

Investigation of SnO₂ thin film evolution by thermoanalytical and spectroscopic methods

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Abstract

The thermal evolution process of a SnO₂ thin film from SnCl₂·2 H₂O precursor dissolved in ethanol was followed by thermogravimetry combined with mass spectrometry (TG-MS), diffuse reflectance Fourier transform infrared spectroscopy (DRIFT) and infrared emission spectrometry (IRES). The precursor salt solution was deposited on a titanium metal sheet. After evaporation of the solvent, the gel-like film was heated in a thermobalance in an oxidative environment to 600°C. Mass spectrometric ion intensity curves showed the liberation of chlorinated species, alcoholic fragments and CO₂ as combustion product and from the decomposition of surface carbonyls, carboxylates and carbonates. The presence of O-H, C-H and C-O bands in the infrared spectra was confirmed and their assignment was made by the deconvolution of the recorded curves.

Keywords: SnO₂ thin films, Sol-gel process, Thermogravimetry-mass spectrometry (TG-MS), Infrared emission spectroscopy, Diffuse reflectance Fourier transform infrared spectroscopy

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1. Introduction

Tin oxide (SnO_2) semiconductive layers with rutile structure have been widely used for technical applications such as gas sensors, solar cells and transparent electrodes for optoelectronic devices [1-3]. In addition, tin oxide is a promising anode material to be used in microbatteries, as well [4,5]. Thin oxide films can be synthesised by numerous techniques such as chemical vapour deposition [6], spray pyrolysis [7], sputtering [8], and sol-gel deposition [9]. The advantage of the sol-gel method lies in the fact that the doping level, solution concentration and homogeneity can be controlled easily without using expensive and complicated equipment. The control of porosity by this method seems to be quite attractive for promoting sensing properties [10].

In the present work the mechanism of formation of a SnO_2 film prepared by the sol-gel method from an ethanolic solution of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ precursor onto a titanium metal support is followed by thermogravimetry - mass spectrometry as well as by reflection and emission FT-IR spectroscopic techniques.

2. Experimental

Thin film preparation

The precursor salt - $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich, Steinheim, Germany)- was dissolved in ethanol and a 0.05M stock solution was made. The gel-like film was prepared onto titanium metal support (size 4 mm x 4mm, thickness 0.1mm) etched in boiling oxalic acid (10%) for 15 minutes, washed with distilled water, rinsed with acetone and dried at room temperature. The coating was made by applying the precursor salt solution (after a 10-fold dilution with ethanol) drop by drop onto the support and removing the solvent by hot air (60°C). This procedure was continued until a measurable quantity of the gel-like film (1-5 mg) corresponding to a relatively thick (400-800 nm) layer was deposited.

Thermoanalytical investigations

Thermoanalytical investigations and the heat treatment of the gel-like coating were carried out in a Netzsch (Selb, Germany) TG 209 type thermobalance in a flowing gas atmosphere containing 19.8% oxygen and 80.2% argon (Messer Griesheim, Hungary). The purity of the gas mixture was 99.995%, and the heating rate was 10 °C/min. In order to simultaneously follow the evolution of the gaseous decomposition products over the temperature range from ambient to 600 °C, the thermobalance was connected to a Balzers MSC 200 Thermo-Cube type mass spectrometer (Balzers AG, Lichtenstein). The transfer line to introduce gaseous decomposition products into the mass spectrometer was a deactivated fused silica capillary (Infochroma AG, Zug, Switzerland; 0.23 mm o.d.) temperature controlled to 150 °C to avoid condensation of high-boiling organic matter.

