



Morphological engineering of SnO₂ and In₂O₃ films deposited by spray pyrolysis

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Abstract. This article demonstrates the possibility of controlling the morphology of deposited metal oxide films by the preliminary formation of the seed-layers of the appropriate oxide on the substrate surface using a simple and cheap method such as successive ionic layer deposition. The study focuses on SnO₂ and In₂O₃ due to their importance in the field of various chemical microsensors.

Keywords. Metal oxides; deposition; spray pyrolysis; morphology control; seed-layer; successive ionic layer deposition.

1. Introduction

When developing any devices, especially such as metal-oxide gas sensors, the problem arises due to the deposition of films with the required morphology. This task is very important, since the electrophysical and surface properties of polycrystalline metal oxide films as well as the parameters of devices based on these materials depend strongly on the morphology of the films, described by parameters such as the size and the shape of grains and crystallites, film texturing, surface roughness and porosity [1]. It has been found that these structural parameters of the films can be controlled by selecting an appropriate substrate, deposition temperature, properties of the precursors, doping elements, film thickness or deposition method [1–6]. However, these approaches optimizing the morphology of the film have significant limitations on the possible change in the film structure that can be obtained. In particular, the materials used in the device can limit the range of temperatures that can be used for film deposition. The electrophysical properties and gas permeability that a film must have after deposition also impose restrictions on the possible changes in the film composition and film thickness required to achieve the desired morphology. For example, additives used for influencing a film structure can greatly affect the electrophysical properties of the films, whereas a change in the film thickness may be accompanied by a strong change in the size of the crystallites and gas permeability. It follows that in order to solve the above problems it is necessary to have methods that could enable to influence the structure of the films without changing the deposition temperature, the composition of the solution or the thickness of the film.

Panchapakesan *et al* [7], developing SnO₂-based gas sensors, showed that the preliminary modification of the substrate surface by seed-layers of metals such as Co, Fe, Cu, Ag and Ni with a thickness of 1.6 nm using thermal evaporation, allows influencing the morphology of films deposited by a chemical vapour deposition (CVD) method and thereby controlling the gas sensitive characteristics of the sensors. These seed-layers could play the role of growth centres during deposition of metal oxides and thus can affect the structural properties of these films [7]. Later it was shown that this approach can be used in the formation of various metal oxide films by the methods of sol–gel technology, electrochemical deposition, aerosol-assisted CVD, chemical bath deposition and so on [8–12]. It was shown that the pre-coating of glass and silicon substrates by seed-layers affected texturing and crystallinity and was crucial for the formation of metal oxides with controlled properties.

In this paper, we show that a preliminary modification of the substrate surface by metal hydroxides is a powerful factor affecting the morphology of the films deposited by spraying pyrolysis. The pyrosol is a film deposition method that involves the preliminary preparation of a solution of metal salts, and spraying this solution onto a heated substrate, where the formation of metal oxide occurs as a result of the pyrolysis reaction [5,6,13]. We also show that the surface modification of substrates used for the deposition of films can be carried out by successive ionic layer deposition (SILD) [14,15]. The SILD method is based on successive adsorption of the cations and anions from solutions of metal salts that interact with each other at the surface of the substrate and form poorly soluble compounds such as hydroxides and peroxides.

Unlike traditionally used methods of forming seed-layers such as thermal evaporation, sputtering, or CVD [7,8,11], SILD technology has a number of undeniable advantages such as ease of carrying out, the absence of expensive equipment required for the deposition of oxide nanolayers, ease of thickness control during nanolayer deposition, etc. [14,15]. In the absence of proper control over the thickness of the sub-layers formed on the surface of the substrate, it is difficult to achieve the necessary reproducibility of the parameters of the deposited metal-oxide films. To demonstrate the possibilities of the proposed approach, we use SnO₂ and In₂O₃, which relate to materials promising for a wide range of applications from catalysis and displays to gas sensors [16]. Previously, studies in this area were mainly devoted to ZnO [8,9,12].

2. Experiment

In₂O₃ and SnO₂ films with a thickness of ~100 nm were deposited on oxidized monocrystalline silicon substrates by a spray pyrolysis method at $T_{\text{pyr}} = 475\text{--}500^\circ\text{C}$ using the standard mode described in ref. [13]. For these purposes, 0.2 M aqueous solutions of SnCl₄ and InCl₃ were used.

