

A novel strategy for fabrication of mesoporous crystalline tin dioxide films with large pores and fully crystalline walls

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ABSTRACT

We have developed a new facile procedure for manufacturing crack-free crystalline thin films of SnO₂ with a uniform mesoporous architecture and full crystallinity of the walls. The procedure is based on the evaporation-induced self-assembly of pre-hydrolyzed tin oxide precursor directed by a commercially available Pluronic polymer. The precursor sol was prepared by the hydrolysis of tin tetrachloride in the presence of ammonium hydroxide in a mixture of ethanol and butanol. The addition of ammonium hydroxide is necessary for the formation of the tin oxide precursor, which is able to self-assemble into a mesoporous structure. The relative concentration of ammonium hydroxide as well as duration and temperature of the hydrolysis reaction influence significantly the properties of hydrolyzed tin oxide species and the mesostructure assembled from them. The films coated from these precursor solutions and calcined at 300 °C to 400 °C exhibit a well-developed worm-like porosity and high crystallinity.

Keywords: conducting transparent oxides, tin dioxide, evaporation-induced self-assembly, mesoporous films.

1 INTRODUCTION

The evaporation-induced self-assembly is one of the most versatile routes to the preparation of functional metal oxide films with a large interface area and a well-defined nanoporous architecture. Spontaneous self-organization of inorganic building blocks (metal oxide precursors) and micelles of amphiphilic molecules (structure-directing agents) enables the formation of highly ordered periodic nanostructures in a very simple way, avoiding the expensive nanolithography or vacuum technologies. The self-assembling ability of the components strongly depends on their surface properties and their mutual interactions.

Inorganic building blocks are conventionally prepared by sol-gel reactions of suitable metal compounds. Formed hydrolyzed species can easily assemble into periodic structures and afterwards condense to a continuous inorganic framework. However, the control over the nature of the formed products is generally low. Consequently, the recent research has been aimed at the preparation of more

defined building blocks in order to gain more control over the self-assembly and the mesostructure of the formed films. [1-5]

One of the processes, which requires a precise control over the self-assembly, is the formation of tin oxide films with a well-developed porosity and high crystallinity. Tin oxide is one of the technologically important semiconducting materials, which is widely used for sensors and catalysts, due to the marked change in its electrical conductivity upon the interaction with reducing or oxidizing species. However, the formation of such films using the self-assembly approach has been found far from straightforward. Highly crystalline films with periodically ordered large pores were obtained only with a special KLE type amphiphilic polymer, which is however not yet commercially available. The preparation of highly crystalline mesoporous tin oxide films with a larger pore size using commercially available Pluronic polymers has required a rather elaborate and time-consuming post-synthesis treatment.

We have proposed that the weak mesostructuring ability of Pluronic polymers is due to an unfavorable interaction of its micelles with the precursor tin oxide species [6]. Therefore, in the present communication we have aimed at the optimization of the interaction strength and the affinity to self-assemble by the variation of the size, charge and hydrophilicity of the tin oxide precursor. We have found that the key issue in the whole process is the sol-gel formation of suitable colloidal particles of tin oxide precursor, which act as the building units of the assembled mesostructures.

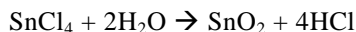
2 EXPERIMENTAL

Mesoporous tin(IV) oxide thin films were prepared according to the following optimized procedure [6]. 0.4 g of SnCl₄ was dissolved in 2 mL of ethanol, afterwards 0.2 mL of distilled water was added. After stirring for about 5 minutes, 2.0 mL of 2M ammonium hydroxide was added. The mixture was stirred for up to 20 h at 20-60 °C, afterwards 0.18 g of Pluronic F127 in 2 ml of butanol was added. The dissolution of Pluronic was accelerated by warming up the reaction vessel to 60 °C. The films were prepared by dip-coating glass or Si wafers with the prepared solution at 23 °C and a relative humidity of 55 %

at a withdrawal rate of 1.8 mm/s. The deposited films were calcined at 300-400 °C for 30 minutes.

3 RESULTS AND DISCUSSION

The formation of the condensed tin oxide framework via hydrolysis of tin tetrachloride is described by the following general scheme:



This seemingly simple reaction equation, however, summarizes a very complex process, which involves a sequence of coupled hydrolysis and branched condensation reactions, as well as the gelation and agglomeration of the formed tin oxide species. Each elementary reaction step has a different reaction rate, and any single equilibrium step can be shifted by a change in the reaction conditions. The reaction mechanism of the sol-gel process of tin tetrachloride is poorly understood. In our work, we have concentrated on the determination of the effect of various processing parameters on the formation of the precursors in order to obtain some basic empirical knowledge, how to control this process and to obtain suitable building blocks for the formation of tin oxide mesostructures. The precursor solution included tin tetrachloride as a tin source, water as a hydrolysis reactant, ammonium hydroxide as a hydrolysis catalyst, Pluronic F127 as a structure-directing agent and a mixture of ethanol and n-butanol as solvents.

