ISSN 0036-0236, Russian Journal of Inorganic Chemistry, 2009, Vol. 54, No. 5, pp. 658–663. © Pleiades Publishing, Inc., 2009.
Original Russian Text © V.V. Kozik, L.P. Borilo, and L.N. Borilo, 2009, published in Zhurnal Neorganicheskoi Khimii, 2009, Vol. 54, No. 5, pp. 717–722.

SYNTHESIS AND PROPERTIES OF INORGANIC COMPOUNDS

Synthesis and Characterization of ZrO_2 Thin Films

V. V. Kozik, L. P. Borilo and L. N. Borilo
Tomsk State University, Tomsk, Russia
E-mail: borilo@mail.ru

Received May 15, 2008

Abstract—Physicochemical processes involved in the preparation of zirconia thin films by sol–gel technology from film-forming solutions (FFSs) on the basis of zirconium oxochloride and ethanol were studied. The phase composition, structure, and properties of the films were determined.

DOI: 10.1134/S0036023609050027

Thin films are important for modern engineering. They are especially successful in rapidly developing electronic engineering, lighting engineering, and civil building. In Russia and other countries, many studies are underway directed to the design of new thin-film compositions, their characterization, and expansion of their application [1, 2]. Special attention is paid to thin-film materials based on Group III–V elements of the Periodic Table. Zirconia-based thin films have a high potential. Zirconia is transparent in the visible; it has high refractive index and bandgap values, good adhesion to substrates (glass, ceramics, silicon, polycor, and sapphire), thermal stability, and corrosion resistance. The synthesis and characterization of nanocrystalline zirconia-based powders prepared by various methods are found in periodicals [3–8]. Studies of ZrO_2 thin films are, however, few. Therefore, here we study the physicochemical processes involved in the preparation of ZrO_2 thin films on various substrates by sol–gel technology from film-forming solutions (FFSs) and the phase composition, structure, and properties of these films as dependent on the synthesis parameters.

EXPERIMENTAL

Thin films were prepared by sol–gel technology from FFSs. The FFSs were prepared from 96% ethanol and zirconium oxochloride $ZrOCl_2 \cdot 8H_2O$ (pure for analysis); the solution concentration was 0.4 mol/L. Films were prepared on glass, single-crystal silicon, quartz, polycor, and sapphire using centrifugation at 4000 rpm or pulling at 5 mm/s and subsequent heat treatment at 60°C for 30 min and at 600–1000°C for 1 h.

The film-forming power of solutions as a function of aging time was studied viscometrically on a glass capillary viscometer (the capillary diameter was 0.99 mm; temperature was 25°C). Reduced viscosity η_{sp}/c was determined as a function of zirconium oxochloride concentration by diluting the FFS with ethanol; oxochloride concentrations ranged within 0.5–3.3 g/dL. The concentration dependences were processed after Bogoslovskii et al. [9].

The thermolysis of the dried FFS was studied on a Q-1500 derivatograph (25–1000°C, calcined Al_2O_3 as reference, air, heating at 10 K/min, Alundum crucibles). A microbalance based on a quartz piezocrystal resonator was used in the thermoanalytical experiments; the weighing accuracy was 10^{-8} g [10]. IR absorption spectra were recorded for films on KBr substrates annealed at various temperatures within 400–4000 cm^{-1} on a Perkin-Elmer Spectrum One spectrometer. The composition of films was determined on a DRON-3M diffractometer (CuK_α radiation, $\lambda = 1.5418$ nm, Ni filter). The refractive index and film thickness were determined on an LEF-3M laser diffractometer. The optical parameters were calculated using the uniform nonabsorbing layer on an isotropic substrate model [11]. Reflection and transmission spectra in the visible and IR were recorded on SF-20 and Perkin-Elmer Spectrum One spectrometers. Dielectric constants were calculated by Kramers–Kroning relations from the reflection and transmission spectra. The bandgap width was calculated from the absorption edge position. Adhesion was determined by scleroscopy on a PMT-3 microhardness tester.

