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Nanophysics, Nanomaterials, Interface Studies, and Applications

Selected Proceedings of the
4th International Conference
Nanotechnology and Nanomaterials
(NANO2016), August 24-27, 2016, Lviv,
Ukraine

Chapter 5

Thermogravimetric Study of Nano-SnO₂ Precursors

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5.1 Introduction

Adsorption-sensitive thin film elements on the basis of nanoscale oxide materials, especially nanoscale tin dioxide, are widely used in the modern gas analyzers. Well-known production methods of nanoscale metal oxide like tin dioxide are liquid phase chemical methods: sol-gel method, chemical solution deposition, chemical vapor deposition, etc. [1–3]. One of the main stages in such technologies is the decomposition of one, thermally unstable, compound to produce tin dioxide as the final product. The production of such compounds is limited enough. The limited and contradictory literature data on their physical and chemical properties determined the necessity to find a suitable precursor for nanosized tin dioxide production. Previously, authors [4] by means of the method of chemical precipitation from solution proposed the preparation technique for SnO₂ film production with polyvinyl acetate (PVA) as a structuring additive. The complex bis(acetylacetonato)dichlorotin (BADCT) was used as a precursor of tin dioxide. In [5], it was firstly mentioned the fact of obtaining of BADCT (Sn(C₅H₇O₂)₂Cl₂) in 1903. Earlier in the literature [5–8], it was reported the BADCT production using chloroform [5] or dry toluene [8] as solvents. A special feature of our method is using of water as a solvent.

In [9], it was reported the thin films' ZrO₂ preparation with similar compounds, namely, zirconium acetylacetonate. Using of BADCT-based complex, prepared by

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O. Fesenko, L. Yatsenko (eds.), *Nanophysics, Nanomaterials, Interface Studies, and Applications*, Springer Proceedings in Physics 195,
DOI 10.1007/978-3-319-56422-7_5

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the authors by the different from the prior method, makes it possible to obtain transparent thin film of tin dioxide with nanoscale grains [4].

The precursor complexes for comparative studies were prepared by two methods differing only in the last stage: the drying process. In the Odessa I. I. Mechnikov National University (ONU), Odessa, Ukraine, the drying was performed in an air and, in Akdeniz University, Antalya, Turkey, in a vacuum. Presumably, the difference in the drying process is determined by the preservation of water molecules in the precursor complex, which, on our opinion, has an impact on the resulting film structure.

In the presented paper, the precursor complexes were investigated by thermographic methods (thermogravimetry, TG; derivatography, DTG; differential thermal analysis, DTA), allowing to investigate in a programmable heating the nature and thermal parameters of physical and chemical processes in the material. The relevance of these studies is determined by the specifics of the processes at the precursor decomposition. This contributes to the creation of a reproducible technology for nanoscale films of it. The aim of the work was a comparative thermographic study of complexes, obtained by the two abovementioned methods thus establishing which one provides a tin dioxide layer of a nanoscale structure.

5.2 Precursor Preparation and Research Methods

Preparation of precursor complexes was carried out in several stages. The first stage is production of the working solution N 1: 50 ml (0.5 mol) of acetylacetone was mixed with 250 ml of distilled water and left for 24 h until complete dissolution. Then N 2 working solution was prepared: 14 ml (0.12 mol) of tin tetrachloride was added to 100-ml-volume conical flask with the subsequent addition of 50-ml-cooled (2–5 °C) distilled water. The heating of the resulting mixture is observed. In the second stage, the working solutions N 1 and N 2 were mixed in 1.0 l flask with further addition of 5 ml of 20% aqueous NH₃ solution. The resulting mixture was stirred for 2 h at 40 °C using a magnetic stirrer. As a result, a dense white precipitate fell out. Then 600 ml of distilled water was added to this same flask. After standing for 10–15 min, the supernatant was decanted. The precipitate was separated by vacuum filtration on a sinter (residual pressure of $P = 500$ mm Hg), washed with 100 ml of distilled water, and dried at 20–25 °C for 3 days. Then it was washed with benzene and dried for 5–6 h at 60 °C complex N 1, in air, and complex N 2, in vacuum.

