

EMANATION THERMAL ANALYSIS STUDY OF A SOL–GEL PRECURSOR FOR SILICA–TITANIA WAVEGUIDES

V. Balek^{*1}, *Z. Málek*¹, *J. Šubrt*², *M. Guglielmi*³, *P. Innozenzi*³,
*V. Rigato*⁴ and *G. Della Mea*⁴

¹Nuclear Research Institute Řež plc, CZ-250 68 Řež, Czech Republic

²Institute of Inorganic Chemistry ASCR, 250 68 Řež, Czech Republic

³Department of Mechanical Engineering, University of Padova, 35131 Padova, Italy

⁴I.N.F.N., Legnaro National Laboratories, 35020 Legnaro, Italy

Abstract

Emanation Thermal Analysis (ETA) was demonstrated as a tool for the characterization of microstructure changes of a sol–gel precursor for silica–titania layers deposited on the glass plate to be used as planar waveguides. Temperature ranges of 280–330 and 380–500°C, respectively, in which the densification of the layers took place, were determined by ETA under in situ conditions of the sample heating. Results of thermogravimetry were compared with the ETA data.

Keywords: densification, emanation thermal analysis, planar waveguides, silica–titania layers, sol–gel

Introduction

By means of the sol–gel technique the silica based planar waveguides with low losses were prepared. When using the sol–gel processing the refractive index may be controlled by the composition of the starting solution of titanium alkoxides and other suitable precursors [1–3]. SiO₂–TiO₂ sol–gel films have been widely used as planar waveguides because of the easy tunability of the refractive index and losses lower than 1 dB cm⁻¹ [4].

In the preparation of planar waveguides deposited on the substrate by the sol–gel technique, the thermal treatment of the intermediate products is frequently used with the aim to obtain well-consolidated (dense) layers. Methods making possible to characterize the microstructure evolution of coatings are, therefore, of interest in this field.

In this study the emanation thermal analysis (ETA) [5–7] was used to characterize the microstructure development of the sol–gel silica titania layers to be used as optical waveguides. In our previous studies the ETA was already applied to characterize the thermal behavior of titania based materials as powders [8] and sol–gel prepared thin films [9]. This method monitored the development of surfaces and sub-surfaces microstructure during the preparation of adsorbents and catalysts on heating

* Author for correspondence: E-mail: bal@ujv.cz

their precursors, such as metal hydroxides, e.g. aluminium hydroxide (gibbsite) [10] or double layer hydroxides (like hydrotalcite) [11].

Experimental

Preparation of samples

The sol-gel method was used for the fabrication of planar optical waveguides on soda lime glass plate. We obtained the films for this application from an ethanol solution of $\text{Si}(\text{OC}_2\text{H}_5)_4$ and $\text{Ti}(\text{OC}_4\text{H}_9)_4$ with water for the hydrolysis reaction ($\text{H}_2\text{O}/\text{TEOS}=2$) and hydrochloric acid as a catalyst ($\text{HCl}/\text{TEOS}=0.01$). Titanium oxide is used to obtain a final film with a refractive index higher than that of the substrate. The nominal molar composition used is 70% silica and 30 % titania, in order to have a refractive index of about 1.7. The concentrations of the final oxides in solutions were 50 or 100 g L^{-1} . The solution also contained acetylacetone to stabilize the $\text{Ti}(\text{OC}_4\text{H}_9)_4$ in the solution. After the deposition by dipping at a temperature of 30°C and 40% humidity, the films were dried at 60°C.

Films deposited by the dip coating and dried at 60°C were labelled by the radionuclides [7] for the ETA measurements. The TG measurements were performed using the powders obtained for the solutions poured into Petri dishes and maintained in a thermostatic chamber for 1 day at 60°C.

Methods

Thermogravimetry (TG) measurement was performed in air at the heating rate of 10°C min^{-1} using the Netzsch STA 409/429 analyzer. ETA and DTA measurements were carried using the Netzsch DTA-ETA 409 analyzer.