RESULTS AND DISCUSSION

The solutions from which thin films can be deposited by sol–gel technology should conform to several requirements. When precursors are dissolved in the solvent, some period is needed for so-called solution ripening or sol formation. This period ranges from several minutes to several days, depending on the precursor. At this stage, the true solution transforms to a colloidal one because of solvation, hydrolysis, complex formation, and condensation. The resulting associations are capable of being anchored to the surface when the solution is applied to the substrate.

We used viscosity as a measure of the film-forming power of the solution [12–14]. Solution viscosities were plotted as function of time and possibility of film preparation from these solutions. Our studies showed that a fresh zirconium oxochloride-based ethanolic solution has not film-forming properties. The film-forming ability appears 2–3 days after the solution was prepared. The solution viscosity increases strongly during this period because of the solvation of zirconium oxochloride and the formation of hydroxo complexes $[Zr_4(OH)_8(C_2H_5OH)_x(H_2O)_{16-x}]Cl_8$ [2–4]; as a result, a stable sol is formed in the solution. Good films with reproducible properties can be prepared if the solution viscosity reaches 2.3×10^{-3} Pa s.

The processes occurring in the FFS during storage and operation change the composition of the complex: the number of molecules of water of coordination decreases, more OH groups appear linked to zirconium, some water molecules are displaced from the inner coordination sphere, and the hydroxo cation charge decreases:

$$[Zr_4(OH)_8(C_2H_5OH)_x(H_2O)_{16-x}]Cl_8 \longrightarrow [Zr_4(OH)_{12}(C_2H_5OH)_x(H_2O)_{12x}]Cl_4 + 4HCl,$$

$$[Zr_4(OH)_{12}(C_2H_5OH)_x(H_2O)_{12-x}]Cl_4 \longrightarrow [Zr_4(OH)_{16}(C_2H_5OH)_x(H_2O)_{8-x}] + 4HCl,$$

$$[Zr_4(OH)_8(H_2O)_{16-x}(C_2H_5OH)_x]^{8+} \longrightarrow [Zr_4(OH)_{8+y}(H_2O)_{16-x-y}(C_2H_5OH)_x]^{(8-y)+} + yH^+.$$

As a result, the system loses stability because of coagulation, and the solution viscosity increases dramatically and exceeds 3.5×10^{-3} Pa s. The films prepared from such solutions have nonuniform thicknesses and low refractive indices. Thus, the film-forming properties of the solution (the ability to form films) exist within a limited period time, namely, while the solution is ripening and aging. The optimal viscosities of zirconium oxochloride-based solutions for preparing ZrO_2 films are $(2.3 \text{ to } 3.5) \times 10^{-3}$ Pa s.

The zirconium oxochloride-based FFS being a solution based on a polymeric hydroxo complex, Kolen'ko et al.' approach [8] is suitable for the quantitative description of colloid interactions in this solution. In this context, we studied the viscosity of the zirconium oxochloride-based FFS as a function of dilution and calculated the covalent and electrostatic terms of the Gibbs free energy of mixing. To describe reduced viscosity η_{sp}/c as a function of concentration, we used a linear extrapolation equation, namely, Huggins's equation

