Hybrid sol-gel silica films with (TiO$_2$-CeO$_2$) binary nanopowders

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Abstract. In the present work the preparation of hybrid sol-gel silica coatings doped with binary TiO$_2$-CeO$_2$ nanopowders was studied. The oxide powder was embedded in the hybrid matrix either by in-situ generation or by previously prepared powder dispersion. The main objective of the work was to establish a correlation between the method of generation of the dopant particles in the system and the properties of the films. The films were deposited on silicon wafer and glass substrates by the ‘dip-coating’ method and characterized in the as-prepared stage and after annealing at 120 °C. The optical and morphological properties of the films deposited on glass and silicon wafer were determined by spectroscopic ellipsometry (SE) and atomic force microscopy (AFM).

1. Introduction

It is well known that hybrid coatings with complex compositions are usually prepared using several substituted siloxane precursors. The most common precursors for the hybrid films preparation include: phenyl-trimethoxysilane (PTMOS), methyltriethoxysilane (MTEOS), 3-glycidoxypropyl-trimethoxysilane (GPTMS), trimethoxysilyl-propyl-methacrylate (TSPM), methyImethacrylate (MMA) and methacrylic acid (MA) [1-10], as well as mixtures of organically substituted and un-substituted Si-alkoxides.

In this work, we used the sol-gel method approach to prepare hybrid coatings in the SiO$_2$-TiO$_2$-CeO$_2$ (abbreviated as SiTiCe) system.

The binary TiO$_2$-CeO$_2$ powder was selected for investigation taking into consideration its very good anticorrosive properties. The main objective was to establish a correlation between the method of embedment of the dopant particles in the system and the optical and morphological properties of the resulting films.

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2. Experimental

2.1. Film preparation
The system chosen consists of methyltriethoxysilane (MTEOS) as a SiO\textsubscript{2} matrix and TiO\textsubscript{2}-CeO\textsubscript{2} powder in a TiO\textsubscript{2}:CeO\textsubscript{2} = 4:1 ratio used as a dopant. The oxide powder was embedded in the hybrid material either by “in-situ generation” or by dispersion of powder previously prepared (“powder dispersion”). The thermal treatment of the coatings was realized at the low temperatures of 120 °C. In the case of “in situ” particles generation, the solution for the matrix was previously prepared and mixed with the solution containing the TiO\textsubscript{2} and CeO\textsubscript{2} precursors.

The preparation of the TiO\textsubscript{2}-CeO\textsubscript{2} powder was reported earlier [10]. Ti(iOPr\textsubscript{4}) (Aldrich) and Ce(NO\textsubscript{3})\textsubscript{3}.6H\textsubscript{2}O (Aldrich) as starting precursors in EtOH medium were used. The metal oxide powder preparation was achieved using an NH\textsubscript{4}OH NH\textsubscript{3} 25% aqueous solution. The resulting powder was filtered, washed with distilled water, dried in the oven for 48 h at 100°C and then annealed for 1 h at 400°C to eliminate the water and organic residues. In both cases, the solutions were prepared corresponding to the 90 mol% SiO\textsubscript{2} – 10 mol% (TiO\textsubscript{2}-CeO\textsubscript{2}) molar composition. From both type of solution prepared as mentioned above, thin films on glass and silicon substrates were deposited by “dip-coating” with a withdrawal rate of 5 cm/min. For all types of samples, a thermal treatment of 30 min at 120 °C with a heating rate of 1°C/min was applied for better film consolidation.

2.2. Characterization methods
The TiO\textsubscript{2}-CeO\textsubscript{2} powders were characterized by XRD and FTIR in the conditions mentioned before [10]. The optical and morphological properties of the films deposited on glass and silicon wafers were determined by spectroscopic ellipsometry (SE) and atomic force microscopy (AFM). The SE measurements were performed in a wide spectral range using Woollam equipment consisting of a VASE ellipsometer for the UV-VIS-NIR range. The AFM measurements were performed in order to examine the surface morphology by model EasyScan2 of Nanosurf® AG Switzerland.