Taking into account that the ETA is non common method, the background information necessary for the description and interpretation of the ETA results are presented. The emanation thermal analysis (ETA) [5, 6] consists in the measurement of radon release rate from the samples previously labeled. Atoms of radon ^{220}Rn are formed by the spontaneous α -decay of ^{228}Th and ^{224}Ra according to the scheme:



The thorium nuclide ^{228}Th used for labeling samples to be tested, has a suitable half-life (1.9 years) to serve as a quasi-permanent source of radon ^{220}Rn (half-life 55 s). The half-life of ^{220}Rn ensures that the steady state between ^{224}Ra and ^{220}Rn is established within several min, which makes it possible to investigate even rapid changes in the solids and on their surface. Radon formed by the spontaneous α -decay of ^{228}Th and ^{224}Ra was incorporated to the depth of several tens of nanometers from the surface due to the energy (85 keV/atom) of recoiled atoms, as determined by Monte Carlo method using the TRIM code [12].

It was supposed that radon atoms can be directly released by recoil or trapped at the lattice defects, vacancy clusters, grain boundaries and pores. The defects in the solids can serve both as traps and diffusion paths for radon. As it follows from theo-

ries of diffusion and recoil processes [13], the radon release rate depends on the surface area of the solid-gas and solid-liquid interfaces, and on the radon diffusion parameters in the solid matrix.

The rate of radon release from the sample (called also the emanation release rate, E) can be expressed in a simplified way as follows:

$$E = E_{\text{recoil}} + E_{\text{diffusion}} = S[K_1 + (D/\lambda)^{1/2}K_2] \quad (1)$$

where E_{recoil} is the part of the radon release due to recoil, $E_{\text{diffusion}}$ is the diffusion part of the released radon, S is the surface area, K_1 is the temperature independent constant, proportional to the penetration depth of Rn recoiled atoms, D is the coefficient of radon diffusion in the sample, λ is the decay constant of Rn, K_2 is constant depending on temperature.

The release of radon atoms previously incorporated into the sample is measured, serving as a probe of microstructure. The increase in the radon release rate (E) indicates an opening of the structure and/or the increase of the surface area of the interfaces, whereas the decrease in E reflects a densification of the structure, closing pores and/or the decrease in the surface area of the interfaces.

Preparation of samples for ETA and radioactivity measurements

The samples for ETA measurements were labeled using adsorption of radionuclides of ^{228}Th and ^{224}Ra from acetone solution on the sample surface. The specific activity of the sample was 10^5 Bq g^{-1} . For one measurement approximately 0.1 g of the sample was used. The labeled samples were stored at least three weeks prior to the ETA measurements in dry condition to allow the radioactive equilibrium between the ^{228}Th and ^{224}Ra nuclides to be established. The layer of the maximum depth of 80 nm was labeled by ^{224}Ra and ^{220}Rn recoiled atoms as determined by TRIM code [12], whereas the remaining atoms of ^{228}Th were adsorbed on the sample surface, serving as a source of ^{224}Ra and ^{220}Rn .

Equipment for ETA

ETA equipment (Fig. 1) consists of the sample holder situated in a furnace, the detector of α -radioactivity, the counts-meter and the carrier gas system [7]. The sample was heated in the constant flow (50 mL min^{-1}) of air, which took the radon released from the sample into the measuring chamber of radon radioactivity.

The ETA results are presented as a temperature dependence of the radon release rate E (in relative units); $E = A_{\alpha}/A_{\gamma}$, where A_{α} is the alpha radioactivity of radon released in unit time from the labeled sample, and A_{γ} is the total gamma radioactivity of the labeled sample.

The A_{α} value is proportional to the rate of radon formation in the sample. Semiconductor and NaI (T_1) detectors were used for the α - and γ -radioactivity measurements, respectively.

