SPRAY-PYROLYSIS, DEEP- AND SPIN-COATING DEPOSITION OF THIN FILMS AND THEIR CHARACTERIZATION

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ABSTRACT

Short review is presented on the authors investigations on the application of spray-pyrolysis and deep- and spin-coating for the preparation of thin films from α-Fe₂O₃; Y₂O₃; CeO₂; La₂O₃; Y₂Fe₂O₇; Y₂Fe₂O₇; Ce; YFeO₃; yttria-stabilized zirconia (YSZ); YSZ:Pt; LaMnO₃; LaMnO₃:Ca; TiO₂; TiO₂:La₂O₃ and Ru(II) complex immobilized in Si-based matrix for microelectronics, photocatalysis and oxygen sensors. The stoichiometry, phase composition, crystal structure, morphology and some functional properties (magnetic, electrical, optical, photocatalytic, response to oxygen) are determined.

Keywords: citric complexes, deep-coating, spin-coating. Ru-complexes, spray-pyrolysis, sol-gel technology.

INTRODUCTION

The interest to non-vacuum methods for thin films deposition has increased in the last decade. The solution based processes have several advantages: simplicity of process, access to a wide range of metal oxide stoichiometries, precise composition control, applicability to substrates of any size. These peculiarities are rather important for some of the practical application of the layers, for example in the superconducting devices. Despite its limitations the spray pyrolysis method meets practically all of the requirements to the methods for films deposition on large substrate. Exact stoichiometry, phase homogeneity and high crystallinity are, in many cases, the crucial requirements to the films deposited. The polymerized complex method (PCM), a version of the sol-gel technology, proved itself as an effective method for production of mono- and polymetal oxides meeting these requirements. The method is based on the formation in ethylene glycol (EG) medium of complex(es) of the respective metal(s) with hydroxopolycarboxilic acid. It was shown that in number of systems mixed-metal citric complexes are formed thus ensuring mixing of the metals at atomic level and enhancing the final product formation [1]. The usage of non-aqueous medium is an additional advantage of the method when easily hydrolysable compound are used as metal source. In number of works which will be shortly reviewed in this paper it was proved that the EG or EG-water solutions of such complexes may be successfully used as starting material for spray-pyrolysis deposition of films.

The type of precursors cited above is only one type of the possible starting materials to be used in spray-
pyrolysis methods. We show that water- or organic solvents-suspensions are rather convenient for production of photocatalytically efficient TiO₂ coatings on different substrates.

On the other hand, the sol-gel technology can be successfully combined with other methods for films deposition such as deep- and spin coating. The methods are especially suitable for production of films from thermally unstable compounds and composites. The application of such procedures for Pt-doped YSZ and for Ru-complex immobilization in Si-based matrix, both used as oxygen sensors, will be shortly reviewed.

EXPERIMENTAL

1. Starting materials preparation. EG solutions of the citric complexes were prepared by addition of metal salt(s) or propoxide(s) to an EG solution of CA (or in some cases of tartaric acid, TA). The molar ratio metal(s):CA:EG=1:5:20 was set, strictly adjusting the desired ratio between metals when polymetal product was produced. Aqueous solution of YZr-citic complexes [2], water or methanol suspensions containing 1% of commercially available or preliminary mechaonactivated TiO₂, with addition (0.24%) of polyethylene glycol (PEG) 2000 (to improve film adhesion and to increase its porosity) were also used as starting material for spray pyrolysis.

Zr-Y-Pt sol for deep-coating production of YSZ:Pt was prepared by the method described in [3]. The luminesphore doped sol solutions were prepared by mixing Ru(II) tris (4,7-diphenyl, 1,10-phenantralene) dissolved in C₂H₅OH (2.5 g/dm³) with SiO₂ - sol, C₁₉H₄₀O₂Si (TEOS), C₁₉H₃₂O₂Si (MTEOS), C₁₄H₃₀O₂Si (Octyl-triEOS) were used as precursors.