The best mesostructure periodicity of films prepared by coating sols of the tin oxide precursor was obtained when the Pluronic to tin oxide molar ratio was 0.8. As a solvent for the preparation of colloidal sols, a 1:1 v/v mixture of ethanol and n-butanol was found the most suitable. The hydroxide to tin ratio, the aging time and temperature were found the most important parameters. The formation of periodic mesostructure occurred only when ammonium hydroxide was added to the solution, the OH/Sn molar ratio of 2.6 ± 0.1 being found the best.

The coating solution has to be aged for a certain time in order to form hydrolyzed tin oligomers suitable as building blocks in the EISA process. At room temperature, the minimum aging time is about 20 hours. The solution pH, which increases initially after the addition of ammonium hydroxide, decreases continuously during the aging process, which can be attributed to the hydrolysis reaction releasing HCl according to the Scheme 1. The aging process can be accelerated by an increase in the aging temperature. At 40 °C, 3 hours are already sufficient to obtain an ordered mesostructure. At 60 °C, however, the hydrolysis and condensation processes became too rapid. Generally, the acceleration of the aging process in this system by increasing the temperature leads to a deterioration of the mesostructure ordering of the films. The deterioration is apparently due to the less controllable course of the hydrolysis and condensation processes,

leading to a broader distribution of the shape and size of the formed oligomers.

By the variation of the processing parameters the best mesostructure ordering was obtained when the coating solution contained tin tetrachloride and ammonium hydroxide at a OH/Sn molar ratio of 2.6 ± 0.1 in a 1 : 1 v/v mixture of ethanol and n-butanol, and was aged for one day at room temperature. The films coated from such a solution were calcined in air at 300 to 400 °C in order to condense and crystallize the inorganic framework and to remove the template. The formation of a mesoporous structure of the films calcined at 300 °C is apparent from the SEM and TEM images. The SEM images show the uniform crack-free surface of the films featuring channel-like pores with a low degree of pore organization. The FFT of the images reveal a periodic repeating unit of 18 ± 0.7 nm (Figure 1a, b). The TEM proves a uniform pore structure (Fig. 2), the FFT exhibiting a ring corresponding to a periodicity of 17 ± 0.5 nm (Fig. 2a, inset). The HRTEM images demonstrate that the walls are completely crystalline, being composed of nanocrystals 2.5 - 3 nm in size (Fig. 2b).

The mesostructure is preserved after the calcination at 400 °C. Surprisingly, the SEM images of the films (top-views) show that the mesostructure unit increased to 18.5 ± 0.5 nm (see Fourier transform in the Fig. 1c, inset) and the pores became more open. This can be attributed to the densification of the inorganic walls due to the further crystallization, leading to an asymmetric change in the pore shape. At the same time, the size of the crystals composing the walls increased to 3 – 3.5 nm (Fig. 1f). The XRD measurements of the films prove that they are crystalline if calcined above 300 °C - the XRD patterns contain broad diffraction lines typical of cassiterite. A quantitative XRD analysis shows that the films' crystallinity increased two-times if the calcination temperature was increased from 300 to 400 °C.

The texture properties and the accessibility of the internal surface of the tin oxide films were studied by krypton adsorption at 77 K. The films calcined at 300 and 400 °C exhibit a well-developed mesoporosity without any pore-blocking and a broad pore size distribution, including also rather small pores. However, there are several characteristic differences in the film porosity due to different calcination temperatures. The increase in the calcination temperature leads to an increase in the specific surface area related to 1 cm² of the support by ca 22 % (from 40 to 49 cm²/cm²), as well as to an increase in the pore volume by ca 29%. The character of the porosity also changes to a certain extent. The film calcined at 300 °C contains a greater percentage of smaller pores and a smaller percentage of pores larger than ca 10 nm than that treated at 400 °C. The toluene adsorption isotherms provide surface area of 45 and 55 m²/g for the films calcined at 300 °C and 400 °C, respectively, which corresponds well to the 66 m²/g found for pure bulk mesoporous SnO₂ assembled from crystalline nanoparticles.

