was 4 °C/min.

Thermal decomposition of the dried FFS of the composition $ZrOCl_2$ – Hacac – C_2H_5OH has a complicated character (Fig. 2). Seven stages of FFS destruction till ZrO_2 of monoclinic modification can se revealed in the DTG curve (according to the XPA data, Table 1); four endothermic effects are observed in the DTA curve with the maxima at 370, 388, 448, 473 K, and two exothermal effects with maxima at 531, 733 K; the second exoeffect is a sum of two effects (according to the DTG data). Endothermic effects within temperature range 321–487 K are likely to be due to a stepwise removal of the residual ethanol and water, as well as the products of decomposition of zirconium compounds with chloride ion. Exothermal effects within temperature range 487–873 K characterize the combustion of ligand, which results in complete decomposition of the FFS with the formation of zirconium oxide.

Thermal analysis of the dried FFS of the composition $HfOCl_2$ – Hacac – C_2H_5OH also indicates seven main stages of decomposition. Three endoeffects with the maxima at 403, 448, 508 K and two exoeffects with the maxima at 693 and 825 K are observed. The latter exoeffect corresponds to the sum of two effects. Hafnium dioxide of the monoclinic modification (see Table 1) is formed at a temperature of 873 K.

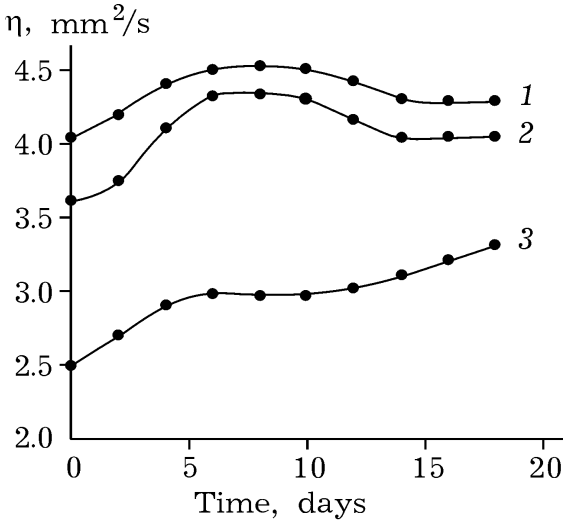

Fig. 2. Thermogram of the decomposition of dried FFS based on ZrO_2 – Hacac – C_2H_5OH.

TABLE 1

X-ray diffraction characteristics of the final products of FFS decomposition

SnO_2				ZrO_2				HfO_2			
d, Å	d, Å ASTM	I/I_0	I/I_0 ASTM	d, Å	d, Å ASTM	I/I_0	I/I_0 ASTM	d, Å	d, Å ASTM	I/I_0	I/I_0 ASTM
3.35	3.34	100	100	3.37	3.63	20	24	5.01	5.07	18	20
2.64	2.64	84	63	3.19	3.19	100	100	3.69	3.68	35	40
2.37	2.36	23	18	2.85	2.85	78	80	3.61	3.61	23	30
1.76	1.75	63	63	2.64	2.63	30	32	3.17	3.15	100	100
1.67	1.67	14	10	2.55	2.55	18	16	2.82	2.82	95	100
1.59	1.58	8	5	2.10	2.09	23	24	2.59	2.59	59	60
1.49	1.49	10	14	1.82	1.81	44	40	2.53	2.52	50	50
				1.71	1.70	20	20	2.33	2.32	45	50
				1.49	1.486	16	16	2.20	2.196	60	60
				1.43	1.426	14	16	2.17	2.171	30	30
								2.00	2.006	40	40
								1.90	1.981	56	60

Determining the quantitative chemical composition of the FFS of the composition $SnCl_2 \cdot 2H_2O$ – Hacac – C_2H_5OH dried at 333 K with the help of micro X-ray spectral analysis (MXSA) using Camebax Microbeam microanalyzer with the accelerating voltage of 20 keV we established that it is a mixture of two substances. Concentrations of tin and chlorine were locally calculated for different parts of the samples, mass %:

	Sn	Cl
Detected in FFS	52.49	34.75
	43.75	24.16
Calculated for $SnCl_2 \cdot 2H_2O$	52.59	33.46
Calculated for $SnHacacCl_2$	42.96	24.49

The results obtained demonstrate that $SnCl_2 \cdot 2H_2O$ and $SnHacacCl_2$ are present in the powder.

