



Research

Thermal Analysis of Supported Thin Films within the Nanostructurome Pipeline

Cerc Korošec Romana^{1,*} and Lavrenčič Štanga Urška¹

¹ University of Ljubljana, Faculty of Chemistry and Chemical Technology, Večna pot 113, SI-1000 Ljubljana, Slovenia

* Correspondence: romana.cerc-korosec@fkkt.uni-lj.si

Citation: Cerc Korošec R, Lavrenčič Štanga U. Thermal Analysis of Supported Thin Films. Proceedings of Socratic Lectures. 2025, 12(III), 89 – 93.

<https://doi.org/10.55295/PSL.12.2025.III11>

Publisher's Note: UL ZF stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2025 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

Abstract:

A comparison of the results obtained with thermoanalytical techniques can show considerable differences between thin film samples and the corresponding xerogels/powders. One reason for this is that the substrate material itself influences the properties and morphology of the deposited films. It therefore makes sense to carry out measurements for thin film samples that have been deposited on a substrate. Thermogravimetric and differential scanning calorimetry measurements on thin films are possible even if the mass of the thin film on a massive substrate is very small. With the described approach, it is shown that each chemical system behaves differently depending on the type of precursor and deposition method, but nevertheless the results of the thin film measurements are helpful in optimising the properties of the final films for a specific application.

Keywords: Thermal analysis; Thin films; Supported films; Thermogravimetry; Differential scanning calorimetry; Nickel oxide

1. Introduction

The applicability of different types of thin films is becoming increasingly important both in science and in many areas of modern technology (Leskelä et al., 1993). They change the chemical and/or physical properties of the substrate and can be used for various purposes, e.g. as surface protection against corrosion, wear and abrasion, as optically active coatings or as coatings for certain chemical applications (Niinistö, 1999), including photocatalytic coatings (Šuligoj et al., 2022). The preparation of thin films involves several steps, from the synthesis of precursors to the final application. The characterization of the prepared films as well as the understanding of the processes by which they are prepared are important for the optimization of the preparation process.

After the film has been deposited on the substrate using one of the chemical or physical deposition techniques, thermal treatment is required. During heating, sufficient adhesion of the film to the substrate is ensured; in addition, certain chemical reactions can occur, during which the structure suitable for the application is formed. For the latter, thermoanalytical techniques allow the determination of the temperature window within which it is essential to monitor the development of the structure using *ex-situ* diffraction and/or spectroscopy techniques.

Thermoanalytical measurements on thin films (thickness below 1 µm) deposited on a planar substrate are a demanding procedure and routine measurements are not yet common. The reason for this is that in thermogravimetry (TG) the mass changes are in the range of buoyancy and aerodynamic effect, while in differential scanning calorimetry (DSC) the heat released or consumed by the sample diffuses into a more massive substrate, so the thermal changes are often below the detection limit (Niinistö, 1999; Cerc Korošec and Bukovec, 2006). Therefore, measurements are performed on the corresponding xerogel powders instead. There are several reasons why thermally induced effects occur at different temperatures for both types of chemically equivalent samples (Przyłuski et al., 1981; Cerc Korošec et al., 2008). Since explanation of the properties of thin films based on TG and DSC measurement results of the xerogels could lead to misinterpretations, it is important that the measurements are performed for thin films themselves.

In this contribution, a protocol for TG and DSC measurements of thin films deposited on planar substrates is briefly presented.

2. Materials and Methods

2.1. Preparation of Thin Films for Thermoanalytical Measurements

Thin film can be deposited from the sol (colloidal solution) by dip or spin coating. Various substrate materials can be used: microscope cover glass (**Figure 1A**), thin platinum foil (thickness 0.025 mm), aluminium foil (**Figure 1B**) (Cerc Korošec et al., 2003). The substrate must be inert (must not react with the thin film) and must withstand the high temperature. For example, microscope cover glass is not a suitable substrate for temperatures above 650 °C because it undergoes a glass transition; in this case, Pt foil can be used. After drying, the microscope glass covered with a thin film is placed between two clean sheets of paper and pressed so that the glass broke into small pieces (**Figure 1C**), which could be placed in a 150 µL Pt crucible (**Figure 1D**).

For DSC measurements, two circles large enough to cover the thermocouples can be cut out of the Pt foil mentioned above; the uncoated circle is used as a reference, while the other is covered with the sample. The underside of this circle is cleaned, dried and placed directly on the sample side of thermocouples (the thin film is deposited to the top side of this circle).