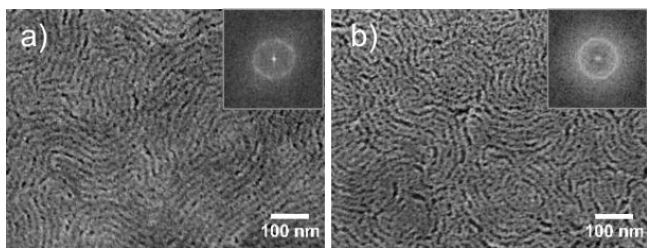


Figure 1: SEM image (top view) of the mesoporous SnO₂ films prepared from OH-hydrolyzed solutions (OH/Sn molar ratio of 2.6, aging for one day) calcined at 300 °C (a) and 400 °C (b) demonstrating their mesoporous structure and crack-free character. Bright areas show the SnO₂ network whereas the black ones the pores. The insets show the corresponding FFT images.

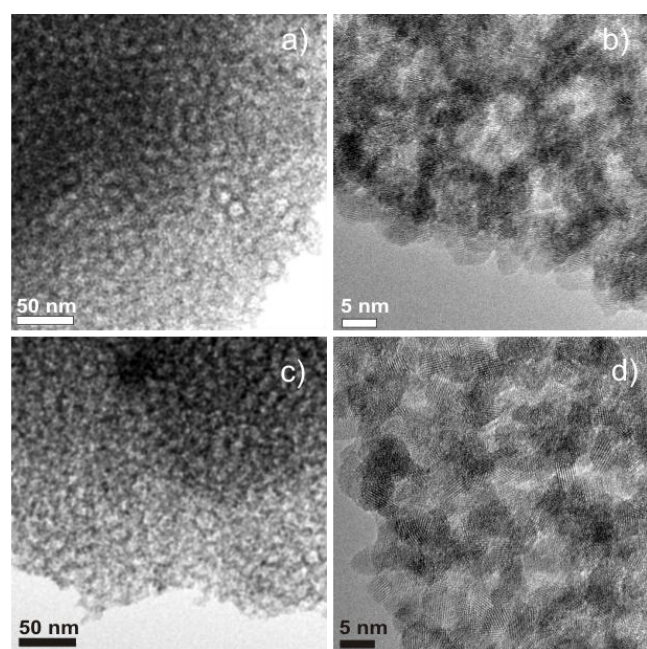


Figure 2: TEM images of the mesoporous SnO₂ films prepared from OH-hydrolyzed solutions (OH/Sn molar ratio of 2.6, aged for one day at room temperature) after calcination at 300 °C (a, b) and 400 °C (c, d). The dark areas correspond to the SnO₂ network, while the white ones to the pores.

The films obtained by the described procedure are not completely transparent. The optical quality of the films is influenced by the amount of ammonium hydroxide added and by the aging conditions. The films prepared from a solution, which does not contain any ammonium hydroxide, are completely transparent, but do not possess any mesoporosity. While the solutions aged with the added ammonium hydroxide are clear, the mesoporous films coated from them turn opaque after calcination. The optical quality of the films was found to deteriorate with the increasing amount of ammonium hydroxide added, with the

increasing aging temperature and aging time, and also Pluronic polymer is present in the reaction mixture during the aging process. The deteriorated optical quality can be attributed to the presence of larger aggregates which scatter the incident light. The acceleration of the hydrolysis/condensation processes leads to a formation of aggregated species and thus to decreased films' transparency.

The dynamic light scattering (DLS) monitoring of the solution containing 2.6 mol/mol of OH/Sn detected the formation of species ca. 3 nm in size shortly after the addition of the ammonium hydroxide to the tin tetrachloride solution (Fig. 3). The size of the species continuously increased with the reaction time, reaching a maximum of 8 ± 3 nm after ca. 19 hours, i.e. the time of the precursor solution aging required for the mesostructure to be formed. Similar analysis of the solutions, which do not contain any ammonium hydroxide, did not detect any formation of comparable species in the same time range. Therefore, we suggest that the ca. 8 nm oligomers are important mesostructure precursors suitable for the self-assembly around the Pluronic micelles. The formation of oligomers of such a size by the hydrolysis and oligomerization catalyzed by bases seems a general characteristic for various metal oxides and differs from more common acid-catalyzed processes. The size of the species observed in the DLS is bigger than the size of the crystallites composing the walls of the mesoporous SnO₂ film. This can be understood taking into account the significant increase in the density upon the crystallization of the amorphous phase. Besides the mentioned 8 nm species, a formation of much larger species roughly 100 to 600 nm in size was also detected in a limited extent, which could correspond to the higher condensation products or agglomerates of smaller colloidal particles.

