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SnO_2 and CeO_2-doped SnO_2 materials obtained by sol–gel alkoxide route

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Abstract

Tin dioxide-based materials have interesting electrical and optical properties being used as gas sensor, catalysts and inorganic ion-exchanger. In this paper a study on the preparation of the SnO_2 and CeO_2-doped SnO_2 powders and films by a sol–gel method, starting from the corresponding metal alkoxides, has been performed. The stabilized tin and tin with cerium organic sols were used for deposition of the thin films on glass and silicon single crystal. Powders were obtained after thermal treatment of the gels formed by the gelation of the solutions in air, at room temperature. The films have been deposited by dip coating on glass and silicon wafers and were characterized by X-ray diffraction and atomic force microscopy and the powders by DTA/TG analysis, X-ray diffraction, IR spectroscopy and specific surface area analysis.

Keywords: Sol–gel

1. Introduction

The Sn–Ce–O materials with typical optical and electrical properties present interest due to their use in a wide variety of applications. Sensors obtained by doping of SnO_2 with CeO_2 present a good sensitivity, high selectivity and quick response to H_2S and CH_4 even at room temperature.[1–3] The redox properties of $Sn_{1-x}Ce_xO_2$ powders allowed their use as high-activity catalysts.[4–7] Tolla et al.[8] studied the oxygen exchange properties in the new pyrochlore solid solution $Ce_2Sn_2O_7$–$Ce_2Sn_2O_8$. The semiconducting properties of the cerium-doped SnO_2 obtained both by classical oxide method and by thermal decomposition of some selected precursors have been also previously established.[9–11]

Mixed CeO_2/SnO_2 film electrodes were used as photoanodes in a new generation of nanophase solar cells.[12] Tin dioxide-doped ceria materials are potential electrolytes for solid oxide fuel cells (SOFC).[13]

Interest has been increasing during the last years in the preparation of thin films and oxide powders by the sol–gel process. With this method multicomponent large scale oxide powders and films can be obtained easily and with lower cost than with other methods, such as CVD, sputtering or vacuum evaporation.

The sol–gel process can be successfully applied for depositing electrochromic films, transparent electronic conductors, ion conductors and counter electrodes.[14] The first passive counter electrode film based on CeO_2–TiO_2 was made by the sol–gel method.[15]

Generally, the most often used precursors for the sol–gel method are metal alkoxides, and gels are formed by hydrolysis and polycondensation reactions.[6–18] For the SnO_2–CeO_2 system, the previously mostly used precursors were tin and cerium salts, especially $SnCl_2$, $SnCl_4$ and $Ce(NH_4)_2(NO_3)_6$.[9,20] However, in some cases, the presence of the inorganic anions could have a negative influence on the properties in the final product. In order to avoid this inconvenience the alcoholic route preparation using cerium and tin alkoxides is recommended.

In this paper, a study on the preparation of SnO_2 and CeO_2-doped SnO_2 powders and films by a sol–gel method, starting from the corresponding metal alkoxides, has been performed.

2. Experimental

The precursors for obtaining of SnO_2 and CeO_2-doped SnO_2 powders and thin films were Sn(IV)–isopropoxide isopropanol adduct (INORGTECH) and Ce(IV)–methoxy-ethoxyde (laboratory synthesized).

The conditions of obtaining stable SnO_2 sol were established as a function of precursor/alcohol and alcohol/catalyst molar ratio.

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Table 1
Initial solutions composition

Solution composition	Molar ratio
$EtOH/Sn(OC_3H_7^i)_4$	366
$EtOH/[Sn(OC_3H_7^i)_4 + Ce(OMe)_2(OEt)_2]$	366
$Sn(OC_3H_7^i)_4/Ce(OMe)_2(OEt)_2$	97.5/2.5
$EtOH/HNO_3$ (vol.)	80

Table 2
Experimental conditions

Reaction time (min)/temperature (°C)	60/30
Gelling time of unsupported gel (h)	24
Gelling temperature of unsupported gel (°C)	30
Withdrawal temperature (°C)/speed (cm/min)	30/5
Thermal treatment (film) 1 h at	500 and 850 °C
Thermal treatment (powder) 1 h at	200, 500 and 1000 °C

Sn(IV)–isopropoxide was dissolved in EtOH, previously treated with HNO_3. The as obtained solution was mixed by stirring for 1 h in a closed system. The SnO_2 and CeO_2-doped SnO_2 supported films on glass and silicon wafer substrates have been obtained by dip coating, using the solutions of composition given in the Table 1. Gels were obtained from the previously prepared solutions by gelling at room temperature. Both materials (film and gel) have been thermally treated according to the results of DTA/TG analysis, previously performed.