$$\eta_{sp}/c = [\eta]a + k'[\eta]^2c, \quad (1)$$

and nonlinear extrapolation equations, namely,

$$\eta_{sp}/c = a + b\exp(-dc), \quad (2)$$

$$\eta_{sp}/c = a + b_1\exp(-d_1c) + b_2\exp(-d_2c). \quad (3)$$

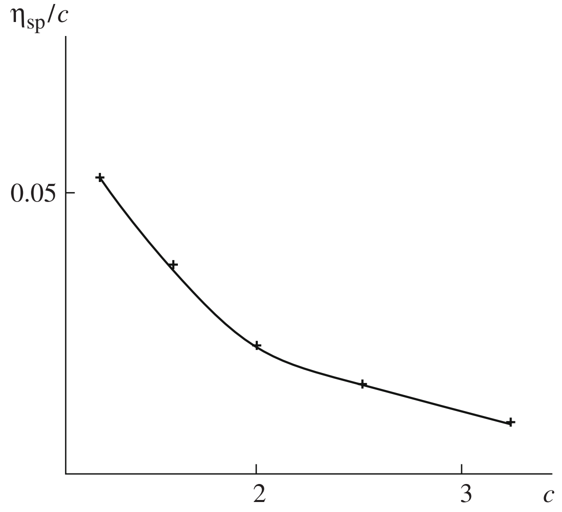


Fig. 1 Reduced viscosity η_{sp}/c for the zirconium oxochloride-based FFS vs. zirconium oxochloride concentration c (g/dL).

Here, a, b_i, and d_i are empirical solvation factors, which depend on the dipole moment, donor and acceptor numbers of the solvent and have the dimension of the molar volume. Various functions for the description of empirical reduced viscosity versus temperature dependences give numerical values of the characteristic viscosity η. Variation in reduced viscosity of the zirconium oxochloride-based FFS (Fig. 1) can be described by Eqs. (1)–(3). For this solution, we calculated the Huggins constant k' and characteristic viscosity from these three equations (Table 1).

The Huggins constant has a negative value ($k' = -2.41$). Probably, this is explained by the effect of hydrogen bonds, which are ignored by the Huggins theory. Comparing the variance and correlation coefficients for the three equations, Eq. (3) most adequately describes the experimental dependence in question; the reliable characteristic viscosity value is 0.102 dL/g. Table 2 lists the solvation energies (in kJ/mol) for the tested FFSs derived from η according to Eq. (3). In solutions containing zirconium oxochloride, there are insignificant electrostatic interactions ($\Delta G_a = 3.5$ kJ/mol) and specific donor–acceptor interactions ($\Delta G_{b1} = -3.64$ kJ/mol, $\Delta G_{b2} = 2.60$ kJ/mol). This is due to the high propensity of zirconium to form bulky polymeric complex structures; these structures, which have high characteristic

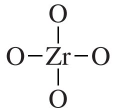
Table 1. Viscometric parameters of the zirconium oxochloride–based FFS (calculated from Eqs. (1)–(3))

Equation	[η], dL/g	k'
(1)	0.059	–2.41
(2)	0.137	–
(3)	0.102	–

Table 2. Worksheet for the calculation of solvation energies

a	b_1	b_2	ΔG_a,	ΔG_{b1}	ΔG_{b2}	d_1	d_2	$[\eta]$, dL/g	ΔG_{mix}, kJ/mol
			kJ/mol						
0.145	–0.150	0.107	3.5	–3.64	2.60	0.063	0.686	0.102	2.46

Table 3. Assignment of IR bands for films and powders annealed at various temperatures

Vibrations	Annealing temperature, °C					
	25	50	100	175	300	450
Stretching vibrations of O–H	3350 –	3340 –	3330 _3350_*	3340 *3370*	3330 *3340*	No *3370*
Bending vibrations of O–H in H_2O	1625, 1635 –	1625, 1635 –	1620, 1635 *1635*	1635 *1635*	No *1610*	No *1625*
Bending vibrations of Zr–O–H	1540, 1575 –	1505, 1540 –	1535, 1560 *1575*	1505, 1540 *1560*	1540 *1540*	No *1540*
 $O-\underset{\underset{\textstyle O}{|}}{\overset{\overset{\textstyle O}{|}}{Zr}}-O$	– –	– –	– *Unobserved*	– *Unobserved*	870 *Unobserved*	870 *860*
Zr–O in the ZrO_2 lattice	– –	– –	–	584 –	584 –	584 470
Vibrations in Zr–O–Zr	610, 620 –	610 –	610, 620 *625*	620 *620*	615 *630*	*Unobserved* *630*

* Data for the dry residue of the FFS are in italics.

viscosities, are responsible for the good film-forming properties of alcoholic solutions of zirconium oxochloride.

