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THERMOANALYTICAL METHODS IN THE STUDY OF INORGANIC THIN FILMS

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Thermoanalytical (TA) methods are relatively seldom applied for assessing the physical and chemical properties of thin films, but they can be used in studies of composition, phase transitions and film–substrate interactions. In the present paper the possibilities of TA methods in thin film studies are reviewed. The thermoanalytical methods considered are the classical TG and DTA/DSC methods but some complementary methods will also be briefly mentioned. The main emphasis is given to true thin films. Details of sample preparation are also given. An important application of TA methods is characterization of precursors for the CVD growth of thin films, and this is also discussed.

Keywords: DTA/ DSC, TG, thin films

Introduction

Thin films of different types play an important role in modern science and technology. Among the various deposition techniques, gas phase processes, especially CVD, are increasing in importance. To obtain films of high quality in a reproducible manner it is important to be able to control the whole deposition process, starting from source chemicals to final characterization of the processed films. In characterization of thin films, important properties to be determined include composition, thickness, structure, orientation, trace element content, possible dopant ion concentration, and film-substrate interaction. In addition, there are a number of special properties associated with the function or application of the thin films which must also be determined.

Numerous diffraction and spectroscopic methods can be applied for characterization of thin films. Thermoanalytical (TA) methods are seldom employed but may have useful applications in studies of composition, phase transitions and film–substrate interactions.

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Recently, Sawada and Mizutani [1] reviewed this topic in a comprehensive paper which unfortunately is available only in Japanese. According to them the number of papers dealing with TA investigations on thin films is approaching 300. The number of papers is significantly smaller if only studies of true thin films prepared from gas or liquid phase are taken into account. The other available review on thermal analysis of thin films by Gallagher [2] is also very recent. It highlights applications in electronic materials and contains 16 references.

In the present paper the possibilities of TA methods for thin film studies are reviewed. Thermoanalytical methods considered are classical TG and DTA/DSC methods. Main emphasis is given for true thin films and the more often studied thick films and free standing films are mentioned only briefly. Details of sample preparation are given because it is one of the most difficult steps in these studies. Sensitivity and its enhancement in TA measurements will also be discussed.

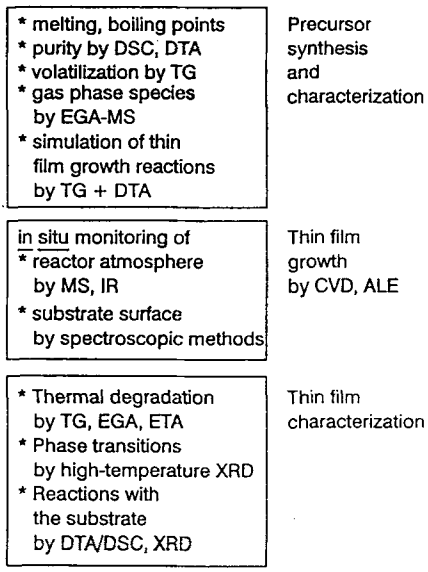

Fig. 1 Thermoanalytical methods in the study of thin films chemically deposited from the vapour phase

Figure 1 shows the various stages in preparation and characterization of thin films and lists the TA methods which can be used to study the preparative processes and the properties of resulting films.

One specially important application of TA methods is the characterization of precursors for the CVD growth of thin films where the use of solid source materials is increasing. The use of TA methods in the studies of volatility of the source materials and composition of gas phase will also be discussed.

Thin film samples

Thin film samples can be divided into different types [1]:

1. Substrate-free films
(i) films separated from substrate prior to measurement
(ii) free-standing films

2. Supported films
(i) films on planar substrates
(ii) films on powder substrates

The free-standing, substrate-free films are usually thin foils of alloys, so-called metallic glasses, prepared by fast quenching of a liquid phase. Several TA studies using DTA and DSC techniques have been carried out on crystallization of amorphous foils [Refs 3–5]. Films of oxide glasses can also be prepared by rapid quenching and their crystallization has been studied by DTA [6, 7]. Amorphous oxide glass films prepared by the sol–gel process comprise the other type of substrate-free films. The solution is spread, for example on polystyrene, dried and then the film is peeled off. In TA studies the weight and temperature changes during gelation and glass transition in the film can be studied [8]. Since the free-standing films are usually thicker than 10 μm, a piece of several milligrams can easily be broken off and studied as a bulk sample.