Diffuse Reflectance Fourier Transform Infrared Spectroscopic (DRIFT) measurements

DRIFT spectra of the tin-chloride film heated to different temperatures were recorded by means of a Bio-Rad Digilab FTS 60A spectrometer. Five hundred twelve scans were obtained at a resolution of 2 cm⁻¹ with a mirror velocity of 0.3 cm/s. Spectra were co-added to improve the signal-to-noise ratio. Reflected radiation was collected at ~50% efficiency. Background spectra were obtained by using etched, uncoated titanium sheets and the recorded spectra were ratioed to the background. The reflectance spectra expressed as Kubelka-Munk unit versus frequency curves are very similar to absorbance spectra and can be evaluated accordingly.

Fourier Transform Infrared Emission Spectroscopic (IRES) analyses

In infrared emission spectroscopy the infrared source is the heated sample itself. In principle, the emitted radiation (from thermally excited vibrational levels) can give exactly the same spectra as in absorption spectroscopy, but the signal to noise ratio (which is inherently low due to the low sample temperature) should be improved by the accumulation of spectra. FT-IR emission spectroscopic measurements were carried out in a Digilab FTS-60A spectrometer, which was modified by replacing the IR source with an emission cell. The infrared emission cell consists of a modified atomic absorption graphite rod furnace, which is driven by a thyristor-controlled AC power source capable of delivering up to 150 amps at 12 volts. A platinum disk acts as a hot plate to heat the titanium sheets with the coatings on top. An insulated 125 µm type R thermocouple was embedded inside the platinum plate in such a way that the junction was <0.2 mm below the platinum surface. The operating temperature

was controlled to ± 2 °C using an Eurotherm Model 808 proportional temperature controller, connected to the thermocouple. The cell was flushed with high purity argon gas to exclude water vapour during the measurements. The emission spectra were collected at 50 °C intervals in the 150 - 750°C range. The spectra were acquired by coaddition of 64 scans at a resolution of 4 cm^{-1} .

3. Results and Discussion

The thermogravimetric (mass loss, TG) and derivative thermogravimetric (rate of mass loss, DTG) curves of 2.19 mg $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ gel on titanium metal support are given in Figure 1. The mass spectrometric ion intensity curves of the $m/z = 29$ (C_2H_5^+), $m/z = 44$ (CO_2^+) and $m/z = 53$ (O^{37}Cl^+) are also shown. By comparing the curves, the following conclusions can be drawn. Below 100 °C residual solvent (ethanol), crystallization water, and hydrogen chloride (as a result of an intramolecular hydrolysis) are lost. In the main mass loss stage (between 100 and 200 °C) alcoholic fragments are liberated in at least two different processes. Chlorinated species evolve mainly in the 20-200 °C range with maximum intensity at approx. 140 °C. Since in the presence of water chloride-containing decomposition products forms hydrochloric acid (which strongly adsorbs to the silica capillary), water evolution cannot be followed directly. The broad evolution pattern of chlorinated species is an indirect evidence of the liberation of water as well. Over 200 °C a monotonous decrease can be observed in the mass loss curve indicating the formation of the final SnO_2 film by approx. 400 °C. It is interesting to note that a small amount of CO_2 is formed below 200 °C and between 300 and 350 °C, indicating the occurrence of combustion processes as well. The low temperature CO_2 formation is due to the burning (oxidative cracking) of residual alcohol, while its occurrence at high temperature can be explained with the combustion/decomposition of carbon containing surface species (and that of elemental carbon formed by solvent cracking and trapped in the film).

In order to completely follow the process of thin film evolution, the changes in composition of the film should be followed as a function of the temperature, as well. Although infrared spectroscopy is a common tool to identify film composition, non of the traditional transmittance or reflectance methods can be used for the study of porous films on metal supports. The information available in the literature on the interpretation of infrared and Raman spectra of tin-compounds prepared on different surfaces from organic (mostly alcoholic) solutions is rather limited. In assigning vibrational spectra, some DFT calculations

[11] or some vibrational spectroscopic data relating to tin-containing supported catalysts and semiconductors [12-16] can be relied on.