We used a set of mutually supplementing methods to study the physicochemical processes involved in the formation of thin films and powders of zirconia from the FFS during heat treatment. Our studies showed that the powder prepared from the zirconium oxochloride–based FFS is thermolyzed differently than $ZrOCl_2 \cdot 8H_2O$.

$ZrOCl_2 \cdot 8H_2O$ is thermolyzed as follows:

$$ZrOCl_2 \cdot 8H_2O \xrightarrow{40\text{–}80^\circ\text{C}} ZrOCl_2 \cdot 5H_2O \xrightarrow{80\text{–}110^\circ\text{C}} ZrOCl_2 \cdot 4H_2O \xrightarrow{110\text{–}130^\circ\text{C}} Zr(OH)_2 \cdot 0.7H_2O \xrightarrow{400\text{–}480^\circ\text{C}} ZrO_{2(\text{amorph.})}.$$

The thermolysis of the powder prepared from the FFS differs in that it contains the product of zirconium oxochloride thermolysis:

$$[Zr(OH)_2(C_2H_5OH)_x(H_2O)_{4-x}]Cl_2 \xrightarrow{110\text{–}200^\circ\text{C}} Zr(OH)_4 \cdot 2H_2O \xrightarrow{250\text{–}350^\circ\text{C}} ZrO_2 \cdot H_2O_{(\text{amorph.})} \xrightarrow{450\text{–}720^\circ\text{C}} ZrO_{2(\text{cub.} + \text{tetrag.})} \xrightarrow{720\text{–}790^\circ\text{C}} ZrO_{2(\text{monocl.})}.$$

ZrO_2 film formation is a more intricate process, as shown by piezocrystal weighing, IR spectroscopy, and X-ray powder diffraction. This process has the following distinguishing feature: when the solution is applied to the substrate, chloride ions remain in the solution and are not contained in the thin FFS layer on the substrate surface. The solution is anchored to the substrate via the interaction of zirconium hydroxo complexes with the surface hydroxide groups of the substrate as a result of hydrolysis. Schematically, subsequent dehydration in a thin layer can be represented as follows:

$$[Zr(OH)_2(C_2H_5OH)_x(H_2O)_{4x}](OH)_2 \xrightarrow{25\text{–}125^\circ\text{C}} Zr(OH)_4 \cdot 4H_2O \xrightarrow{125\text{–}230^\circ\text{C}} Zr(OH)_4 \cdot 2H_2O \xrightarrow{230\text{–}300^\circ\text{C}} Zr(OH)_4 \cdot H_2O \xrightarrow{300\text{–}355^\circ\text{C}} ZrO_2 \cdot H_2O \xrightarrow{355\text{–}375^\circ\text{C}} ZrO_{2(\text{amorph.})} \xrightarrow{375\text{–}400^\circ\text{C}} ZrO_{2\,(\text{cub.})}.$$

The IR spectra of a freshly applied film contain peaks corresponding to zirconium hydroxide and physisorbed water (Table 3). Film adhesion to the substrate is low; the refractive index is about 1.6, which is not characteristic of zirconia (Fig. 2). The refractive index of the film systematically increases during heat treatment as temperature increases, while the film thickness decreases to reach a steady-state value at 400°C (Fig. 2). The values of 2.0–2.1 for the refractive index mean that the film composition corresponds to zirconia.

In cases where a powder is formed, zirconia crystallization is observed above 450°C and accompanied by two exotherms, at 480 and 720°C. The former is due to the transition of the amorphous phase to the cubic and tetragonal phases; the latter, to the transition to the monoclinic phase. In cases where a film is formed (with thicknesses up to 100 nm), X-ray powder diffraction detects cubic ZrO_2 even at 400°C. This correlates with the Ostwald phase rule, which says that the phase with the lowest thermodynamic stability is the first to crystallize [4]. IR spectra show that the absorption bands associated with the vibrations of water and OH groups disappear as temperature elevates. Table 3 makes it clear that dehydration is accompanied by polymerization and the formation of infinite –Zr–O–Zr– chains whose vibration frequency is about 610–620 cm^{-1}. About ~400°C, the film is restructured to a regular crystal structure. This is made clear by the disappearance of the bands associated with the vibrations of chains and the appearance, instead, of the vibrations of ZrO^{4+} tetrahedra at 870 cm^{-1}.

