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EFFECT OF REAGENTS MIXING ON THE THERMAL BEHAVIOR OF SOL–GEL PRECURSORS FOR SILICA-BASED NANOCOMPOSITE THIN FILMS

Viorica Muşat[1*], *P. Budrugeac*[2] *and C. Gheorghieş*[3]

[1]Department of Metals and Materials Science, 'Dunărea de Jos' University of Galati, 111 Domneasca, 800201 Galati, Romania
[2]INCDIE-ICPE-CA – National Institute for Research and Development in Electrical Engineering, 313 Splaiul Unirii 030138 Bucharest, Romania
[3]Department of Science, 'Dunărea de Jos' University of Galati, 111 Domneasca, 800201 Galati, Romania

The paper presents, based on TG-DTG-DSC data, some results of the thermal decomposition of some complex sol–gel precursors used for the deposition of mesoporous ZnO/SiO_2 nanocomposite thin films for gas sensing applications. The effect chemical composition of the sol and reagents mixing during the sol preparation is discussed. The chemical nature of ZnO source (zinc acetate solid salt, zinc acetate alcoholic solution or ZnO nanopowder) used for the sol preparation significantly affects the thermal decomposition of complex precursor and the microstructure and properties of the nanocomposite thin films.

Keywords: *sol–gel, TG-DTG-DSC, thermal decomposition, ZnO:SiO_2 nanocomposite*

Introduction

Silica-based nanocomposite materials are considered one of the most challenging systems for the quantum confinement of semiconductive nanocrystalline grains, investigated for optoelectronic devices [1–4] and for gas-sensing applications [5–6]. For gas-sensors applications high porous materials are used, both grain size and pore size being very important. The sol–gel method is one of the most cost-efficient chemical methods for the preparation of oxide and silica based nanocomposite thin films as it represents a simple and low-cost processing alternative to the vacuum deposition techniques [7–12]. Sol–gel method is very suitable and widely used for the preparation of porous (micro, meso and macro) materials (bulk and thin films) [9–12]. For the sol–gel preparation of mesoporous thin films, complex sol precursors are used. These sols consist of several reagents, used as sources for semiconductive (usually oxide) nanoparticles, for silica matrix, for porosity generation, catalyzer and stabilizers. A large number of studies on sol–gel preparation of metal oxide silica-based nanocomposites and a relatively small number of papers on Zn–SiO_2 nanocomposite preparation and properties have been published, but very few papers on the thermal decomposition of complex sol–gel precursors for nanocomposite materials can be found [13–15]. The formation of the nanocomposite film from the sol–gel precursor is a multiple-step process, which

Table 1 Chemical components used for the preparation of the sol precursors and the mass of the dried gel samples used for thermal analysis

Samples	Chemical components			Sample mass
	ZnO source	SiO_2 source (TEOS)	Surfactant (CTAB)	$m/10^3$ g
Sample 1	Solid salt: $Zn(CH_3COO)_2{\cdot}2H_2O$	Non-hydrolyzed alcoholic solution	–	21.40
Sample 2	Solid salt: $Zn(CH_3COO)_2{\cdot}2H_2O$	HCl-hydrolized alcoholic solution	–	20.13
Sample 3	Solid salt: $Zn(CH_3COO)_2{\cdot}2H_2O$	HCl-hydrolyzed alcoholic solution	Solid	18.53
Sample 4	Aged liquid alcoholic solution of $Zn(CH_3COO)_2{\cdot}2H_2O$	HCl-hydrolyzed alcoholic solution	Solid	19.45
Sample 5	ZnO nanopowder	HCl-hydrolyzed alcoholic solution	Solid	21.30
Sample 6	Aged liquid alcoholic solution of $Zn(CH_3COO)_2{\cdot}2H_2O$	–	–	21.15

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[*] Author for correspondence: vmusat@ugal.ro and vio52musat@yahoo.com

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

involves decomposition and pyrolysis of organic compounds, removal of water and residual organics from the resulting network followed by nucleation and growth of the metal oxide crystallites. The thermal decomposition behavior of the gel precursor plays an important role in oxide crystallites size and in film porosity. This paper presents, based on TG-DTG-DSC data, some results of the thermal decomposition of some complex sol–gel precursors used for the deposition of mesoporous ZnO/SiO_2 nanocomposite thin films for gas sensors application. The effects of chemical composition of the sol and the mixing of zinc oxide precursor used for the sol preparation are discussed.