The resulting product is a fluffy white powder which melts at 200–220 °C and ignites spontaneously in air at a temperature 250–270 °C. Preliminary chemical analysis (for chlorine and tin) revealed that the resulting compound contains 1.9 of chlorine atoms and 2.2 water molecules for one tin atom.

Simultaneous thermogravimetric and differential thermal analysis was performed for the precursor complexes by means of derivatographs (Q-1500 Hungary D production) for complex N 1 and (Perkin-Elmer 6000) for complex N 2 in air

and nitrogen at a heating rate of 10 °C/min. The powder mass loss resulted during thermogravimetric studies is shown below.

5.3 Experimental Results and Discussion

As soon as tin tetrachloride (SnCl₄) and acetylacetonate (C₅H₈O₂) were used for obtaining precursor, this gives the possibility to suppose the presence of bis(acetylacetonato)dichlorotin and tin tetra acetylacetonate in the precursor. The presence of chlorine in complex N 1 was determined analytically and was 17.5%. In [10], it was also confirmed the presence of chlorine in complex number 2 in the amount of 16.50 ± 0.60%. Such an amount of chlorine in both complexes indicates a predominant content of BADCT in both of them. The thermal decomposition of the precursor complex has to include the stages of decomposition specific for its components.

Figures 5.1 and 5.2 show the results of TG, DTG, and DTA studies of complexes number 1 and number 2, respectively.

The DTG curve for complex number 1 (Fig. 5.1) clearly shows a peak at 100 °C, and the loss of mass on TG curve was 8%. If it is considered that the basic substance is a precursor complex crystalline BADCT (Sn(C₅H₇O₂)₂Cl₂•2H₂O), then the calculated percentage of the coordinated water in its structure is of 8.5% order. As it is shown, the resulting TG value is close to the mass loss calculated for the coordinated water content, thus indicating the presence of water in complex N 1. In addition to the evaporation of coordinated water, the evaporation of adsorbed water may also occur, amount of which is smaller compared with the coordinated one.