2. Film deposition. The spray device shown in [4] with a diameter of the pneumatic nebulizer nozzle 0.7-1.0 mm (depending on the material viscosity) was used. The parameters of the process: the initial solution or suspension concentration, the flow rate of the pressurized O₂ (1.0 - 1.5 d/min) used as carrier gas, the angle of pulverization (30-60°, most often 45°), the temperature of the substrate heating (100-500 °C), the time of spraying (typically 30 s), the time intervals between consequent sprayings (30-300 s) and heating temperature during the intervals depend on the nature of the spraying material, the substrate and the final product and, rather strongly, on the film thickness desired. These parameters were optimized for every one of the systems studied. The films thickness is easily controlled by the number of sprayings.

The device shown in [5] was used for deep-coating deposition of Pt-doped YSZ [6] and for Ru(II)-complex immobilized in Si-based matrix films [7; S. Anastasova, M. Milanova, E. Kashchieva, D. Todorovsky, to be published]. Deep speeds between 0.2 and 0.4 mm/s and 1-7 number of immersion were applied.

The deposition of SiO₂/Ru(II) composites have been performed by means of Spin Coater KW-4A (Idex Corp., USA). Spinning speed of 2000-6000 rpm and cycle time of 20-60 s were used.

3. Post-deposition annealing. In some of the systems studied, films with a satisfactory crystal structure (Y₆Fe₂O₁₂, CeO₂) can be obtained in situ, i.e. in the course of the spray-pyrolysis deposition. In most of the cases additional heat treatment (at conditions defined accounting for the final product chemical nature) must be applied. The drying time for the SiO₂/Ru(II) composites depends on the nature of the Si-precursors used [7, 8].

The influence of combined laser-magnetic field post-deposition treatment of YFeO₃ and Y₆Fe₂O₁₂ films by Nd:YAG laser pulses (energy density 110 mJ/cm², 700 µs) and synchronized magnetic-field pulses (0.5 T, 900 µs) was also studied [8, 9].

4. Analysis and characterization. The thickness of the films was measured by a Talystep profilometer. The crystal structure, the stoichiometry, morphology and optical transparency of the films and metals oxidation state were determined. Some functional properties - magnetic (saturation and permanent magnetization and coercive force, photocatalytic properties (degradation of methylene blue, malachite green and phenol) and the response to O₂-content in the atmosphere were established for α-Fe₂O₃ and Y₆Fe₂O₁₂; TiO₂ and TiO₂/La₂O₃; YSZ and YSZ:Pt films, respectively.

RESULTS AND DISCUSSION

The films produced, the main characteristics of the initial materials preparation procedures, the deposition methods, the post-deposition treatment and the methods applied for films characterization are summarized in Table 1.

The stoichiometry of the polymetal samples correlates well with the composition of the initial solu-
Table 1. Deposition and characterization of thin films