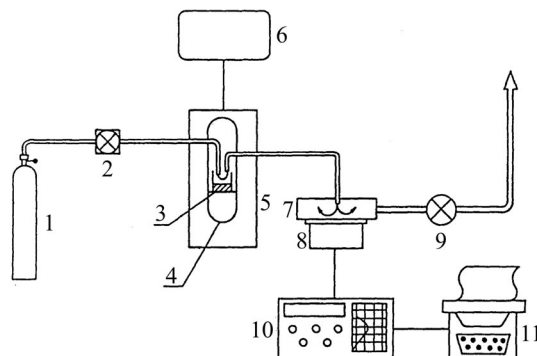


Fig. 1 Schematic diagram of the ETA apparatus; 1 – gas supply, 2 – gas flow stabilizer, 3 – labelled sample, 4 – sample holder, 5 – thermostat, 6 – temperature controller, 7 – measuring chamber, 8 – radioactivity detector, 9 – flow rate meter, 10 – counts-meter, 11 – data processor

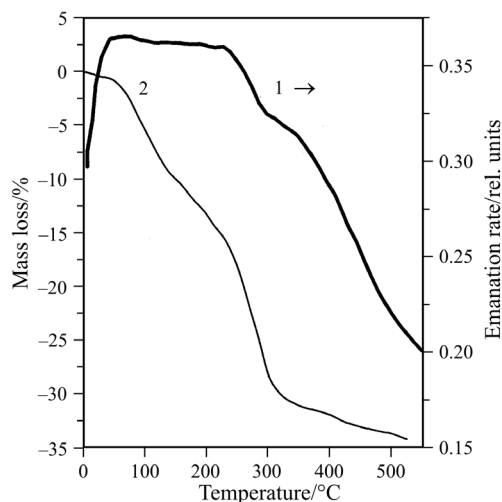


Fig. 2 Results of thermogravimetry (curve 1) and emanation thermal analysis (curve 2) obtained during heating of $\text{SiO}_2\text{-TiO}_2$ gels (70:30 mol) in air

Results and discussion

From the TG results measured on heating in air (Fig. 2, curve 1) it follows that the mass loss took place in several steps, namely:

- in the temperature range 60–130°C, which was ascribed to the release of water from the sample (this process was accompanied by the endothermal DTA effect with the maximum at 100°C),
- in the temperature range 150–310°C, ascribed to the combustion of the residual $-\text{O}-\text{C}_2\text{H}_5$ groups (being accompanied by the exothermal DTA effect with the maximum at 300°C),

- in the temperature range 320–470°C, ascribed to the combustion of the residual –O–C₄H₇ group (being accompanied by the DTA exothermal effect with the maximum 380°C) [14].

From the ETA results (Fig. 2, curve 2) following conclusions can be done regarding the microstructure development of the sample: in the range 60–90°C the increase of radon release rate indicated exposure of surface as the result of water release from the sample.

No changes of the sample microstructure were indicated in the range 100–270°C. In the range 280–330°C – can be considered as the 1st step of the densification of the silica–titania layer characterized by the decrease of the radon release rate E (after the combustion of the –O–C₂H₅). The temperature range 380–500°C – can be considered as the 2nd step of the densification of the layer characterized by the decrease of the radon release rate, E (after the combustion of –O–C₄H₉).

Consequently, the temperature of 500°C was recommended for the preparation of the consolidated sol–gel silica titania layer. The silica–titania planar waveguide (thickness 190 nm) obtained from the sol–gel precursor after heating to 500°C for 1 h was transparent and colorless.

Conclusions

The results of ETA made it possible to determine the temperature intervals where the densification of the sol–gel silica-titania layers took place during thermal treatment. The results of thermogravimetry supported the interpretation of the ETA results.

The ETA can be recommended as a suitable tool to characterize the microstructure development of the sol–gel layers (coatings) under in situ conditions of drying, heating and other technological treatment.

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