Experimental

For the preparation of the investigated sol–gel precursors, the following reagents were used: zinc acetate ($Zn(CH_3COO)_2{\cdot}2H_2O$, Merck 99.5%) as ZnO semiconductive nanoparticles source, tetraethoxysilane (TEOS, Sigma Aldrich, 98%) as a silica matrix source and cetyl trimethylammonium bromide (CTAB, Sigma Aldrich, 95%) as a surfactant for porosity generation. Starting from these reagents, three different procedures were used for the preparation of the investigated sol precursors (Table 1): zinc acetate solid salt was directly dissolved into the pre-hydrolyzed TEOS solution (I), a sol based on zinc acetate salt was firstly prepared and then it was added into the pre-hydrolyzed TEOS solution (II) or ZnO nanopowder was added into the pre-hydrolyzed TEOS solution (III).

The aged liquid solution (sol) of zinc acetate used as ZnO source was prepared by dissolving the solid salt in ethanol. The solution was stirred at 60°C for 60 min with reflux. The HCl-hydrolyzed TEOS solution in ethanol was aged for one day at room temperature. The CTAB was directly dissolved in the hydrolyzed TEOS solution. The molar ratio of TEOS:C_2H_5OH:H_2O:HCl:CTAB was 1:25:7:0.14:0.05. The investigated samples were solid gel precursors obtained by drying the liquid precursors (sols) in air at RT and then heated at 80°C for one hour. The TG/DTG, DSC curves were recorded simultaneously in static-air atmosphere, at the heating rate of 10 K min^{-1}, using about 20 mg mass samples (Table 1) and a STA 409PC Netzsch-Germany equipment.

Results and discussion

Figure 1 shows the TG-DTG-DSC curves of a simple zinc acetate based sol–gel precursor (Sample 6) and a complex precursor obtained by adding the simple zinc acetate precursor over a HCl-prehydrolyzed TEOS

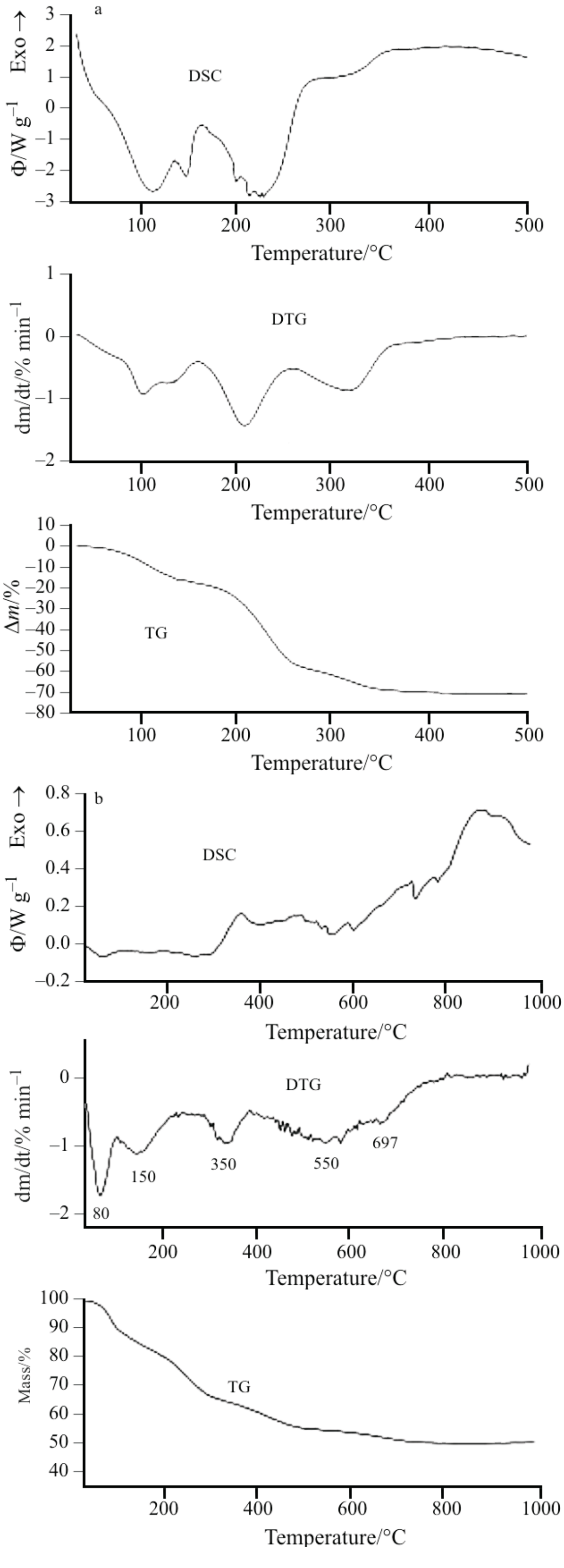

Fig. 1 TG-DTG-DSC curves of the a – Sample 6 and b – Sample 4

solution containing also CTAB surfactant (Sample 4). As expected, the TG-DTG-DSC curves show significant differences between the thermal behavior of the simple and complex precursors. Figure 1a shows three endothermic mass loss steps for the simple precursor: 30~150°C (water removal), 170~250°C (zinc acetate decomposition) and 250~350°C (residual organics removal). Some results concerning the thermal behavior of simple precursors generating ZnO thin films were also presented in previous papers [15–17]. Figure 1b shows the thermal decomposition process of the complex precursor. No DTG peak at about 220°C, corresponding to the decomposition of zinc acetate [15, 17], can be observed. From these results, one can also conclude that two steps of water removal (100 and 150°C) occur in both cases (Fig. 1a, b). Second observation is that an exothermal mass loss process (T_{max}=376°C) and a very complex decomposition step between 400–800°C occur only for the complex precursor.