<table>
<thead>
<tr>
<th>Compound</th>
<th>Method</th>
<th>Initial solution</th>
<th>Deposition</th>
<th>Characterization</th>
<th>Other parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Initial solution</td>
<td>Heating</td>
<td>Substrate</td>
<td>Post-deposition annealing</td>
</tr>
<tr>
<td>a-Fe_{2}O_{3}</td>
<td>spray-pyrolysis</td>
<td>FeCl_{3}, CA, EG, H_{2}O (30%)</td>
<td>60</td>
<td>30</td>
<td>silica</td>
</tr>
<tr>
<td>Y_{2}O_{3}</td>
<td>spray-pyrolysis</td>
<td>YNO_{3}·6H_{2}O, CA, EG</td>
<td>120</td>
<td>30</td>
<td>silica, β-quartz</td>
</tr>
<tr>
<td>CeO_{2}</td>
<td>spray-pyrolysis</td>
<td>Ce(NO_{3})<em>{3}, TiO</em>{2} or Ce(NO_{3})<em>{3}, 6H</em>{2}O, CA, EG</td>
<td>65</td>
<td>80</td>
<td>silica, β-quartz</td>
</tr>
<tr>
<td>YFeO_{3}</td>
<td>spray-pyrolysis</td>
<td>Y(NO_{3})<em>{3}·6H</em>{2}O, FeCl_{3}, CA, EG</td>
<td>90</td>
<td>30</td>
<td>silica</td>
</tr>
<tr>
<td>YFeO_{3}</td>
<td>spray-pyrolysis</td>
<td>Y(NO_{3})<em>{3}·6H</em>{2}O, FeCl_{3}, CA, EG</td>
<td>95</td>
<td>15</td>
<td>silica, YAG (100)</td>
</tr>
<tr>
<td>YSZ</td>
<td>spray-pyrolysis</td>
<td>Y(NO_{3})<em>{3}·6H</em>{2}O, ZrCl_{4}, CA, EG</td>
<td>120</td>
<td>30</td>
<td>silica, β-quartz, ESZ,</td>
</tr>
<tr>
<td>YSZ : Pt</td>
<td>spray-pyrolysis</td>
<td>Y(NO_{3})<em>{3}·6H</em>{2}O, ZrCl_{4}, H_{2}PtCl_{6}, CA, EG</td>
<td>120</td>
<td>30</td>
<td>silica, β-quartz, ESZ,</td>
</tr>
<tr>
<td>La_{2}O_{3}</td>
<td>spray-pyrolysis</td>
<td>La(NO_{3})<em>{3}·6H</em>{2}O, Ti(OH)_{4}, CA, EG</td>
<td>120</td>
<td>30</td>
<td>silica</td>
</tr>
<tr>
<td>La_{2}O_{3}</td>
<td>spray-pyrolysis</td>
<td>La(NO_{3})<em>{3}·6H</em>{2}O, MnCl_{2}·4H_{2}O, Ca(CH_{3}COO)<em>{2}·2H</em>{2}O, EG, CA</td>
<td>120</td>
<td>40</td>
<td>silica, β-quartz, SiO_{2}</td>
</tr>
<tr>
<td>CdSe</td>
<td>spray-pyrolysis</td>
<td>CdSe, EG, H_{2}O</td>
<td>-</td>
<td>-</td>
<td>silica, glass, YSZ on silica</td>
</tr>
<tr>
<td>TCO</td>
<td>spray-pyrolysis</td>
<td>La(NO_{3})<em>{3}·6H</em>{2}O, Al(NO_{3})<em>{3}·9H</em>{2}O, CA, EG</td>
<td>100</td>
<td>30</td>
<td>silica</td>
</tr>
<tr>
<td>SiO_{2}</td>
<td>spray-pyrolysis</td>
<td>SiO_{2}, H_{2}O</td>
<td>70</td>
<td>18</td>
<td>glass</td>
</tr>
<tr>
<td>SiO_{2}</td>
<td>spray-pyrolysis</td>
<td>SiO_{2}, H_{2}O</td>
<td>70</td>
<td>18</td>
<td>glass</td>
</tr>
</tbody>
</table>

1) Erbia stabilized zirconia 2) Polyvinyl alcohol
3) D. Todorovsky, R. Todorovska, M. Milanova, D. Kovacheva, to be published.
4) S. Anastasova, M. Milanova, E. Kashchieva, D. Todorovsky, to be published.

Some deviations were found in the preparation of YFeO_{3} and LaMnO_{3}:Ca films [12, 18]. The crystal structure is closed to that of the referent materials and is reached at temperatures usually slightly below the ones used at the preparation of the materials in bulk form by the same method. As a rule not less than 500 °C must be applied at post-deposition annealing to achieve complete burning of the organic components. Texturing is observed when single crystals substrates were used. The morphological grains size depends on the concentration of the initial solutions and the nature of the medium. Columnar structure is probably formed at Y_{3}Fe_{2}O_{12} deposition [13]. Very good magnetic properties are measured for this film and they can be influ-
enced by a post-deposition laser-magnetic field treatment [8]. TiO₂ coatings show satisfactory photocatalytic properties for degradation of dyes and phenol in wastewaters [19-22]. Doping with La₂O₃ increases the activity. The role of the preliminary mechanocatalytical activation of the TiO₂ on the photocatalytic efficiency is rather complicated [26]. Spray pyrolysis deposition of films with thickness above 1.5-2.0 µm requires more special deposition technology [15].

CONCLUSIONS

Uniform, stoichiometric, phase homogeneous films with good adhesion and thickness between 0.1 and 20 µm with controlled porosity are obtained from a number of uni- and polymetallocxides, CdSe and SiO₂-Ru(II) complex composite by combining PCM and spray pyrolysis or sol-gel technology and deep- or spin coating.

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REFERENCES