For the interpretation of the DRIFT spectra, temperature intervals that can be related to some events in the TG curve shall be considered. Therefore, spectral changes in the 20-100, 100-120, 120-150, 150-200 and the 200-400 °C temperature interval are investigated. It should also be considered that in the 20-200 °C range several overlapping thermal decomposition processes take place. In the ambient to 100 °C range most of the residual organic solvent is liberated. At the same time part of the remaining crystallization water is lost and -as a result of intramolecular hydrolysis- tin-oxihydroxide is formed accompanied with hydrogen-chloride formation. The FT-IR (DRIFT) spectra of the SnCl₂ film heated to different temperatures in the thermobalance and cooled back to room temperature are shown in Fig. 2. The resolved bands of the 1500 to 1350 cm⁻¹ and the 1400 to 800 cm⁻¹ ranges are shown in Figure 3 and Figure 4, respectively. The infrared emission spectra of the film recorded at different temperatures are given in Figure 5. The peak positions of the resolved bands in the O-H and C=O stretching vibration range are summarized in Table 1 with the indication of the types of vibrations, as well. Intramolecular hydrolysis can take place to some extent even at room temperature as evidenced by the bands at 880 and 970 cm⁻¹ in the DRIFT spectrum. These bands can be identified as OH libration bands. The residual solvent shows strong coordination as evidenced by the changes in relative intensity of the bands. The O-H deformation bands (in the 1420 - 1380 cm⁻¹ range) decrease, while the δ_sCH₃ (1390 cm⁻¹), δ_{as}CH₃ (1470 cm⁻¹) and βCH₂ (1445 cm⁻¹) bands increase in intensity as the firing temperature increases. At the same time, the overlap of the bands and bandwidths show a decreasing tendency. Coordination of the alcohol is made most likely via the O-H group. These processes are most intense in the 120 150 °C range, since the mass spectrometric ion intensity curves show maxima at 130 and 150 °C. Over 150 °C the coordination of the residual solvent is somewhat changed, as indicated by the relative intensity increase of the alcoholic O-H deformation bands (1423 1400 cm⁻¹) and the increased diffusivity of the peaks. At the same time, the relative intensity and bandwidth of deformation bands of O-H groups connecting to tin are increased (970 -910 cm⁻¹). Considering that the O³⁷Cl⁺ (and also the Cl₂⁺) ion intensities decrease considerably until 200 °C, tin-hydroxy-chlorides and tin-oxides/hydroxides will be present at the end of the thermal decomposition process. As a consequence broad, closely overlapping characteristic Sn - O bands appear in the 750 - 430 cm⁻¹ range [11-17]. The appearance of tin-oxides is accompanied with the increase of the

oxidation number of tin as well, resulting in the presence of Sn^{II}- and Sn^{IV}-oxides in the film. Since the residual solvent and its decomposition products are strongly connected to the film, ν CH and β CH bands are still present in the DRIFT spectrum even at 300 °C (in the 3000 - 2800 and 1500 - 1350 cm⁻¹ ranges).

The cracking of strongly coordinated organic species starts over 200 °C and is not finished by 350 °C, since C-H deformation bands can still be found in the DRIFT and IRES spectra in the 1500 - 1350 cm⁻¹ range (Figs. 3 and 5).