The investigation on the thermal decomposition of the complex precursor was oriented to emphasize the effect of CTAB surfactant, sol preparation (reagents mixing and chemical nature of ZnO source) and the effect of HCl catalyst used to hydrolyze TEOS.

The effect of HCl catalyst (used to hydrolyze TEOS) on zinc acetate thermal decomposition

Figure 2 shows the TG-DTG-DSC curves of sol–gel precursors which differ by the method of the preparation of TEOS solution. One precursor was prepared using a non-hydrolyzed TEOS solution (Sample 1) while the other precursor was obtained by using a HCl–hydrolyzed TEOS solution (Sample 2). An observation of these curves reveals that the endothermic peak at around 230°C (Fig. 1a), attributed to zinc acetate decomposition [15–17], is present only for the precursor that contains non-hydrolyzed TEOS. The presence of the strong acid (HCl) used as a catalyst for the pre-hydroxylation of TEOS leads to chemical transformation of zinc acetate.

The effect of CTAB surfactant

Figure 3 shows the TG-DTG-DSC curves of two sol–gel precursors that were prepared with and without CTAB surfactant (Samples 3 and 2, respectively). All other experimental conditions in the preparation of the precursors were similar. An exothermal mass loss decomposition peak at T_{max}=376°C can be observed only for the precursor containing CTAB surfactant (Fig. 3b), which means that this peak corresponds to the oxidative decomposition of CTAB.