The dehydration character is also revealed by the activation energies and orders of reactions for these stages calculated after Metzer and Horowitz [15] (Table 4). The activation energy of the initial stage does not exceed 70 kJ/mol; such values imply that the products are desorbed from the surface. The order of reaction at this stage for films is less than unit; therefore, diffusion processes are dominant. The activation energies of subsequent stages (100–200 kJ/mol) are indicative of the occurrence of chemical processes; the order of reaction is about unity or higher. The examination of the data in Table 4 makes it clear that processes in a thin layer occur at lower temperatures. The activation energies of stages in thin films are lower than in disperse powers. The rate-controlling stage of oxide formation in thin layers is also different, first, because of an insignificant diffusion retardation in thin layers and, secondly, because of a specific condition of the thin surface film and the influence of the surface energy of the substrate on kinetic parameters.

One important feature of thin films is the dependence of their fundamental properties not only on the composition but also on the physicochemical parameters of the substrate material. The films on glass or amorphous quartz have the lowest refractive indices because they are amorphous on these substrates. On polycrystal (polycor) and single-crystal (quartz) substrates, films in part contain a crystalline phase and an amorphous phase, depending on their formation temperature. At high annealing temperatures, polycrystalline films are formed on such substrates, as verified by their higher electrical conductivities and refractive indices [16].

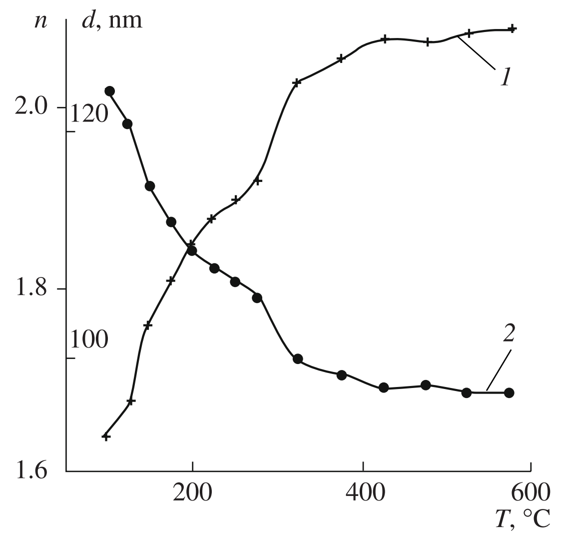


Fig. 2. (*1*) Refractive index and (*2*) thickness vs. temperature for ZrO_2 films.

The films in our experiments have good adhesion to glass, quartz, silicon, polycor, and sapphire substrates. These films are insulators with a high bandgap width. Table 5 compiles selected physicochemical properties of the films.

CONCLUSIONS

Zirconia thin films with thicknesses of 40–120 nm on glass, single-crystal silicon, quartz, polycor, and sapphire substrates have been prepared from zirconium oxochloride and ethanol FFSs. The physicochemical processes involved in film formation and the phase composition and properties of the films have been studied. The film-forming power of the FFS is controlled by the formation of zirconium hydroxo complexes in the solution; the optimal viscosities of FFSs for the deposition of quality films are within $2.3–3.5 \times 10^{-3}$ Pa s. Thermally induced zirconia formation occurs in several stages involving removal of solvolysis products and ZrO_2 crystallization. The films prepared on glass or quartz substrates are amorphous; those on silicon, poly-

Table 4. Kinetic parameters of stages in the formation of zirconia films and powders