2.2. Instrumental

Measurements were performed on a Mettler Toledo TG/SDTA 851^e Instrument and DC analysis on a Mettler Toledo 20 Cell; all in dynamic air atmosphere and with a heating rate 5 K/min.

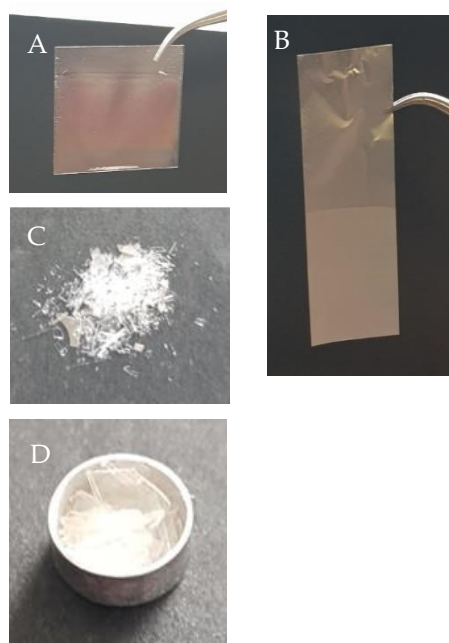


Figure 1. Thin film, prepared by sol-gel method and deposited on a microscope-cover glass by dip-coating – A, on aluminium foil – B; broken pieces of microscope cover glasses with deposited film – C, and pieces of the latter in 150 µL Pt crucibles – D.

3. Results

Figure 2A shows a comparison of the dynamic TG curves of thin film and corresponding xerogel. The thin film was prepared by alternately dipping deposition from NiSO_4 and a LiOH solution, while the xerogel was formed by mixing the two solutions and drying the slurry at room temperature. Onset temperature at which NiO forms differs by more than 100 degrees (220°C for the thin film and 325°C for the xerogel sample). The reason for this is the formation of carbonate anions in the thin film structure (they are formed during the reaction between atmospheric CO_2 and the alkaline surface of the thin film), while sulfate anions are present in the xerogel samples (they originate from the precursor) (Cerc Korošec et al., 2008). The reason for the large difference in thermal stability is therefore different anionic species; sulfate anions stabilize the primary hydroxide structure that forms at room temperature. From **Figure 2B** it is evident that the temperature difference for NiO formation in sol-gel films and xerogels is only 30 degrees. In this case, the reason most likely lies in the smaller aggregates of colloidal particles in the thin film sample, which have a higher surface energy. **Figure 2C** represents the results of the DSC measurement of the thin film described above (**Figure 2B**); when the film was applied to aluminium foil, cut into small pieces and placed in a crucible covered with a pierced lid, a curve was obtained. If the film was applied to a Pt circle and placed directly on the thermocouples (as described in Materials and Methods), a different result was obtained, which is shown in curve b). The reason for this difference lies in the fact that in an open system the gasses formed during thermal decomposition can easily leave the system. Therefore, the initial temperature is lower (265°C) compared to a partially closed system in which an equilibrium reaction $\text{A(s)} \leftrightarrow \text{B(s)} + \text{C(g)}$ raises it (295°C), according to Le Chatelier's principle. The results of thermal treatment optimization, based on TG measurements of thin films, are for NiO sol-gel films for electrochromic applications summarized in (Cerc Korošec and Bukovec, 2006).