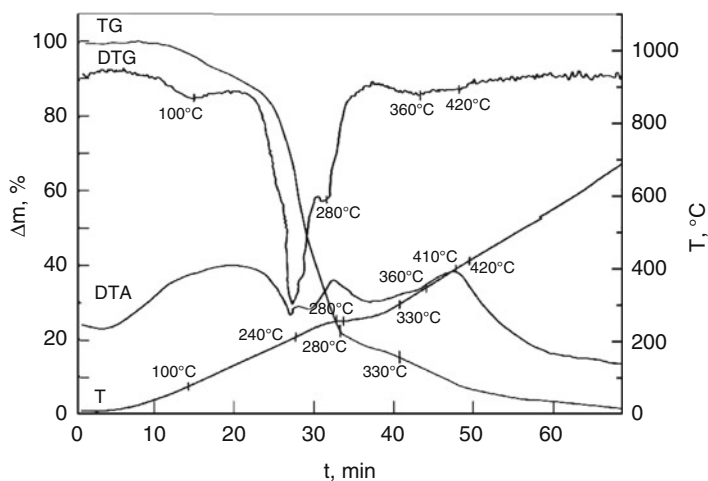


Fig. 5.1 TG, DTG, and DTA results of complex N 1

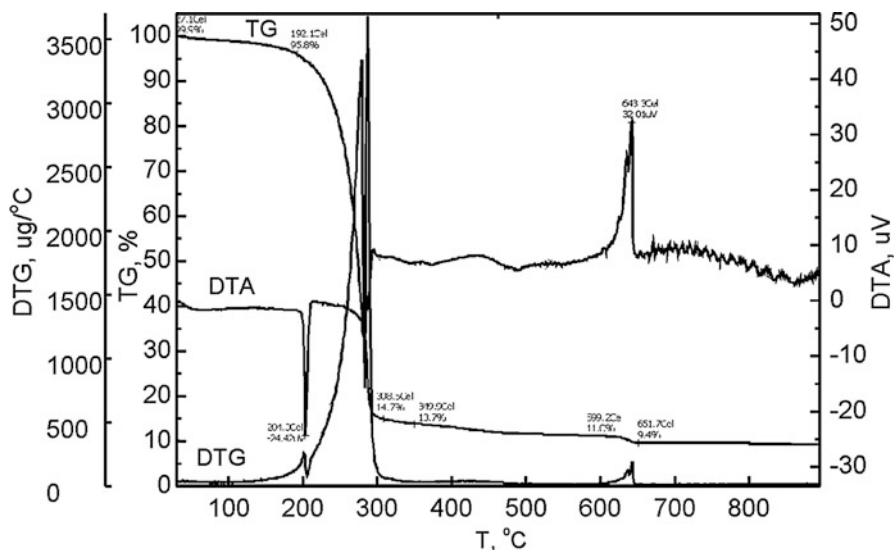


Fig. 5.2 TG, DTG, and DTA results of complex N 2

At heating up to 190 °C on the DTG curve of complex N 2, the change in mass is less than 4%, thus indicating the much less water molecule presence in complex N 2. In [10], the quantitative content of hydrogen (3.41%) in complex number 2 corresponds to the anhydrous BADCT. According to other authors [11], water after 200 °C is almost not detectable in tin compounds, i.e., except for dehydration, other changes in the phase composition of the material at a temperature below 190 °C are unlikely. Consequently, the mass change in complex N 2 up to this temperature is supposed to be connected with evaporation of adsorbed water.

The DTA curve for complex N 1 (Fig. 5.1) contains the endothermic process peak at about 240 °C. According to TG and DTG curves, the process beginning corresponds to 200 °C. The absorption but not the release of energy is attributed to the substance phase transformation (i.e., melting or evaporation of the material). In the processes of thermal decomposition of the complexes, the flammable release of energy, not absorption, is observed. The coincidence of DTA and DTG that peaks at 240 °C shows that there has been not only the melting but the intensive evaporation of the complex. This assumption is confirmed by the loss of mass, visible on the TG curve for complex number 1 in the range of 200–240 °C. For complex N 2 (Fig. 5.2), the DTA peak at 200–210 °C is of endothermic type, but significant mass loss is not observed in this case, i.e., in the specified temperature range, this complex just melted. The gradual evaporation of complex number 2 occurs at higher temperatures up to 280 °C, which is evident due to its mass loss on the TG and DTG curves and to energy absorption in the DTA curve.

For complex N 1 at 280 °C and for complex N 2 at a higher temperature (286 °C), the exothermal distinct peaks on the DTA curve are accompanied by the

intensive mass loss, thus indicating that the complexes burned away in the oxygen of air. Subsequently (280–310 °C), the DTA curve for complex N 1 exhibits an endothermic process with a mass loss, which is reflected in the TG and DTG curves and is associated with intense final reaction product evaporation at the complex decomposition.

The further study shows another strong exothermic effect: for complex N 1 at 410 °C and for complex N 2 at 640 °C. Obviously, the residue of SnO is oxidized up to SnO₂. This is confirmed by the data of [12], where it was shown that the oxidation of the SnO up to SnO₂ takes place before 650 °C. For complex N 1, this process occurs at a temperature of 230 °C lower than for complex N 2. This difference is explained by the influence of the oxidized SnO particles' sizes. Complex N 1 is a hydrated BADCT. Upon separation of water, it is loosened, which promotes the formation of small mass particles. The further decomposition up to oxide occurs simultaneously with the evaporation of the gas phase (confirmed by corresponding changes in the above-described curves: TG, DTA, and DTG). Upon decomposition of anhydrous N 2, apparently, complex oxide is formed with larger particles' size and mass. Therefore, for complex N 1, no residue remains after thermogravimetry, and for complex N 2, about 10% of the material remains (by the experience of decomposition studies of acetylacetonates of other metals of group IV [13], the residue is a tin dioxide). As it can be seen from the TG, DTG, and DTA results of the study of complex N 1 (Fig. 5.1) at 700 °C, the weight loss was 100%, i.e., it is completely evaporated.