3. Results and discussion
Under the experimental conditions mentioned above, quasi-crystalline powder with anatase structure was obtained, as illustrated by the XRD and FT-IR spectra presented in figure 1.

![Figure 1. XRD (a) and FT-IR (b) spectra of TiO\textsubscript{2}-CeO\textsubscript{2} powder.](image)

The AFM images of coatings deposited on glass and silicon substrates before and after thermal treatment show adherent, homogeneous, continuous and smooth films, as presented in figure 2. It could be observed that SiTiCe films deposited on glass (figure 2, a-d) generally exhibit higher roughness values as compared to those on silicon (figure 2, e-h). In the case of glass substrates, higher roughness is obtained for the coatings prepared by “powder dispersion” in comparison with the films prepared by “in-situ generation”. This could be due to the nanopowder agglomeration in the hydrophobic hybrid SiO\textsubscript{2} matrix. A more uniform morphology is observed for the films deposited on silicon by the “in situ” method (figure 2, e and f) as compared with those deposited by “powder dispersion” (figure 2, g and h). For the films deposited on silicon substrates, the roughness remains rather low, less than 8 nm.
Figure 2. AFM images showing 3D topographic view of the SiTiCe films deposited on glass (a-d) and silicon (e-h); below each image the RMS roughness values and method of added powders are presented. TT means thermally treated films. Images from the left columns (a, b, e and f) were obtained using “in situ” procedure, while those in the right columns (c, d, g and h), by the “powder dispersion” method.

Figure 3. Refractive indices of the coatings deposited on: (a) glass and (b) silicon.

| Substrate | Sample          | d_{SiTiCe} (nm) | E_g (eV) |
|-----------|-----------------|----------------|----------|
| Si        | SiTiCe_in-situ  | 50.35          | 3.71     |
|           | SiTiCe_in-situ_TT | 48.90          | 3.62     |
|           | SiTiCe_powder   | 2.26           | 3.80     |
|           | SiTiCe_powder_TT | 3.12           | 4.23     |
| Glass     | SiTiCe_in-situ  | 57.62          | 2.98     |
|           | SiTiCe_in-situ_TT | 51.54          | 2.97     |
|           | SiTiCe_powder   | 87.02          | 3.38     |
|           | SiTiCe_powder_TT | 89.24          | 3.53     |

The analysis of the experimental SE data used the following model: substrate (glass or silicon) / Si-Ti-Ce film / roughness. In the case of films deposited on silicon, an interfacial layer composed by native SiO_2 (2-3 nm thick) was added. The SiTiCe film thickness and optical band gap of the films deposited on glass and silicon substrates are presented in the table 1, while the refractive index dispersion is presented in figure 3. It can be seen that: the thickness and the refractive index of the films studied depend on the preparation method and on the type of substrate used; the films deposited by “powder dispersion” exhibit the highest thickness differences between the coatings deposited on silicon and those on glass, due to their low adherence to the Si substrate; no significant differences in the optical and microstructural properties of the films were noticed after thermal treatment, except for the
coatings deposited on Si by “powder dispersion”; the optical band gap energy ($E_g$) increases after thermal treatment for the samples prepared by “powder dispersion”.

Conclusions
Sol-gel coatings of the SiO$_2$-TiO$_2$-CeO$_2$ (SiTiCe) system deposited on silicon and glass substrates were successfully prepared by both “in situ” and “powder dispersion” methods. The embedment of the pre-synthesized oxides is a better way of determining the composition of the particles introduced in the hybrid matrix. The “in situ” generation allows coatings to be obtained with a more homogeneous distribution of particles the coating. When pre-synthesized particles were used, their tendency to aggregate in the hybrid hydrophobic silica matrix was observed. The spectroscopic ellipsometry results showed a strong influence of the method of dopant generation and substrate on the optical properties of the resulting films. The preparation of these films could be expanded on other substrates, such as aluminum or magnesium due to their potential applications as corrosion protective layers.

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