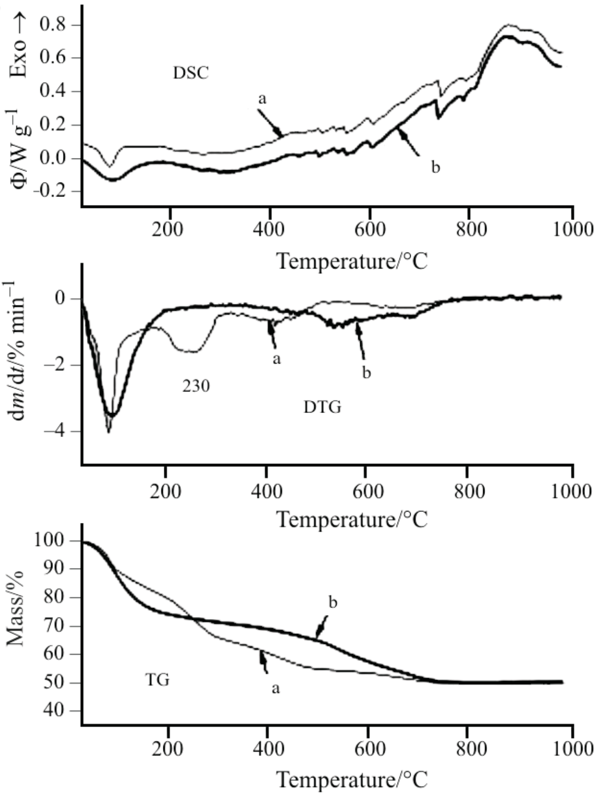

Fig. 2 TG-DTG-DSC curves of the a – Sample 1 and b – Sample 2

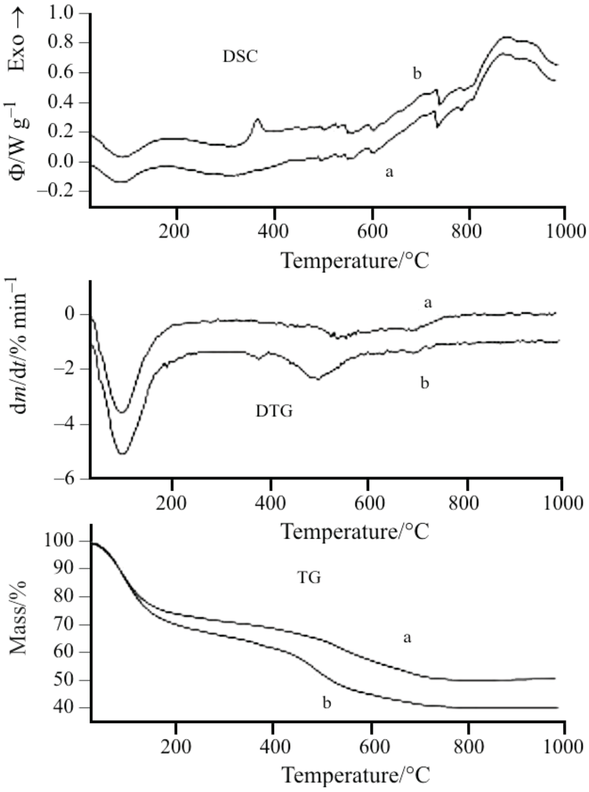

Fig. 3 TG-DTG-DSC curves of the a – Sample 2 and b – Sample 3

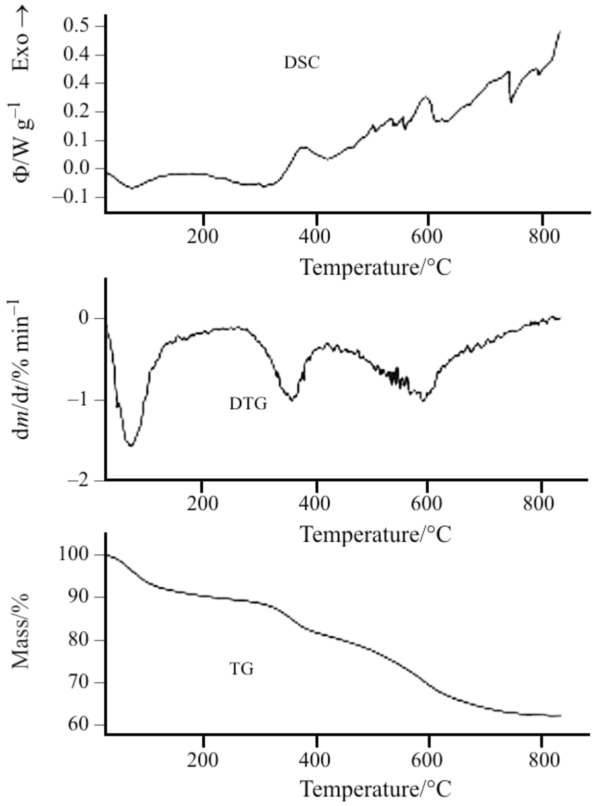

Fig. 4 TG-DTG-DSC curves of the Sample 5

The effect of sol preparation (reagents mixing)

As mentioned in the experimental part, three different procedures were used for the preparation of the complex sol precursors (Table 1):

I: zinc acetate solid salt ($Zn(CH_3COO)_2 \cdot 2H_2O$) was directly added (dissolved) into the pre-hydrolyzed TEOS solution (Sample 3).
II: a simple sol based on zinc acetate salt was firstly prepared, similar to Sample 6 and then it was added into the pre-hydrolyzed TEOS solution (Sample 4).
III: ZnO nanopowder was added into the pre-hydrolyzed TEOS solution (Sample 5).

Figure 4 shows the TG-DTG-DSC curves of the precursor prepared with ZnO nanopowder (Sample 5). The TG-DTG-DSC curves for the precursors which have been prepared using the other two above mentioned procedures have been presented in Fig. 1b (Sample 4) and Fig. 3 (Sample 3).

An analysis of the curves presented in Figs 1b, 3 and 4 leads to the following conclusions:

- although the decomposition process is complex, three thermal decomposition steps can be observed: 20–300°C (water removal and decomposition of zinc oxide source), 300–400°C (exothermic decomposition of CTAB) and 400–800°C (complex decomposition/ transformation of TEOS);
- there is no peak (around 230°C) corresponding to the decomposition of zinc acetate, in the case of complex precursors (Samples 3, 4 and 5);
- when the complex sol is prepared by adding an aged zinc acetate-based solution into the pre-hydrolyzed TEOS solution, the water existing in the gel precursors is well structured and two steps of water removal (100 and 150°C) can be observed (Sample 4 in Fig. 1b);
- the peak which corresponds to the oxidative decomposition of the CTAB surfactant (~380°C) is present in the case of all complex precursors.

Conclusions

The thermal decomposition of complex precursors based on zinc acetate for mesoporous nanocomposite films can be generally divided into three steps: 20~300°C (water removal and decomposition of zinc oxide source), 300–400°C (exothermic decomposition of CTAB surfactant) and 400–800°C (silica matrix generation by complex decomposition of TEOS and crystallization of ZnO nanoparticles). The presence of HCl as a catalyst for the pre-hydrolyzing of TEOS affects the decomposition of zinc acetate used as zinc oxide source. The procedure of sol preparation significantly affects the thermal decomposition of complex precursors and the microstructure and properties of ZnO/SiO_2 nanocomposite thin films obtained from these precursors.

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