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# FROM PRECURSORS TO THIN FILMS – Thermoanalytical techniques in the thin film technology*

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## Abstract

Processing thin films for advanced applications, for instance in electronics and optoelectronics, involves several steps starting from precursor synthesis and ending up with the devices. Especially when optimizing the first steps of this chain of processes, thermoanalytical techniques play an important role. The review will focus on the main chemical deposition methods (CVD, ALE, spray pyrolysis, sol-gel) giving selected examples of problem-solving by thermal analysis. The techniques discussed are TG, DTA/DSC, EGA and their combinations. High-temperature X-ray diffraction (HTXRD) is also a powerful tool for *in situ* studies of thin films. The examples are taken from solar cell, superconductor and flat panel electroluminescent display technologies.

**Keywords:** ALE, CVD, DSC, DTA, EGA, EL display, solar cell, sol-gel, spray pyrolysis, superconductor, TG, thin films

## Introduction

From the very beginning thermal analysis (TA) has been used to study inorganic materials, first exclusively in the bulk form [1, 2]. With their present high level of sophistication the thermoanalytical techniques and instruments are now capable of investigating thermally induced changes occurring also in thin films where the amount of available sample is small, typically below 1 mg $cm^{-2}$. This widens the application range of thermal analysis to thin film technology which plays a key role in developing new materials, processes and devices especially for microelectronics and optoelectronics industries [3, 4].

Recent examples of new materials with a high application potential both as thin films and powders include the fullerenes and high-temperature superconductors. In both cases thermal analysis was employed to study these novel materials immedi

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ately after their discovery and especially for the synthesis and characterization of superconductors the thermoanalytical methods have proven to be indispensable [5–7].

In general, thermal analysis is now becoming a frequently used group of techniques to solve problems in depositing and characterizing materials in the form of thin films [8]. The enhanced use of TA is due to several factors including the increased use of chemical deposition methods for thin films where the precursors and processes can be conveniently studied by thermal analysis. Also the general trend towards soft chemistry ('chimie douce') favors the development of new processes which aim at savings in materials, energy and environment [9]. Thin films and lower processing temperatures contribute towards this goal.

## Thin films and their deposition processes

A generally accepted definition for thin films is not available but a common usage is to define them by thickness, i.e. layers below 1 μm are called thin films. According to another definition, thin films are layers prepared by a thin film deposition method even if the layer thickness is some μm. Most electronic and optoelectronic devices employ thin films with layer thicknesses below 1 μm, however.

**Table 1** Examples of thin film applications

| | |
|---|---|
| Protective coatings | TiN, TiC for wear protection |
| Transparent optical coatings | ZnSe for wide range of transparency |
| Contacts, interconnects | Various metals such as W, Pt, Ag, Au, Cu, Al |
| Semiconducting films | GaAs for devices |
| Photoconductive films | CdTe for solar cells |
| Superconducting films | $YBa_2Cu_3O_{7-\delta}$ for SQUIDS |
| Insulating films | $Al_2O_3$, $SiO_2$ |
| Luminescent films | ZnS:Mn for displays |
| Lubricant films | $MoS_2$ |
| Antireflection coatings | $CeO_2$ |
| Transparent conductors | $In_2O_3$–$SnO_2$ (ITO) |
| Gas sensors | $SnO_2$ |
| Thin film capacitors | $BaTiO_3$, $PbTiO_3$ |
| Piezoelectric films | $LiNbO_3$ |

The applications of thin films are widespread in modern technology. Table 1 gives some examples of inorganic thin film materials and their uses.

## Thin film deposition methods

A practical way to divide the thin film deposition methods into two groups is to look at the nature of the deposition process: physical or chemical. The physical methods include evaporation, laser ablation, molecular beam epitaxy (MBE) and sputtering. The chemical methods comprise gas phase deposition methods and solution techniques. The gas phase methods are chemical vapor deposition (CVD) [10] and its novel variant, atomic layer epitaxy (ALE) [11, 12], while spray pyrolysis, sol-gel, spin and dip coating methods employ precursor solutions. As the final material is a solid thin film, the CVD and ALE processes involve the volatilization of the solid or liquid precursor and its transport and subsequent reaction on the substrate surface, viz. the sequence *s/l* → *g* → *s*. In solution techniques the sequence is *l* → *s*.

## Thermoanalytical techniques in the study of thin films

Although the thermoanalytical techniques and their combinations are essential for the analysis and development of materials [13], they are seldom directly applied to thin films. This is due to the fact that sensitivity is in most cases not high enough for a standard TA technique because of the minute amount of sample available and it being on top of a substrate [3]. Practically the only exception to this rule is the use of high-temperature X-ray diffraction (HTXRD) which can directly measure the diffractogram from a thin film with a thickness of some tens of nanometers laying on top of the substrate (Fig. 1).