Si substrates used to deposit SnO₂ layers have been pre-modified with seed-layers of Fe, Ce or Zr hydroxides. The seed-layers were formed by the SILD method. The thickness of the deposited seed-layers is controlled by the number of deposition cycles, one cycle of which consists of treating the substrate in an aqueous solution of metal salts with a subsequent treatment in a slightly alkaline solution to convert the precipitate in an insoluble state and washing with water. As a result of this reaction, a hydroxide layer is formed on the surface of the substrate with an average thickness of 0.4–0.8 nm that depended on the type of metal used [14,15]. For deposition of Fe, Ce and Zr hydroxides, 0.01 M aqueous solutions of (NH₄)₂Fe(SO₄)₂, Ce(NO₃)₃ and Zr(OAc)₄ were used. During the precipitation of Fe and Ce hydroxides, a solution of NH₄OH contained an additional oxidizing agent, H₂O₂. The repetition of mentioned operations is accompanied by the deposition of a second layer of the same thickness on the surface of the substrate. The number of such cycles ranged from 4 to 16. The substrate with the deposited seed-layers of hydroxides was then heat-treated at a temperature >300°C to transfer hydroxides formed in the oxide state and to stabilize their properties [15].

For the structural characterization of deposited films, X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used. XRD measurements were carried out by a Rigaku Rotaflex X-ray diffractometer with a rotating anode source, working with K α of Cu. For the structural characterization, we used the $\theta/2\theta$ mode of measurements. The average size of the crystallites in the deposited films was estimated by the Scherrer formula. For SEM measurements, we used the scanning electronic microscopes Philips XL30 and Stereoscan JS360 Cambridge Instruments.

3. Results

As a result of the conducted studies, it was established that the preliminary modification of the substrate surface with a seed-layer prior to the deposition of In₂O₃ and SnO₂ films does have a significant effect on their morphology. An example of this effect is shown in figures 1 and 2. It is important to note that (1) the effect of preliminary modification of the substrate on the morphology of the films deposited by spray pyrolysis and their XRD patterns is much more pronounced for In₂O₃ films than that for SnO₂ films and (2) for the appearance of a pronounced effect in the morphology of the film, the number of deposition cycles should exceed four, which corresponds to the average thickness of the seed-layer (d_s) equal to ~1.6–2 nm. If, however, the number of deposition cycles exceeds 8–10, i.e., $d_s > 4\text{--}5$ nm, then the morphology of the films ceases to change appreciably with increasing number of deposition cycles. This means that 8–10 deposition cycles are sufficient to modify the surface of the substrates.

In addition to changes in the morphology of the films, a change occurs in the size of grains and crystallites, in the dispersion of the size of crystallites and in the texturing of the films. Moreover, these changes occur without changing the deposition temperature, the film thickness and the composition of the solution for deposition, which is a significant advantage of the proposed method. It is also important that the effect of film's morphology transformation depends strongly on both the metal hydroxide used for the modification, and the metal oxide deposited on the modified substrate. For example, the studies showed that the use of the CeO₂ seed-layers promoted a decrease in the grain size dispersion in SnO₂ films (figure 2b). If the grain size in the SnO₂ films deposited on the unmodified substrate varied from 18 to 80 nm, then the change in the grain size in the films deposited on the modified substrate did not exceed ± 4 nm. In addition to that the average grain size in films deposited on a modified substrate increased from 30 to 64 nm. Interestingly, XRD patterns have not changed much.

At the same time, in the case of In₂O₃ films, the modification of the substrate surface by the CeO₂ seed-layers was accompanied by an increase in both the average grain size from 30 to 60 nm and the grain size dispersion (figure 1c). Of the other most pronounced effects, one can single out a cardinal change in the morphology of In₂O₃ films deposited on substrates modified by ZrO₂ (figure 1b). In the case of SnO₂ films, the morphology of the film changes not so noticeably (figure 2d), but XRD measurements show (figure 3) that these changes occur. The observed change in the intensity of individual peaks on the XRD pattern indicates a change in the orientation of the SnO₂ grains involved in the formation of the SnO₂ film.