A competing method for studying crystallization of films is hot-stage X-ray diffraction, which is more frequently used to study phase transitions, reactions and crystallizations in powder samples [9]. The applicability of hot-stage XRD has significantly improved recently due to utilization of position-sensitive detectors and efficient data storage and display. Several papers on crystallization of amorphous alloy foils studied by hot-stage XRD have been published [10, 11]. *In situ* studies of reactions are also possible if the apparatus allows the use of various atmospheres.

Films on powder substrates can be studied by TA methods by treating them as usual powder samples, provided that the amount of film compared to the amount of substrate is high enough. The substrate, if inert, only reduces the thermal effects to be monitored. For example, in our study on TiO_2–mica pigments where the mica substrate flakes are fully covered by TiO_2 films (TiO_2 content 20–40%), TA measurements could be used to determine (i) the amount of TiO_2, (ii) the Ti precursor used, (iii) the deposition process used, and (iv) the type of mica substrate used [12].

In this review most attention is paid to films on planar substrates. The thickness of the films is usually less than 1 μm. For example, thin film structures needed in electroluminescent displays, consist of 0.5 μm thick II-VI sulfide layers and 0.25 μm thick oxide layers [13]. The amount of material in a sulfide layer is about 0.2 mg/cm^2 and in the oxide layer about 0.05 mg/cm^2. Problems to be studied by TA methods in these films include the thermal stability of the sulfide film, the possible OH^- and Cl^- impurity contents of the oxide layers, and diffusion

of ions between different layers. The oxide films prepared from metal chlorides and water in the gas phase may easily contain OH^- group. If only 10% of the material is hydroxide the sensitivity problems in TA measurements are obvious.

Preparation of samples

The most common way to prepare a sample is to separate the thin film from the substrate, after which TA measurements can be carried out for powders although handling of a small sample may be difficult. The usual way to separate the film from the substrate is by scraping [13–16]. Gallagher *et al.* [17] used a razor blade for detaching iron oxide thin films. Scraping is a practical method for thicker films (>1 μm) because the normal sample size (few mg) can be obtained from a small area. Problems appear when thin films (<100 nm) have to be studied and when the films adhere very strongly to the substrate.

Sometimes the film and substrate materials have very different thermal expansion coefficients (ceramic film on metal or *vice versa*). Following gas phase deposition at elevated temperatures the film may peel from the substrate during cooling and then a sample is easily available for TA measurements [10, 18, 19]. A common way to get a film to peel off is by thermal shock but this is not possible in preparation of samples for TA characterization.

One possible separation method is dissolution of the substrate. This has been utilized for polymer and metal substrates [19–21]. In the case of multilayer structures the uppermost film can be removed by dissolving the intermediate layer(s). This has been used for chalcogenide/B_2O_3/Si and Al_2O_3/ZnS/glass structures where B_2O_3 has been dissolved by water and ZnS by acid [22, 23]. Ni/Si layer samples for DSC have been succesfully prepared on photoresist/Si (or glass) substrates and the photoresist has been removed by acetone [24–26]. There is, however, a possibility that the solvent affects the composition of the film to be studied or small amounts of solvent remain in the film.

Easton *et al.* [27] studied the properties of EB-evaporated Mo-N films by DSC, XRD and conductivity measurements. The films were collected on a liquid nitrogen cooled Cu substrate and subsequently removed by applying a coating of collodion and stripping the film from the copper.

In some papers it is not clear whether or not the thin films have been removed from the substrate and, if they have been removed, how this has been done [28–30].

Sensitivity enhancements allowing study of films on substrate

Enhancements in TA systems

The sensitivity of balances in TG instruments is of the order of 1 μg and this is sufficient for thin film applications. But in the presence of substrate the film

material is 'diluted' 10^3–10^4 times and the weight changes take place in the range of buoyancy and aerodynamic effects and are difficult to assign. Lieb *et al.* [31] solved the problem by a homemade TG system which allows the use of large-area samples (1 cm width, 5–9 cm long) to ensure the adequacy of the film material. A small hole was drilled into the sample and this hung on a platinum wire.

Gallagher [2] succeeded in determining the content of carbon film on fused silica fibre and monitored a 100 μg weight change in a sample size of 30 mg. In order to achieve this the pure substrate was measured under identical conditions and the curve obtained was used as baseline and subtracted from the film/silica curve. This can be done if the substrate material is inert in the temperature range studied.

The use of so-called high-resolution TG [32] which in fact is the same as quasi-isothermal TG [33, 34], *viz.* heating is slowed down when a weight change begins, may improve resolution of the TG curve up to a level needed for supported films. In dedicated isothermal systems larger sample sizes can often be employed and consequently the amount of film material will be larger [35].