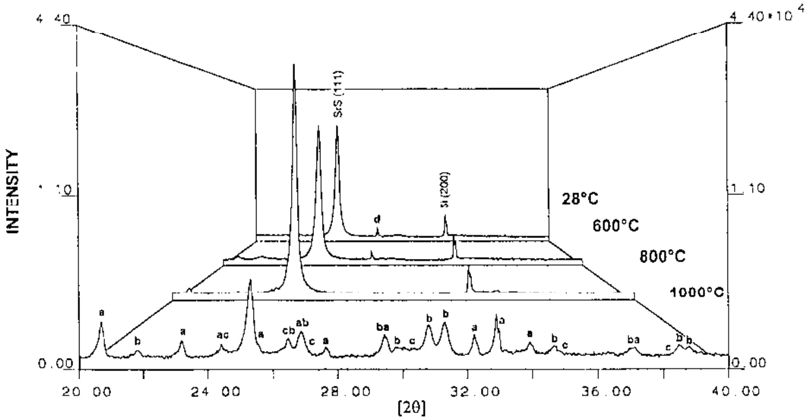

**Fig. 1** SrS thin film sample measured *in situ* by high-temperature X-ray diffraction (HTXRD) at (a) 28, (b) 600, (c) 800 and (d) 1000°C. The identification of peaks at 1000°C show that the thin film had reacted with air and the silicon substrate. Phase identification: a=$SrSO_4$, b=$Sr_2SiO_4$, c=$SrSiO_3$ [33]

Also, a high-sensitivity DTA/DSC instrument can be used in favorable cases to detect phase changes in thin films as seen in the case of polymorphic transformation

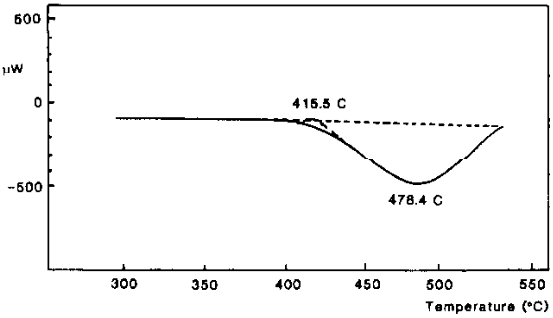

**Fig. 2** DSC curve recorded from a ZnS thin film showing the polymorphic cubic → hexagonal transition with an enthalpy change of 1.0 kJ $mol^{-1}$ [14]

of ZnS (Fig. 2) [14] or melting of $SnI_2$ thin film [15]. In principle, the sensitivity of emanation thermal analysis (ETA) is also high enough for thin film analysis but the interpretation of data is not straightforward [14]. A powerful new combination is simultaneous XRD-DSC which could be used in favourable cases also for the study of thin films [34].

| | |
|---|---|
| * melting, boiling points<br>* purity by DSC, DTA<br>* volatilization by TG<br>* gas phase species by EGA-MS<br>* simulation of thin film growth reactions by TG + DTA | Precursor synthesis and characterization |
| *In situ* monitoring of<br>* reactor atmosphere by MS, IR<br>* substrate surface by spectroscopic methods | Thin film growth by CVD, ALE |
| * Thermal degradation by TG, EGA, ETA<br>* Phase transitions by high-temperature XRD<br>* Reactions with the substrate by DTA/DSC, XRD | Thin film characterization |

**Fig. 3** Thermoanalytical methods applicable for the study of thin films deposited from the vapor phase by chemical methods (CVD, ALE) [3]

However, the picture will be quite different if we look at the possibilities of TA in the complete chain of processes starting from precursors and leading to thin films for applications (Fig. 3). Especially the first step, viz. precursor synthesis and characterization, calls for a comprehensive use of thermoanalytical techniques. For instance, essential information for the development and understanding of a solution deposition process (sol-gel, spray pyrolysis) can be obtained when the precursor decomposition reactions are studied under simulated thin film growth conditions by TG and DTA, preferably in a simultaneous mode.

## Electronic and optoelectronic materials – some selected examples

The following selected examples of the application of thermal analysis are taken from three novel technologies: flat-panel displays, superconductors and solar cells. They also illustrate how thermoanalytical methods can be used when thin films are processed by chemical methods either *via* gas phase (ALE) or *via* solution (sol-gel, spray pyrolysis).

