Physicochemical Processes of Formation and Properties of Thin-Film Materials Based on the Oxides of Zirconium and of the Elements of Iron Triad

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Abstract

Thin-film materials based on zirconium dioxide and the oxides of iron triad elements are obtained. Physicochemical processes of their formation are investigated. It is stated that the films are dielectrics with large refractive index (2.0–2.2), high mechanical and chemical stability, high thermal stability; they absorb radiation in the UV and visible spectral regions. The obtained materials can be used as decorative, sunscreen coatings.

INTRODUCTION

Thin-film coatings are widely used in modern science and technology. Many investigations into physicochemical processes of formation and into the properties of thin films are performed in our country and abroad [1]. Special attention is paid to thin-film coatings based on binary and ternary systems of the oxides of elements of II, IV groups of Mendeleev's Periodic Table [2]. Films based on zirconium dioxide are used as optical filters for UV, visible and IR spectral regions due to large refractive index and wide forbidden band, elevated chemical and thermal stability, good adhesion. Zirconium dioxide doping with the oxides of iron triad elements allows varying optical characteristics of the films. Small width of forbidden band of the mentioned oxides (<2 eV) provides good adsorption of IR radiation.

The goal of the present investigation was to study physicochemical processes of formation and to examine the properties of thin films based on the oxides of zirconium of and iron triad elements.

EXPERIMENTAL

The films were obtained by precipitation from alcohol film-forming solutions (FFS) of zirconium oxochloride, chlorides of iron (III), cobalt (II), nickel (II) on glass and quartz substrates by centrifuging at the temperature of 25 °C and the substrate rotation frequency of 500–4000 rpm. The total concentration of salts calculated for oxides was 0.4 mol/l; the molar fraction of the oxides of iron triad elements in the films was varied within the range of 0–100 %. Preliminary treatment was performed at 50 °C, and subsequent treatment at 50–800 °C. Differential thermal analysis was carried out with Q1500 instrument (Paulic–Paulic–Erdey), X-ray phase analysis was performed with DRON-3 diffractometer. Kinetic parameters were calculated according to Erofeev – Kolmogorov procedure. Optical characteristics of the films were studies with LEF-3M laser ellipsometer and Specord-M 40 spectrophotometer.

RESULTS AND DISCUSSION

The main processes involved in the formation of films from FFS based on zirconium oxochloride are: removal of solvent and adsorbed water, consecutive dehydration of zirconium hydroxide, formation of the crystal structure of the film [3]. The decomposition of dried FFS based on zirconium oxochloride and iron chloride is described in [4]. Thermolysis of the initial iron chloride $FeCl_3 \cdot 6H_2O$ occurs in 3 stages; similar processes take place in FFS, where the temperature range of the stages is shifted to lower temperatures. This is explained by the formation of a solvate due to the substitution of part of the coordinated water by alcohol, which is removed easier than water. Thermal decomposition of cobalt chloride $CoCl_2 \cdot 6H_2O$ (up to 140 °C) results in the formation of anhydrous chloride; water loss occurs in 4 stages. Thermolysis of the dried FFS on this basis occurs in 3 stages. Unlike for the decomposition of salt, the shift of the processes to higher temperature range and the decrease in activation energy are observed for the dry residue of this FFS. This may be due to the change in the inner coordination sphere of cobalt cation. The removal of the solvent and adsorbed water, consecutive dehydration of zirconium hydroxide, thermolysis of the salts of iron triad elements are accompanied by an increase in the film density and an increase in the refractive index (Fig. 1).

The results of X-ray diffraction analysis show that the films, depending on obtaining conditions, can have single-phase structure (cubic, tetragonal, monoclinic modifications of ZrO_2), or can contain a mixture of cobalt, nickel or iron oxides with different modifications of

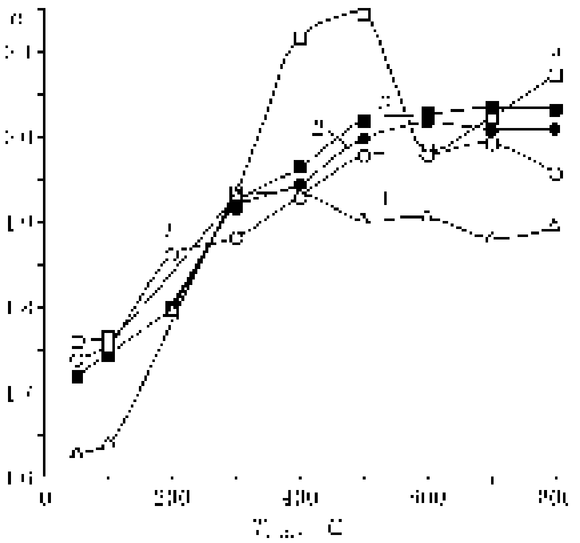

Fig. 1. Effect of annealing temperature on refractive index of the films of zirconium and cobalt oxides. Molar fraction of cobalt oxide, %: 0 (*1*), 10 (*2*), 20 (*3*), 60 (*4*), 80 (*5*).