The presence of ν OH and β OH bands (in the 3630 - 3100 cm⁻¹ and the 1607 - 1600 cm⁻¹ region, respectively) in both the DRIFT and IRES spectra at higher temperatures is of considerable importance. The peak at 1604 cm⁻¹ (as a shoulder of the band at 1567 cm⁻¹) in the IRES spectra (Figure 5) can be assigned as water deformation band. This band can be observed even at 350 °C. Since the IRES spectra were recorded in argon atmosphere at specified temperatures (without subsequent cooling back to room temperature after each step), the uptake of water from the atmosphere can be excluded. A band at 1605 ± 3 cm⁻¹ can also be observed in the DRIFT spectra even at 400 °C. The bandwidth is gradually decreasing up to 150 °C (from 21 to 14 cm⁻¹) then increases again (from 14 to 24 cm⁻¹ till 400 °C). It can be supposed that some kind of coordination water is present in the film. Deconvolution of the ν OH spectral range supports this idea. According to literature data [12] the alcoholic ν OH band does not appear in the spectral range below 3330 cm⁻¹, not even when strong hydrogen bonds are formed. At the same time -as a result of peak deconvolution- a band component of continuously decreasing intensity was obtained in the 3258 - 3108 cm⁻¹ range assigned as ν OH vibration. Since in the DRIFT spectra ν OH bands are still present after the complete removal of organic residues, it can be concluded that tin-hydroxy compounds are formed. According to literature sources [14-17] tin can form Sn(OH)₂-O-Sn(OH)₂-O- type polymer chains in which the OH groups remain stable even at elevated temperatures. Deconvolution of the 1200 - 800 cm⁻¹ range of the film heated to 400 °C results in the appearance of bands at 1053 and 926 cm⁻¹ in the DRIFT spectrum. These bands can be assigned as OH librations in two different chemical environments.

It is important to note that tin-containing catalyst coatings prepared from organic solutions contain residues with C-C and C=C bonds as a result of the firing process [13]. These bonds appear at about 1100 cm⁻¹ and in the 1610 - 1600 cm⁻¹ range. Indeed, deconvolution of the 1700 - 1500 cm⁻¹ range resulted in band components at 1540, 1605, 1640 and 1685 cm⁻¹. The band positions moved to higher frequencies with the increase of the temperature. Since the

1605 cm^{-1} band shows a shift of 3 cm^{-1} only, it is present in the spectrum with practically the same intensity independently of the temperature, it is unlikely that it belongs to fragment with C=C bond.

In the IRES spectra a band at 2086 cm^{-1} is observed in the 150 - 350 °C range. This band cannot be observed in the DRIFT spectra. Since a DRIFT spectrum is recorded from the surface only, while an IRES spectrum provides spectral information on the surface layer, this band can be assigned to terminal $-\text{C}\equiv\text{O}$ group present in deeper layers of the film. Carbon-oxides originating from the decomposition of organic solvents can be connected to surfaces in the forms of carboxylates, carbonyls and carbonates [18-21]. The MS ion intensity curves shows CO_2 evolution at 130, 150, 300 and 380 °C. The bonding of carbon-oxides cannot be assigned to a single structure in a heterogeneous surface thin film of complex structure. It is believed that the bands in the DRIFT spectra in the 1700 - 1500 cm^{-1} range belong to C=O functional groups present primarily in carbonate-type surface species even at 200 °C.

4. Conclusion

The use of thermal analysis combined with different types of spectroscopic techniques is essential to reveal the formation mechanism of a tin oxide thin film prepared by the sol-gel method. The thermal decomposition of the precursor salt is rather complicated leading to the formation of different organic and inorganic surface species as a function of the firing temperature. These processes play an important role in the development of surface morphology and pore structure. Knowing the thermal behaviour of this one-component system, the understanding of the formation of different mixed oxide systems with SnO_2 as one of the components can be attempted. Knowing the thermal history of the films, tailoring the properties of thermally prepared thin films can be facilitated.

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7. Legends

Table 1. Assignment of infrared bands identified in the deconvoluted spectra as a function of the firing temperature.

Figure 1. Thermogravimetric (TG), derivative thermogravimetric (DTG) and mass spectrometric ion intensity curves of a $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ coating ($m/z=44$: CO_2^+ , $m/z=53$: O^{37}Cl , $m/z=29$: C_2H_5^+).

Figure 2. DRIFT spectra of a $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ film heated to different temperatures.

Figure 3. Deconvolution of the DRIFT spectra in the 800 to 1400 cm^{-1} range.

Figure 4. Deconvolution of the DRIFT spectra in the 1350 to 1500 cm^{-1} range.

Figure 5. Emission infrared spectra of a $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ film heated to different temperatures.