It should be noted that in the recent literature there are many other examples of the use of TA techniques for advanced analysis of thin films. For instance, the formation of iridium oxide film electrodes has been studied by emission FTIR spectroscopy coupled with secondary ion mass spectrometry (SIMS) [35].

### *Thin film electroluminescent displays*

The TFEL displays consist of a stack of thin films where the functional core is an insulator-semiconductor-insulator structure [16]. Most research effort is directed towards the improvement of the quality of the doped semiconductor layer which in the case of the yellow monochrome display is manganese-doped ZnS. For full-color displays, rare earth-activated phosphors are commonly used, for instance SrS:$Ce^{3+}$ produces a blue-green emission in a high-voltage field.

A gas-phase deposition technique, ALE, is used in an industrial scale to produce the TFEL displays. TG/DTA measurements under vacuum (1–5 torr) are used to simulate the conditions on an ALE reactor when checking the precursor batches on developing new precursors [17, 18]. Generally the precursors should be completely volatile in a reasonable temperature range (200–300°C) without leaving a solid resi-

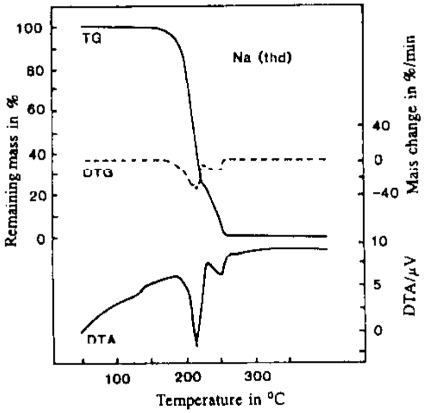

**Fig. 4** TG, DTG and DTA curves for a volatile sodium-diketonate complex Na(thd) (thd=2,2,6,6-tetramethyl-3,5-heptanedione). Sample mass is 10 mg, heating rate 10°C $min^{-1}$ and the pressure 2 mbar [20]

due indicative of thermal decomposition (Fig. 4). Simple inorganic compounds can seldom be used but instead organometallics and complexes with organic ligands which may in the gas phase dissociate and recombine in a complex manner. In order to understand the gas phase behavior, complementary MS studies are necessary [17–20]. Only by combining TG and MS data with crystallographic molecular structure determination it was possible to resolve the complex volatilization mechanism of zinc acetate involving the formation of a tetrameric complex $Zn_4O(CH_3COO)_6$ which led to the observed higher growth rate [21].

## *New oxide-based high-$T_c$ superconductors*

Thermal analysis can be applied to study several aspects of high-$T_c$ superconductor chemistry and physics including synthesis, stoichiometry, thermal expansion, phase transformations and chemical reactions [5]. The thermoanalytical techniques have proven to be especially powerful when determining the oxygen stoichiometry [6, 7] or when developing sol gel processes [22 24].

In a similar way as new precursors for TFEL displays are developed [17], TG can be used to evaluate the CVD precursors for oxide superconductors $YBa_2Cu_3O_{7-x}$ and $Tl_2Ba_2CaCu_2O_8$ [25, 26]. For CVD work it is also important to determine from the TG data the sublimation rate and its stability.

Using solution techniques it would be favorable to use a single-source precursor when preparing materials by thermal decomposition, for instance $SrTiO_3$ can be pre-

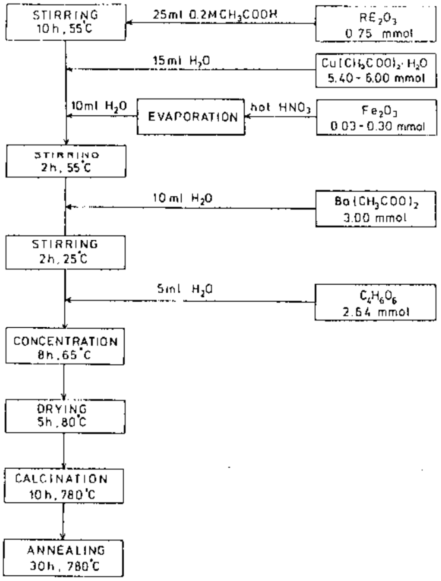

**Fig. 5** Preparation of superconducting $(Y_{1-x}Eu_x)Ba_2(Cu_{1-y}Fe_y)_4O_8$ samples by the acetate/tartrate sol-gel method [23]

pared from strontium titanyl oxalate [27]. A single-source precursor would in most cases guarantee that the decomposition product has the right ratio of the metallic components. For the new superconductors, however, it is not possible to prepare a single precursor containing all the three or more metallic constituents. Instead, the sol-gel process employs a mixing of the components in appropriate ratios and then decomposing the dried mixture. This process easily allows for the use of additional components as dopants as seen in the case of Eu- and Fe-substituted $YBa_2Cu_3O_{7-x}$ for Mössbauer spectroscopic studies (Fig. 5) [23].