Surface modification of the substrates by seed-layers of CeO₂ or ZrO₂ also contributed to the improvement in the stability of the metal oxide/Si-SnO₂ interface at high-temperature treatments ($T_{\text{an}} = 950^\circ\text{C}$). This is manifested in a smaller change in the SEM images and XRD patterns of

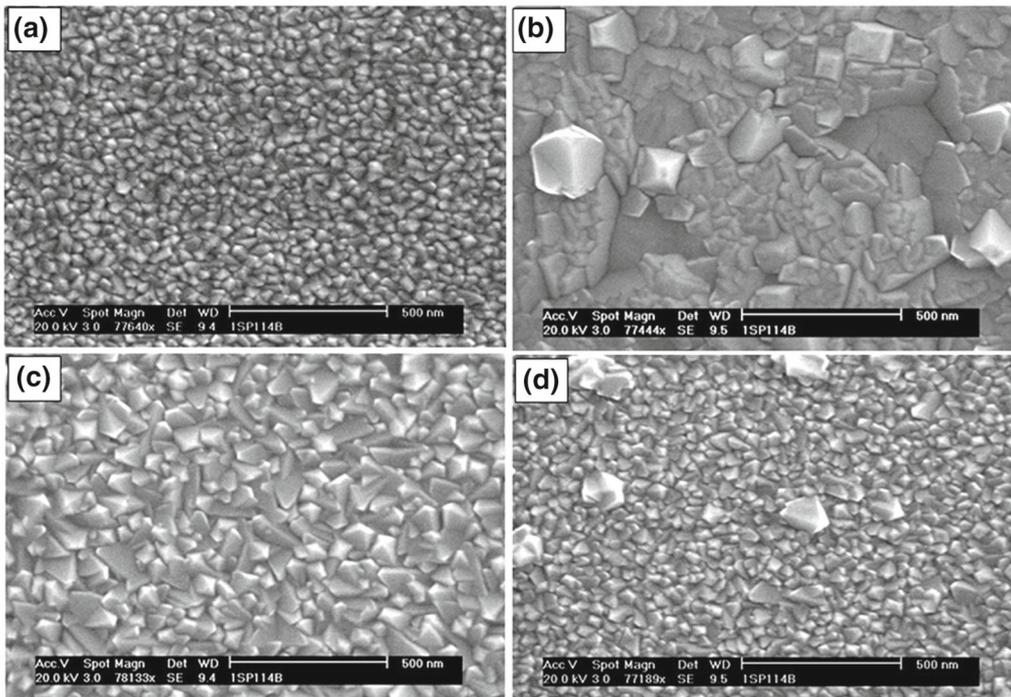


Figure 1. SEM images of In_2O_3 films with a thickness of ~ 100 nm, deposited by the spray pyrolysis method on (a) an unmodified substrate and substrates after modification by seed-layers of (b) ZrO_2 (10 SILD cycles), (c) CeO_2 (eight SILD cycles) and (d) Fe_2O_3 (eight SILD cycles).