The *glass supported films* were thermally treated at 500 °C, for one hour and the *silicon wafer supported films* were annealed at 500 and 850 °C. In both cases the heating rate was 1 °C/min.

In order to establish the phase formation in the *dried gels* thermal treatments at 200, 500 and 1000 °C, for one hour at each temperature, were realized.

Experimental conditions of sol–gel process are presented in Table 2.

A schematic diagram of sol–gel process of CeO_2-doped SnO_2 preparation is given in Fig. 1.

The following methods were used for the powder and film characterization.

Thermodiferential (DTA) and thermogravimetric (TGA) analysis using a MOM-Budapest OD-103 type Derivatograph in the temperature range between 20 and 1000 °C, XRD analysis using a Scintag Diffractometer XDS 200 with Cu Kα radiation, IR spectropscopy in the range 4000–200 cm^{-1} using a Carl-Zeiss-Jena M80 spectrometer, BET method using a laboratory made equipment and AFM measurements.

3. Results and discussion

3.1. SnO_2 and CeO_2-doped SnO_2 powders

The stable sols prepared as mentioned above, used both for SnO_2 and CeO_2-doped SnO_2 films deposition, were transformed in unsupported yellow gels by gelation at room temperature.

The thermal behaviour of the obtained gels was studied by DTA/TG analysis, in comparison with that of Sn-alkoxide.

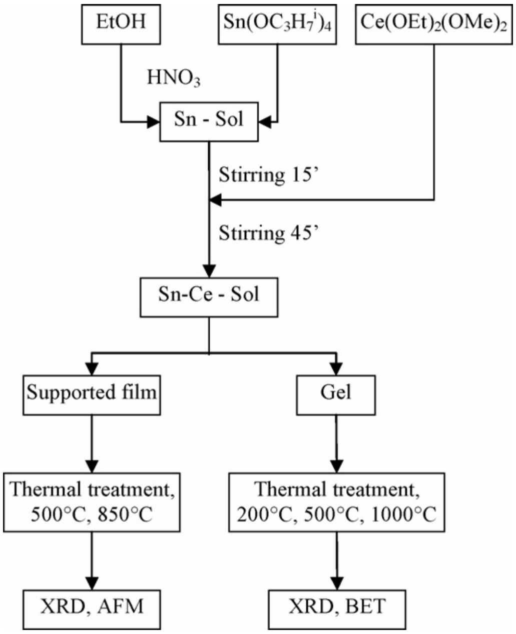

Fig. 1. Schematic diagram of sol–gel process of CeO_2-doped SnO_2 preparation.

The thermal effects recorded for the tin alkoxide decomposition and for the prepared SnO_2 and CeO_2-doped SnO_2 gels are presented in Table 3.

For the tin isopropoxide–$Sn(OC_3H_7)_4$-sample the endothermic effects at 125, 185 and 215 °C are assigned to the alkoxide decomposition and organic radicals evolution, corresponding to a total weight loss of 55.75%. The next exothermic effects at 220 and 315 °C correspond to the oxidation reaction of Sn partially reduced during the $Sn(OC_3H_7)_4$, decomposition and to the oxidation of the high amount of organics resulted by alkoxide decomposition. After 500 °C a slow weight loss is observed, assigned to the desorption of the organic residues from the obtained oxide. The total weight loss determined experimentally is 58.88% in good agreement with the calculated one of 57.80%.

The SnO_2 and CeO_2-doped SnO_2 gels present quite similar decomposition curves, but essentially different from that corresponding to the $Sn(OC_3H_7)_4$ precursor decomposition. Up to 200 °C the adsorbed water and alcohol evolution take place, with a weight loss of 27.11 and 25.82%, respectively. The weight loss is accompanied by the corresponding endothermic effects at 125 and 110 °C, respectively. At higher temperatures the samples present the characteristic thermal behavior of gels that eliminate gradually the water from their composition without a well-defined thermal effect.