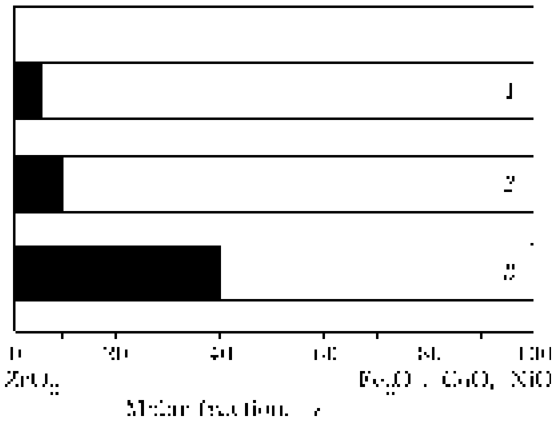

Fig. 2. Region of the existence of cubic modification of ZrO_2 in the systems: ZrO_2–NiO (*1*), ZrO_2–CoO (*2*), ZrO_2–Fe_2O_3 (*3*).

ZrO_2. A solid solution based on the cubic modification of ZrO_2 is formed in the region with high zirconium oxide content. With an increase in the content of the oxides of iron triad elements, the cubic modification is gradually replaced by tetragonal or monoclinic one. In the region of low ZrO_2 content, in addition to the solid solution, oxides are formed additionally: of iron (Fe_2O_3), cobalt (Co_2O_3 or Co_3O_4), or nickel (NiO). In the row Fe–Co–Ni, the region of the existence of fcc structure narrows. This is connected with the decrease of ion radius in this row (Fig. 2), which leads to even more substantial decrease in the mean ion radius of the cation sublattice and to a decrease in the stability of ffc structure of zirconium dioxide.

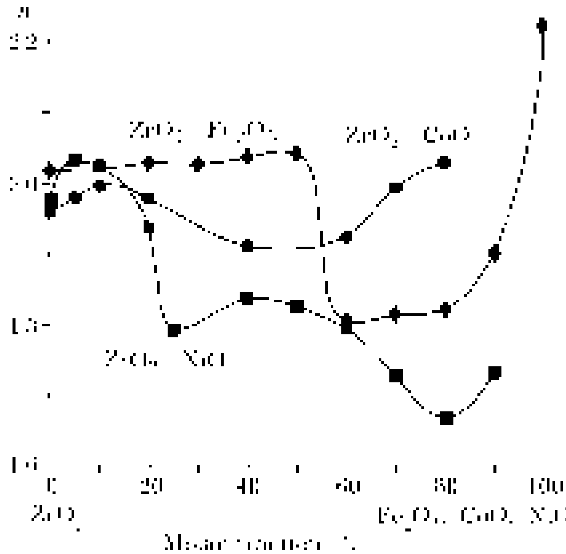

Fig. 3. Diagram: composition – refractive index.

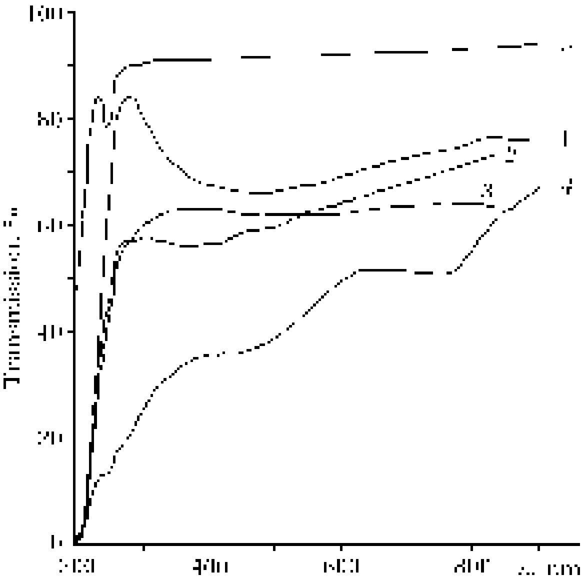

Fig. 4. Transmission spectra of the films obtained on quartz substrates. Molar fraction of cobalt oxide, %: 0 (*1*), 20 (*2*), 30 (*3*), 50 (*4*), *5* – substrate.

As a rule, the cubic modification of ZrO_2, obtained by means of sol-gel technology, is metastable and transforms at increased temperature into monoclinic or tetragonal modification [5].

In the system ZrO_2–Fe_2O_3, in the region of the stability of solid solution of fluorite structure (molar fraction of Fe_2O_3: 0–40 %), the refractive index of the film increases with increasing iron oxide content; in the systems ZrO_2–CoO, ZrO_2 – NiO the refractive index decreases with increasing content of the corresponding oxides (Fig. 3) [6, 7]. This can be connected with the difference in the polarizing ability of the cations Fe^{3+}, Co^{2+}, Ni^{2+}. Examination of transmission spectra of the resulting films within the range of 200–900 nm shows that they absorb in the UV and visible regions of the spectrum. In the case if film composition corresponds to the region of solid solutions based on ZrO_2, the film absorbs light only in the UV region. An increase in the content of the oxides of iron triad elements slightly shifts the edge of absorption to longer wavelengths. This can be observed for the films in the system ZrO_2–CoO as an example (Fig. 4). The release of an oxide of iron triad element as a separate phase leads to the appearance of absorption not only in the UV but also in the visible region; this absorption increases with increasing content of these oxides. Thus, the properties of the obtained films depend on the nature of components and on phase composition.

Thin films based on zirconium dioxide and the oxides of iron triad elements are dielectrics with the large refractive index (2.0–2.2), high mechanical and chemical stability, thermal stability. The investigated films absorb radiation in the UV and visible spectral regions. Thus, thin-film coatings based on zirconium oxide and the oxides of iron triad elements can be used as decorative and sunscreen coatings.

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