Parameter	Film	Powder
Temperature range, K	25–125	–
Relative process rate, g/min	3.1	–
Activation energy, kJ/mol	36	–
Order of reaction	0.7	–
Temperature range, K	125–230	110–200
Relative process rate, g/min	2.9	7.8
Activation energy, kJ/mol	54	66
Order of reaction	1.1	2.2
Temperature range, K	230–300	–
Relative process rate, g/min	2.6	–
Activation energy, kJ/mol	89	–
Order of reaction	0.7	–
Temperature range, K	300–355	250–350
Relative process rate, g/min	3.9	6.3
Activation energy, kJ/mol	130	157
Order of reaction	1.7	1.7
Temperature range, K	355–375	450–720
Relative process rate, g/min	2.4	7.1
Activation energy, kJ/mol	119	200
Order of reaction	0.9	1.8

Table 5. Physicochemical properties of ZrO_2 films

Film thickness, nm	40–120
Refractive index	1.85–2.08
Dielectric constant	4.0
Bandgap width, eV	5.1
Adhesion strength, MPa	0.93

cor, or sapphire have a crystal structure depending on the annealing temperature and film thickness. The resulting ZrO_2 films have high refractive indices, are insulators, and have good adhesion to substrates.

REFERENCES

1. V. I. Vereshchagin, V. V. Kozik, L. P. Borilo, et al., *Polyfunctional Inorganic Materials Based on Natural and Artificial Compounds* (Izd-vo Tomsk. Univ., Tomsk, 2002) [in Russian].
2. L. P. Borilo, *Thin-Film Inorganic Nanosystems* (Izd-vo Tomsk. Univ., Tomsk, 2003) [in Russian].
3. V. F. Petrunin, V. V. Popov, Khunchzhi Chzhu, and A. A. Timofeev, Neorg. Mater. **40** (3), 303 (2004).
4. N. A. Shabanova, V. V. Popov, and P. D. Sarkisov, *Chemistry and Technology of Nanodisperse Oxides* (Akademkniga, Moscow, 2006) [in Russian].
5. N. N. Oleinikov, I. V. Pentin, G. P. Murav'eva, and V. A. Ketsko, Zh. Neorg. Khim. **46** (9), 1413 (2001) [Russ. J. Inorg. Chem. **46** (9), 1275 (2001)].
6. V. I. Pentin, N. N. Oleinikov, G. P. Murav'eva, et al., Neorg. Mater. **38** (10), 1203 (2002).
7. L. G. Karakchiev, E. G. Avvakumov, O. B. Vinokurova, et al., Zh. Neorg. Khim. **48** (10), 1589 (2003) [Russ. J. Inorg. Chem. **48** (10), 1447 (2003)].
8. Yu. V. Kolen'ko, A. A. Burukhin, and B. R. Churagulov, Zh. Neorg. Khim. **47** (11), 1755 (2002) [Russ. J. Inorg. Chem. **47** (11), 1609 (2002)].
9. A. Yu. Bogoslovskii, E. G. Pribytkov, and G. A. Teren'eva, Zh. Prikl. Khim. **71** (2), 294 (1998).
10. V. V. Serebrennikov, G. M. Yakunina, V. V. Kozik, and A. N. Sergeev, *Rare-Earth Elements and Their Compounds in Electronic Engineering* (izd-vo Tomsk. Univ., Tomsk, 1980) [in Russian].
11. B. M. Komranov and B. A. Shapochnykh, *Measurements of Parameters of Optical Coatings* (Mashinostroenie, Moscow, 1986) [in Russian].
12. L. P. Borilo, V. V. Kozik, N. A. Skorik, and V. V. Dyukov, Zh. Neorg. Khim. **40** (10), 1596 (1995).
13. R. V. Gryaznov, L. P. Borilo, V. V. Kozik, and A. M. Shul'pekov, Neorg. Mater. **37** (7), 828 (2001).
14. V. V. Kozik, L. P. Borilo, and A. M. Shul'pekov, Zh. Prikl. Khim. **73** (11), 1872 (2000).
15. M. B. Fialko, *Nonisothermal Kinetics in Thermal Analysis* (Izd-vo Tomsk. Univ., Tomsk, 1981) [in Russian].
16. V. V. Kozik, A. M. Shul'pekov, and L. P. Borilo, Izv. Vyssh. Uchebn. Zaved., Fiz., No. 12, 77 (2002).