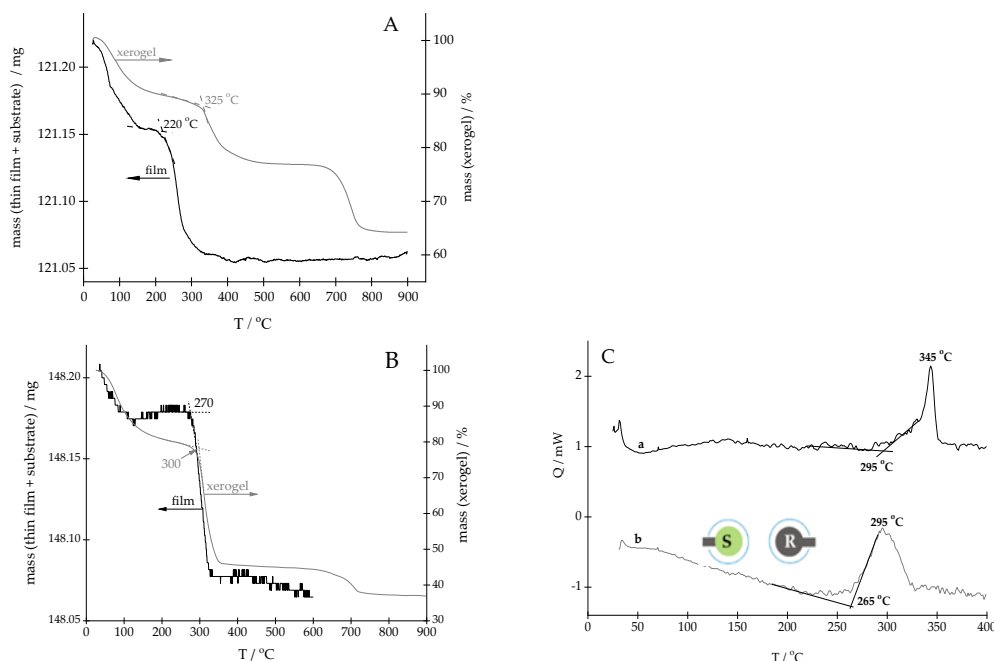


Figure 2. Comparison of TG measurements between supported thin films and corresponding powders for $\text{Ni}(\text{OH})_2$ samples, prepared by alternately dipping deposition – A, sol-gel prepared thin films and xerogels – B, and DSC curves of the films, prepared by the sol-gel method, for two different measurement approaches – C.

4. Data on Procedures and Samples

Data on procedures and samples are given in **Table 1**.

Table 1. Data on procedures and samples

Description of the sample	Sol (colloidal solution) in glass container or solid sample.
Aliquots needed	1
Total volume of the sample	5 mL (liquid) or 10 mg (solid sample)
Time required to obtain results	2 weeks
Manpower	Highly skilled researcher (thin films analysis) or researcher (solid sample)
Estimated cost per sample without manpower	250 EUR (thin films analysis) or 150 EUR (solid sample)
Contact person	Romana Cerc Korošec, romana.cerc-korosec@fkkt.uni-lj.si

5. Discussion

In some cases, the thermal analysis of thin films can be carried out in the usual way as for a xerogel/powder sample: I) when the thin film exists as a free-standing film, e.g. thin metal films or thin films of polymers; II) when the film is deposited on a powdered substrate, e.g. mica or ceramic support, and III) when the thickness of the film exceeds 1 μm , in which case it can be scraped off the substrate. However, the results obtained for deposited thin film samples and the corresponding xerogels/powders may differ significantly. For this reason, and also if the film is very thin (in this case it is impossible to obtain a sufficient mass of the film by removing it from the substrate), it is possible to obtain reliable results from TG and DSC measurements of supported films.

6. Conclusions

Thermal analysis of thin films deposited on planar substrates requires a special approach, but the results are useful for understanding the processes that take place during thermal treatment, even on a larger scale for industrial applications.

Funding: This research was supported by Slovenian Research Agency through the core funding No. P1-0134 and University of Ljubljana interdisciplinary preparative project Nanostructurome 802-12/2024-5.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Cerc Korošec R, Bukovec P, Pihlar B, Padežnik Gomilšek J. The role of thermal analysis in optimising the electrochromic effect of nickel oxide thin films prepared by the sol–gel method. Part I. *Thermochim Acta*. 2003; 402: 57-67. DOI: 10.1016/S0040-6031(02) 00537-3
2. Cerc Korošec R, Bukovec P. Sol-gel prepared NiO thin films for electrochromic applications. *Acta Chim Slov*. 2006; 53: 136-147. WOS:000238295100003
3. Cerc Korošec R, Šauta Ogorevc J, Draškovič P, Dražić G, Bukovec P. Electrochromic nickel oxide/hydroxide thin films prepared by alternately dipping deposition. *Thin Solid Films*. 2008; 516: 8264-8271. DOI: 10.1016/j.tsf.2008.03.014.
4. Leskelä M, Leskelä T, Niinistö L. Thermoanalytical methods in the study of inorganic thin films. *J Thermal Anal Cal*. 1993; 40: 1077-1088. DOI:10.1007/bf02546867
5. Niinistö L. From precursors to thin films: Thermoanalytical techniques in the thin film technology. *J Therm Anal Cal*. 1999; 56: 7-15. DOI: 10.1023/A:1010154818649
6. Przyłuski J, Płocharski J, Bujwan W. Application of thin-film DTA to amorphous selenium layers. *J Thermal Anal*. 1981; 21: 235-238. DOI: 10.1007/BF01914206
7. Šuligoj A, Cerc Korošec R, Žerjav G, Novak Tušar N, Lavrenčič Štangar U. Solar-driven photocatalytic films: synthesis approaches, factors affecting environmental activity and characterization features. *Top. Curr. Chem*. 2022; 380: 51. DOI: 10.1007/s41061-022-00409-2