The accelerated aging of tin tetrachloride based sols by adding a certain amount of ammonium hydroxide enables to obtain suitable building units and to assemble fully crystalline mechanically stable SnO₂ films with a uniform accessible mesoporosity in a very simple procedure. The hydroxide to tin molar ratio of 2.6 used in the optimized procedure is below the stoichiometric ratio of 4 needed to replace all the chloride atoms in the tin tetrachloride molecule. As the solution pH after the addition of the mentioned sub-stoichiometric amount of ammonium hydroxide is still very low of ca. 0.8 – 1.6, the hydrolysis and condensation processes still proceed at very acidic conditions. The interpretation of the results is complicated by the fact that the sol-gel chemistry of tin tetrachloride is not well understood. It is well established that the hydrolysis of tin ion is much faster than that of, e.g., silicon one. It seems, however, that the course of the hydrolysis and condensation of tin differs from the reaction scheme of other metal ions. Thus, the transition metal oxide precursors for the EISA process are usually prepared at strongly acidic conditions in order to suppress hydrolysis and to stabilize the condensation products in the form of small oligomers.

Tin compounds, however, were found to be still present as monomers or dimers at these conditions. We suggest that the addition of hydroxide ions can lead to two possible different scenarios. In the first one, it acts as a reactant for the neutralization of HCl released in the reaction of SnCl₄ with alcohols or water, thus shifting the total equilibrium to the right and triggering the hydrolysis. In the second one, hydroxide ions react directly with the tin cation leading to the formation of tin hydroxide, which can further condensate to higher molecular weight products. In both cases, the reaction conditions are still very acidic, which makes our process different from the basic hydrolysis of tin ions leading as a rule to the formation of compact tin oxide particles several hundreds of nanometers in size.

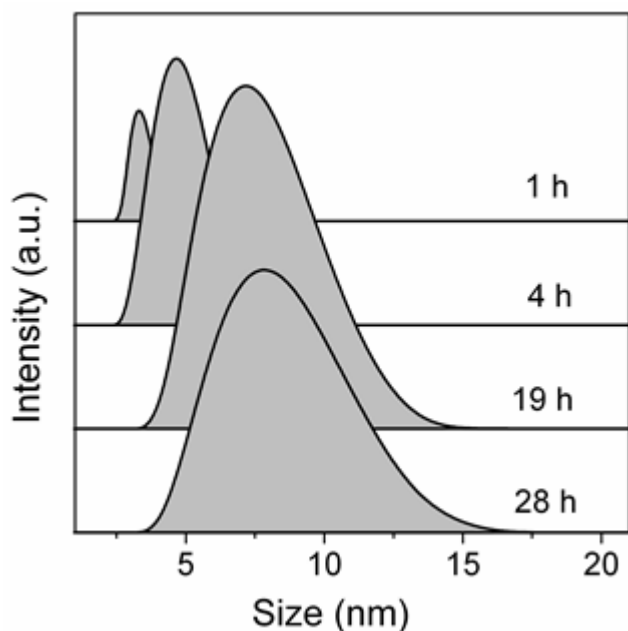


Figure 3: DLS particle size distribution of a colloidal solution containing ammonium hydroxide (OH/Sn molar ratio of 2.6) and aged at room temperature for different times as indicated in the labels.

4 CONCLUSIONS

We have developed a new facile procedure for manufacturing mesoporous crystalline thin films of SnO₂ by the EISA process using cheap and easily available chemicals, especially tin tetrachloride as a source of tin oxide and Pluronic F127 as a structure directing agent. The developed procedure differs from the common base-catalyzed hydrolysis and condensation of tin compounds, but rather resembles the techniques based on preformed nanocrystals. The crucial factor is the formation of a specific oligomeric precursor ca 8 nm in size, whose preparation was triggered by the addition of ammonium hydroxide to an alcoholic solution of tin tetrachloride. Despite the addition of hydroxide, the pH of the alcoholic

solution is still very low of 1.2-1.4. Such a precursor is suitable for the assembly directed by the Pluronic polymer and afterwards relatively easily convertible to a stable mesoporous framework.

The periodicity of the mesostructure ordering and the transparency of the films obtained by the developed approach are inferior to those of films fabricated from the same precursors using delayed humidity (DHT) post-treatment. The developed protocol however offers a practical advantage of a facile and fast preparation. The obtained films could be of a significant interest for applications where the high crystallinity, small crystal size, large pore size, accessible porosity and high surface area are of primary importance, such as in sensorics and catalysis. Further optimization of the films' ordering and their optical properties would require a much deeper insight into the formation mechanism of the precursor species, to their structure and their interaction with the template. Moreover, the developed approach involving formation of the pre-defined metal oxide building blocks can become an efficient way for nanostructuring metal oxides, whose sol-gel chemistry is difficult to control.

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