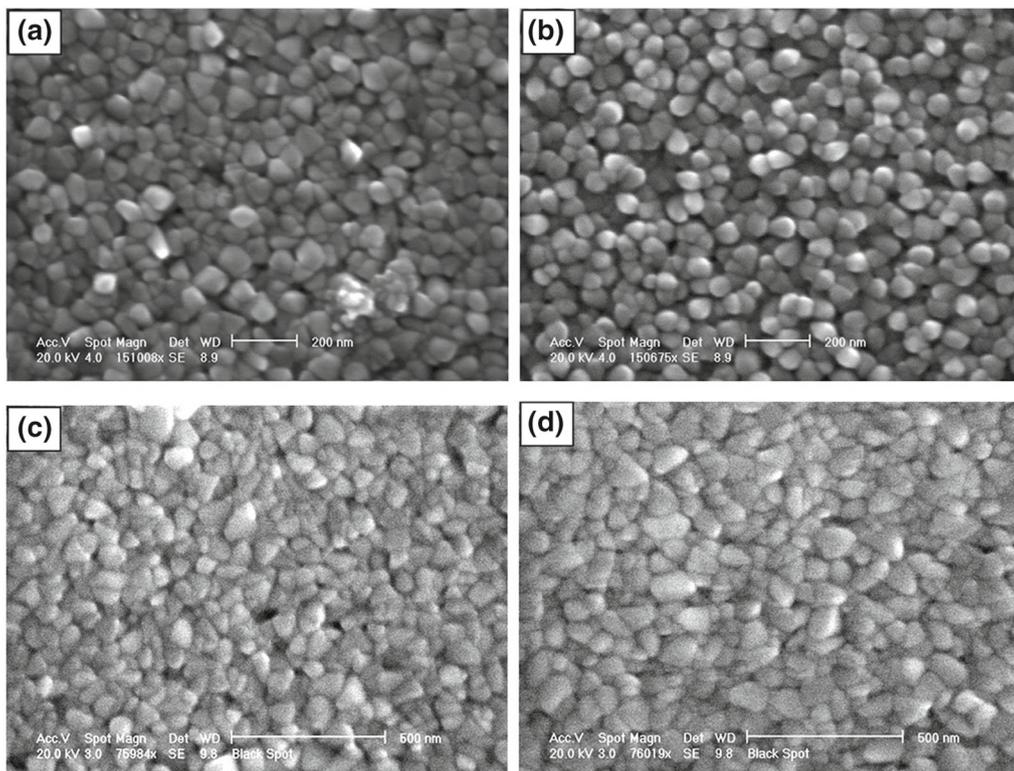


Figure 2. SEM images of SnO_2 films with a thickness of ~ 100 nm, deposited by the spray pyrolysis method on (a) an unmodified substrate and substrates after modification by seed-layers of (b) CeO_2 , (c) Fe_2O_3 and (d) ZrO_2 using eight cycles of SILD.

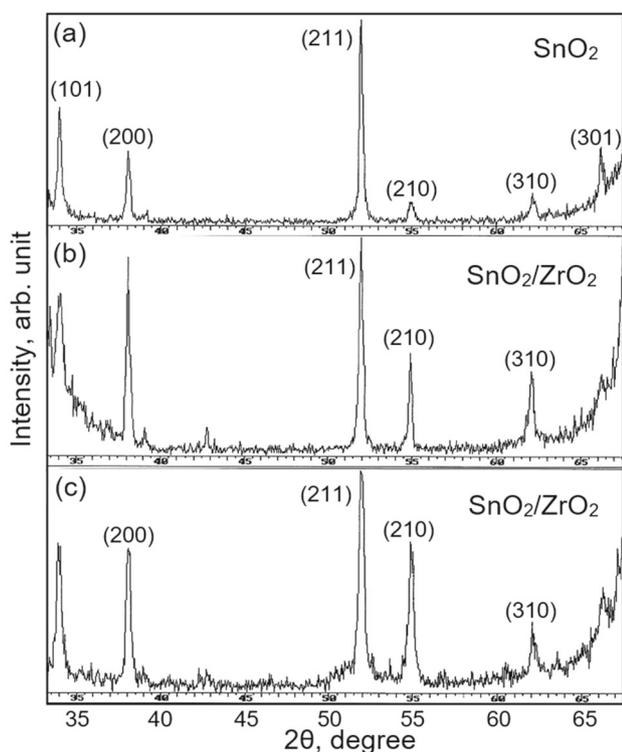


Figure 3. XRD patterns of SnO₂ films deposited by spray pyrolysis on (a) an unmodified substrate and (b, c) substrates modified by seed-layers of ZrO₂ using 4 and 16 SILD cycles, respectively.

these films in comparison with films deposited on unmodified substrate samples. This means that by selecting the appropriate metal oxide used to modify the surface of the substrate, it is possible to achieve the desired result.

4. Conclusion

Our first results show that the approach based on the SILD method of substrate modification by the seed-layer of some hydroxides is effective for controlling the morphology of SnO₂ and In₂O₃ films deposited by pyrolysis. A more detailed study of the structure of the deposited films, the mechanism

of the influence of the seed-layers on the film morphology and the establishment of a correlation between the morphology of the formed films and their electrophysical and instrumental properties are in the second stage of studies.

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