Both gels (SnO_2 and CeO_2-doped SnO_2), thermally treated at 200 °C were amorphous as determined by XRD (Table 4).

The IR spectra of the gels, thermally treated at 200 °C, present well defined bands in the 600–800 cm^{-1} range, assigned to the SnO_2 network vibration.[21,22] The structural OH and H_2O vibrations are also present in both cases in the 3300–3500 cm^{-1} range.

The specific surface area determined by BET method for the Ce-doped SnO_2 sample, thermally treated at 200 °C is

Table 3
DTA/TG analysis of the tin alkoxides and as prepared SnO_2 and CeO_2-doped gels

Sample	Temperature range (°C)	Thermal effects (°C)		Weight variation (%)	Assignment
		Endo	Exo		
$Sn(OC_3H_7{}^i)_4$	20–220	125	–	−22.96	$Sn(OC_3H_7{}^i)_4$ decomposition, $-OC_3H_7{}^i$ evolution
		185	–	−17.98	
		215	–	−14.81	
	220–500	–	220	+0.75	$Sn^{2+} \rightarrow Sn^{4+}$ and carbon combustion
		–	315	−1.48	
	500–1000			−2.59	Organic residues desorption
	20–1000			58.88	
SnO_2 gel	30–200	120	–	−7.76	H_2O and ROH evolution
	200–500	–	–	−19.35	Structural OH evolution
	500–1000			−1 86	
SnO_2:CeO_2 gel	30–200	110	–	−6.61	H_2O and ROH evolution
	160–500			−19.21	Structural OH evolution
	500–1000	–	–	−1.90	

62.89 m^2/g, in good agreement with the mentioned values in the literature.[20]

The structural evolution of the gels thermally treated at different temperatures, as determined by XRD, is presented in Table 4. As mentioned above, at 200 °C both samples appear as being amorphous. At 500 °C the SnO_2 phase with low crystallization degree was identified for both un-doped and CeO_2-doped samples. After thermal treatment at 1000 °C the SnO_2 sample crystallizes with a rutile structure, while in the case of the CeO_2-doped SnO_2 sample, besides of SnO_2 with rutile structure, the presence of traces of CeO_2 could be detected, confirming no interaction between the components at this temperature. However, other studies for the similar composition obtained by different methods have mentioned only the presence of rutile phase of SnO_2, assuming the formation of a solid solution.[23–25] The compositional range and the thermal domain in which the solid solutions in the mentioned system are stable are still under discussion.

3.2. SnO_2 and CeO_2-doped SnO_2 films

As presented in the Experimental part, the sol–gel films obtained by dip coating were thermally treated at 500, and 850 °C, respectively, depending on the type of substrate.

The results of the XRD analysis of the films deposited on glass have shown only the presence of the diffraction lines of the support. In the case of the films supported on silicon wafers a low crystallization of SnO_2, rutile phase, was identified. These results are in good agreement with the literature data that show that the substrate topography influences the crystallization of the deposited films. On crystalline substrate the film itself is more liable to crystallize.[26]

Table 4
Phase composition of the unsupported porous materials

Sample	Temperature of thermal treatment (°C)		
	200	500	1000
SnO_2 gel	Amorphous	SnO_2 low crystallization	SnO_2
CeO_2-doped SnO_2 gel	Amorphous	SnO_2 low crystallization	SnO_2, CeO_2

Fig. 2 shows X-ray diffraction patterns of SnO_2 and CeO_2-doped SnO_2 films supported on the Si wafers thermally treated at 850° C in air, for one hour. At this temperature the materials becomes essentially crystallized.

Only the XRD lines corresponding to SnO_2 could be identified in both samples. The absence of the crystallized CeO_2 in the CeO_2-doped SnO_2 film could be assigned to the low amount of CeO_2 in the film composition. The characteristic lines of the silicon wafer support could be also noticed.