Thermal analysis helps to establish the decomposition temperatures necessary and the mechanism of the decomposition. Preliminary information can be obtained from TG/DTA studies of single components forming the mixture but it should be noted that the final system is not a simple sum of the components. This is illustrated by case of $YBa_2Cu_3O_{7-x}$ preparation from Y, Ba and Cu periodate [28]. While the yttrium and copper periodates decompose around 500°C, the $Ba(IO_3)_2$ resists oxide formation even at 1100°C which is a too high processing temperature for $YBa_2Cu_3O_{7-x}$. However, when a three-component mixture is heated, the decomposition and formation of $YBa_2Cu_3O_{7-x}$ is complete already at 950°C.

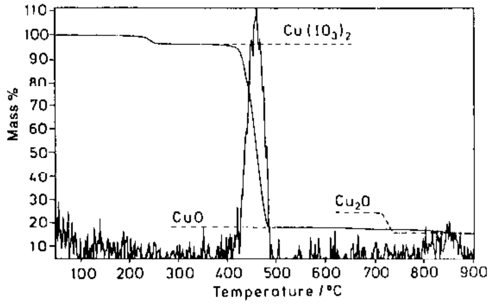

**Fig. 6** A simultaneous TG and EGA-MS study of $Cu(IO_3)_2 \cdot 2/3H_2O$ showing oxygen evolution at 400–500°C [28]

Evolved gas analysis (EGA) is a powerful tool for clarifying the reaction mechanism. In the periodate case, an EGA-MS system [29] clearly showed the oxygen evolution (cf. Fig. 6) [28], while in the study of the acetate/tartrate gel EGA was used to monitor $H_2O$ and $CO_2$ evolution [23].

## *Solar cell materials*

Our last example comes from the solar cell technology where low-cost, large area applications favor a simple chemical deposition technique such as spray pyrolysis. The materials include simple or ternary sulfides among which CdS, $Cu_{2-x}S$ and $CuInS_2$ are most often employed. The materials have also other applications in photodetectors and gas sensors.

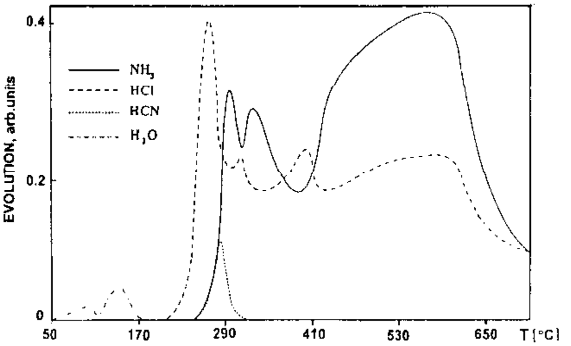

**Fig. 7** The evolved gases by FTIR-EGA from $Cu(SCN_2H_4Cl)\cdot 0.5H_2O$ in a (He+10% $O_2$) mixture [31]

Because spray pyrolysis is a thermal process, TA can be used to study the decomposition mechanism in order to optimize the process as regards temperature, stoichiometry, carbon residues and other parameters. When doing this it is advisable to use model compounds which have the same or nearly the same stoichiometry as spray pyrolysis solutions.

Thus because CdS and $Cu_{2-x}S$ can be prepared by spray pyrolysis from corresponding metal chloride solutions containing thiourea (tu), the model compounds synthesized contained also tu and Cl in various ratios [30–32]. The decomposition process of such compounds is very complex and dependent on atmosphere. Without having *in situ* FTIR-EGA data and *ex situ* XRD results for the residues and intermediates it would not be possible to interpret the TG/DTA curves. Especially the EGA data reveal some surprising details which have influence on the industrial process design and precautions. For instance, it was shown that in the temperature around 290°C some HCN is evolved when the model compound $CutuCl\cdot 0.5H_2O$ is heated in air (Fig. 7) [31].

## Concluding remarks

From the preceding discussion and examples it is obvious that thermoanalytical techniques can make an important contribution to the thin film technology. While direct TA measurements of thin films are still not very common, studies related to chemical deposition processes are rapidly increasing in number. The most successful techniques for direct studies of thin films are high-temperature XRD and DSC/DTA while TG and EGA are applied for precursors and processes. For enhanced information content and a better interpretation of the data it is advantageous to use, instead of a single technique, two or three TA methods which complement each other.

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