The presence of $SnCl_2 \cdot 2H_2O$ in the dried FFS is also confirmed by the XPA data. Analyzing the results of the quantitative MXSA of the dried FFS we may assume that the joint evaporation of ethanol and acetylacetone, as well as partial decomposition of the complex compound, accompanied by the loss of Hacac and the formation of $SnCl_2 \cdot 2H_2O$ occur in the heterogeneous system during drying the solution.

Thermogram of a mixture of $SnHacacCl_2$, $SnCl_2 \cdot 2H_2O$ points to three stages of decomposition (Fig. 3). The first one, accompanied by two endoeffects within the temperature range 323–473 K, is likely to be due to the evaporation of the complex and adsorbed ethanol molecules. The second stage (exoeffect at T = 473–593 K) corresponds to the decomposition of $SnHacacCl_2$ complex *via* removal of Hacac followed by oxidation. At the third stage, within

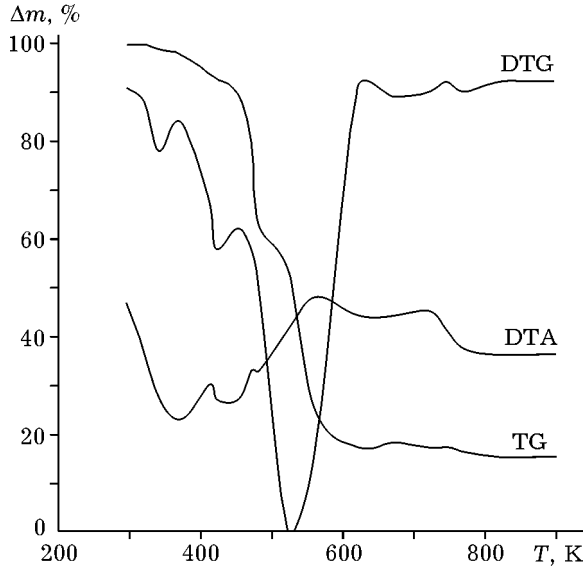

Fig. 3. Thermogram of the decomposition of dried FFS based on $SnCl_2 \cdot 2H_2O$ – Hacac – C_2H_5OH – HCl.

TABLE 2
Film properties

Composition	Refractive index n	Thickness d, nm	Adhesion force F, kg/mm^2
SnO_2	1.84	41.5	0.450
ZrO_2	2.14	65.7	0.801
HfO_2	2.12	58.9	0.765

temperature range 593–873 K, the formation of SnO_2 occurs as a result of $SnCl_2 \cdot 2H_2O$ decomposition to SnO. The latter is oxidized by the oxygen of air forming SnO_2 of rutile-type structure (according to the XPA data, see Table 1).

So, the results of XPA and thermal analysis of the dried FFS show that the final products of their thermal destruction at T = 873 K are zirconium and hafnium dioxides of the monoclinic modification and tin dioxide of rutile-type structure.

The films of zirconium, hafnium and tin dioxides were obtained by centrifuging with the FFS applied on single crystal silicon substrates at the centrifuging speed of rotation 2000–5000 rpm. The temperature of film formation (873 K) for the ZrO_2, HfO_2, SnO_2 films was chosen on the basis of thermal analysis of the dried FFS. It was established experimentally that it is necessary to anneal the films for 1 h in order to obtain stable film properties. Optical characteristics of the films were examined with LEF-3M ellipsometer, electrophysical parameters were measured with E7-8, E7-12 instruments; adhesion was measured with PMT-3 microhardness-meter. The obtained films were thermally stable, chemically inert, possessed good adhesion to silicon of KDB-20 grade (TP). Some properties of the films are shown in Table 2. The SnO_2 films exhibit semiconductor properties, electronic conductivity, and have resistance 10^6. The ZrO_2 and HfO_2 coatings are dielectrics.

The films obtained from FFS exhibit the properties not worse than those of the ZrO_2, HfO_2, SnO_2 films synthesized using other procedures.

CONCLUSIONS

1. Principal possibility to use ethanol solutions of the acetylacetonates of zirconium (IV), hafnium (IV) and tin (II) to obtain oxide films is demonstrated.

2. Optimal temperature and time modes (T = 873 K, τ = 1 h) of obtaining oxide coatings from FFS were determined.

3. The ZrO_2, HfO_2, SnO_2 films exhibiting high adhesion to the silicon substrate were obtained by centrifuging.

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