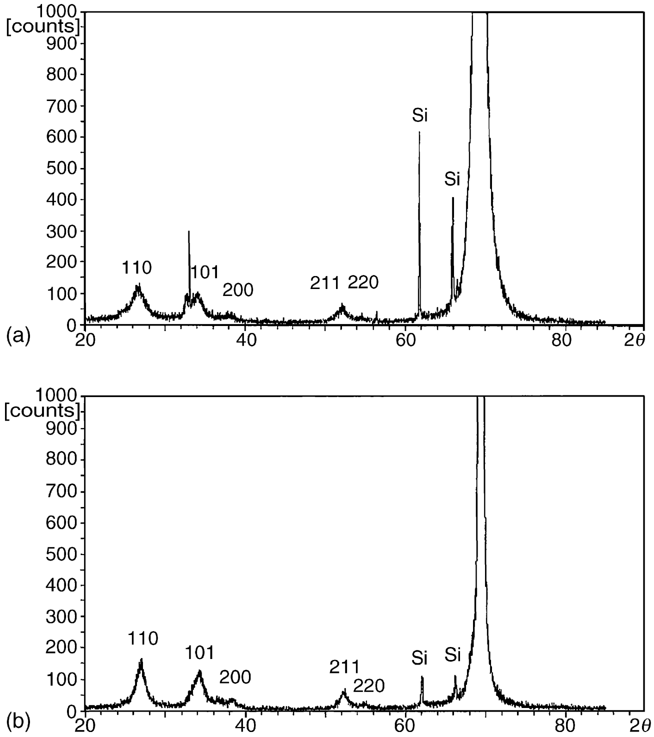

Fig. 2. X-ray diffraction pattern of the films supported on the silicon wafers, thermally treated at 850 °C: (a) SnO_2 film; (b) CeO_2-doped SnO_2 film.

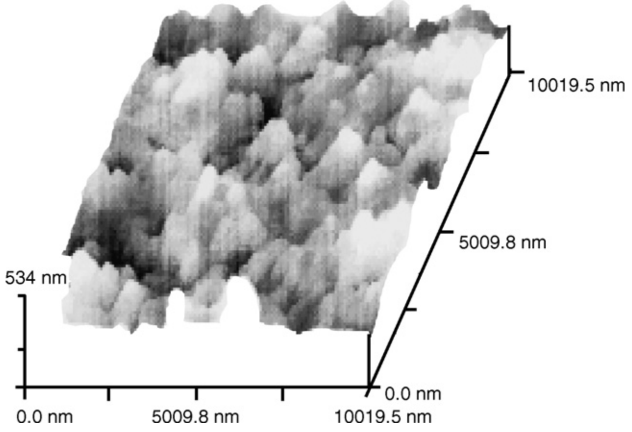

Fig. 3. AFM tridimensional image of CeO_2-doped SnO_2 surface deposited on Si wafer support.

The AFM picture of the doped film is presented in Fig. 3. A rather high thickness of the film was obtained by one layer deposition, but in the same time the average roughness of 69.2054 nm of the film is rather high. The relative high value of the roughness can be assigned to the agglomeration phenomena during the thermal processes of the deposited layer on monocrystalline Si wafer.

The thickness of the film can be modified and the roughness could be improved by appropriate changes of the preparation conditions of the solutions and of the deposition procedure. Our results are quite similar with those mentioned in literature [17] for the Pt and Sb doped SnO_2 layers, obtained by sol–gel method.

4. Conclusions

Tin dioxide and and Ceria-doped tin dioxide materials (powders and films) were synthesized by a sol–gel method starting from the alkoxides of the corresponding metals.

The obtained powders are amorphous and have a high specific surface area. By thermal treatment they undergo the following structural evolution:

- at 500 °C the SnO_2 phase with low crystallinity degree was identified for both un-doped and CeO_2-doped samples;
- at 1000 °C the material obtained by thermal treatment is well crystallized and consists from a mixture of SnO_2 and CeO_2 underlying no interaction between the two components.

In the case of the films obtained by deposition on glass and silicon wafers they are amorphous below 500 °C.

The films deposited on silicon wafer thermally treated at 850 °C are well crystallized and show only the presence of SnO_2 rutile phase.

The powders and the films will be tested as sensors.

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