The thermogravimetric study results for both complexes are summarized in Tables 5.1 and 5.2.

Comparative thermogravimetric studies of complex N 2 in air and in nitrogen were also conducted in the Akdeniz University (Antalya, Turkey). Figure 5.3 shows the TG, DTG, and DTA results of the thermal decomposition of the product.

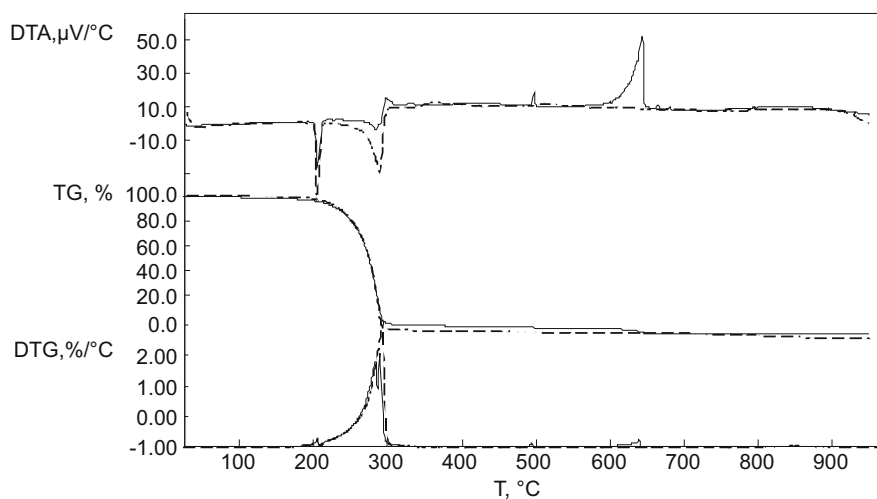
The mass loss observed between room temperature and 192 °C was about 4% and occurred, as mentioned above, due to the evaporation of adsorbed water. Well-seen endothermic peak at 204 °C is associated with the melting point. TG and DTA data (Fig. 5.3) show the complex structuring connected with oxygen in the temperature

Table 5.1 The thermogravimetry results of complex 1

T, °C	TG	DTA	Possible process
100 °C	Mass loss 8%		Coordinated water evaporation
240	Mass loss	Endothermic peak	Melting and intensive evaporation of the complex fragments
280	Intensive mass loss	Exothermic peak	The complex fragments' reaction with oxygen
280–310	Mass loss	Endothermic process	Intensive evaporation of decomposition products of the complex fragments
410	Mass loss	Exothermic peak effect	Oxidation of the complex fragments (SnO oxidized to SnO ₂)

Table 5.2 The thermogravimetry results of complex 2

T, °C	TG	DTA	Possible process
Under 192	Mass loss 4%		Adsorbed water evaporation
204		Endothermic peak	Melting of complex N 2
Over 210	Gradual mass loss	Endothermic peak	Fragment of the complex evaporation
277	Intensive mass loss	Endothermic peak	The complex intensive evaporation fragment
286	Mass loss	Exothermic peak	The complex reaction with oxygen fragments
500	Small mass loss (1.5–2%)	Exothermic peak	Fragments of the complex oxidation
620–650	Small mass loss (1.5–2%)	Exothermic peak	Fragments of the complex oxidation (SnO oxidized to SnO ₂)

**Fig. 5.3** The results of DTA (1), DTG (2), and DTG (3) studies of complex N 2. The solid and dotted curves represent data obtained in nitrogen and in air, respectively

range 192.0–308.5 °C, one at 277.4 °C and the other at 286.6 °C. Comparison of thermogravimetric curves obtained in oxygen and in air shows the presence of two competing processes at a temperature of about 277.4 °C – evaporation and oxidation of the complex fragments. Evaporation is confirmed by a large value of the absorbed energy in the DTA curve, registered at this temperature in nitrogen and a large mass loss (TG curve) also in nitrogen. On the contrary, in air at 277.4 °C, both the endothermic DTA peak value and the mass loss are less. Besides that, the exothermic peak appears in DTA curve at 286.6 °C in the air indicating the complex fragments' reaction with oxygen, before they leave the complex. Thus, the

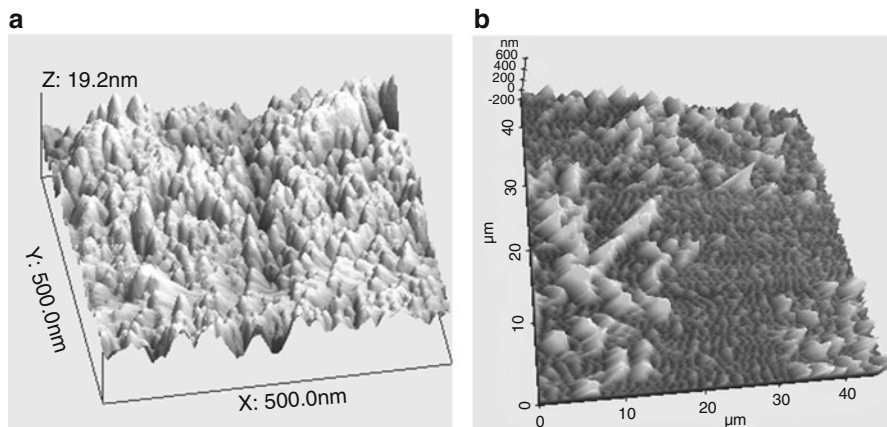


Fig. 5.4 AFM images of the surfaces for films obtained from the precursor complexes N 1 (a) and N 2 (b)

residual mass of fragments studied in the air in the considered temperature interval is more of the fragments' residual mass studied in the nitrogen. These witnesses to the nonvolatility of the reaction products formed in the air due to their comparatively considerable size.

The residual mass at 308.5 °C, Fig. 5.3 (in the air), is approximately 14.7%, which is apparently due to the tin compounds' presence in the product. A small exothermic peak at 500 °C and a strong exothermic peak between 620 and 650 °C for the DTA curve measured in air are not observed on the curve measured in nitrogen. These exothermic peaks observed in the air correspond to a small loss of mass of the complex (about 1.5–2%) and may occur due to combustion of organic residues formed during BADCT decomposition. The further temperature increase does not lead to greater loss of mass.

Due to the method proposed by the authors [4], tin dioxide films were obtained from two precursor complexes. The surface morphology of SnO₂ films prepared from precursor complexes N 1 (a) and N 2 (b) is shown at Fig. 5.4 using an atomic force microscope. The image comparison shows that in case of using of a hydrated precursor (complex N 1), the film with a grain size of 10–20 nm was obtained. At the same time, the size of films' grains obtained from complex N 2 (anhydrous BADCT) is more than 500 nm.

These studies support the preference of using the hydrated precursor complex to obtain tin dioxide film with a smaller grain size of a nanoscale.

5.4 Conclusions

TG, DTG, and DTA studies of two sets of precursors allowed to establish and to compare the main stages of their decomposition: water evaporation, melting, evaporation of materials, and combustion of the material remnants in oxygen. The complexes' decomposition differences are caused by differences in their structure, namely, in the presence (in complex N 1) or absence (in complex N 2) of coordinated water molecules. The formation of a crystalline complex in the case of N 1 happened at the last stage of preparation – the drying step. Air drying facilitated to preserve the crystalline hydrate complex which is important for the further obtaining of nanoscale tin dioxide. In the thermal decomposition of the complex, the water in its structure acts for loosening and subsequent formation of smaller (nanosized) particles. Therefore, the use of precursor complex containing crystalline hydrate (N 1) should be preferred in the preparation of nanosized tin dioxide with a well-developed surface which provides a high sensitivity of its physical parameters to a changing environment and hence the widespread use as sensitive elements of the sensors.

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