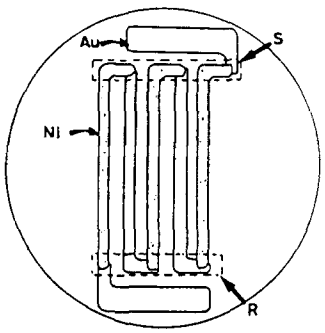

Fig. 2 DTA probe containing three thermocouples. The film is deposited in the *S* region and the reference region *R* is kept clear [42]

In calorimetric studies, the sensitivity can be improved by depositing the films directly onto classical thermocouples or metal ampoules which can be placed in a DTA or DSC instrument [36, 37]. Further improvements have been achieved by thin-film thermocouples [38] which allow enlargement of the measuring area to centimeter size [39]. The use of multiple or patterned thermocouples further improves the sensitivity and the sample sizes of 20–50 μg obtained are large enough for a reliable signal [40, 41]. In the case of V_2O_5 films (area 8 mm^2, thickness 300 nm) a few micrograms could be measured (Fig. 2) [42].

In DSC and DTA studies of supported films, sensitivity can be significantly enhanced by placing the film side in contact with the sensor [43]. Moreover, the reference sample should be of the same kind as that used for analysis. Using this method, films of $TaSi_2$ 150 nm thick and with an area of 15 mm^2 could easily be studied [44].

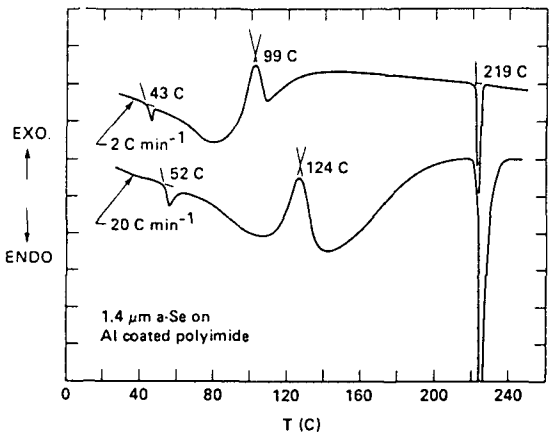

Fig. 3 DSC curves for 1.4 μm thick Se films showing the glass transition, crystallization and melting temperatures for two heating rates [45]

Thornburg [45] studied the crystallization of amorphous 1.4 μm thick selenium films deposited on polyimide or Al-coated polyimide sheets (diam. 6.3 mm) by DSC. Ten sample discs with Se films faced to each other were placed in the DSC pan. This yielded a total sample weight of 61 mg of which less than 2 mg was Se and gave reliable data (Fig. 3). Crystallization of Se and Bi-doped Se films on Al has been studied extensively by Grenet *et al.* [46] and by Atmani *et al.* [47–49] with DTA. In their measurements one sample disc (diam. 6.5 mm) was enough for enthalpy and energy determinations.

The formation of metal aluminides (Ti, Zr, Cr, Nb) in sputtered layers of Al (5 layers 4000 Å thick) and metal (4 layers 400–1200 Å thick) has been studied with DSC by Ball and Todd [51]. The films were deposited on Al foil and the foil was folded such that a sufficient amount of thin film material was available for DSC measurement. Ball *et al.* [51] also studied the influence of Cu and Si on the reaction between aluminium and hafnium metal layers. The kinetics of the intermetallic growth was determined by DSC.

Detection by other techniques combined to TA instruments

The sensitivity of TG measurements can be improved by the use of a magnetic field. Gallagher *et al.* [52] have shown that 1.5 μg of magnetic material or films as thin as 10–20 Å are enough for mesurements. The data yield reaction temperatures and kinetics but the weight change interpretation is not straightforward.

Evolved gas analysis by mass spectrometry (EGA-MS) is, in principle, a very sensitive technique and the TG-MS system can be used in thin film studies even when the TG curve does not show measurable changes. Its applicability has been demonstrated by Gallagher *et al.* in the characterization of an oxidized copper

surface and GaAs/Au contact as well as in the behaviour of hydrogen in boron nitride films [53–55].

Addition of optical detection systems to TA instruments improves the possibilities of observing thermal changes in thin film samples, as shown by Maeda *et al.* [56] in thermoreflectance studies of 165 nm thick Ag-Zn films.

Emanation thermal analysis (ETA) [57], which is based on the implantation and release of radioactive gas atoms during heating, is a sensitive method which can also be applied to study of thin films. When combined with other measurements, for example XRD, ETA measurements have yielded useful information on structural changes in ZnS thin films prepared by the ALE technique from different Zn precursors (Fig. 4) [58].

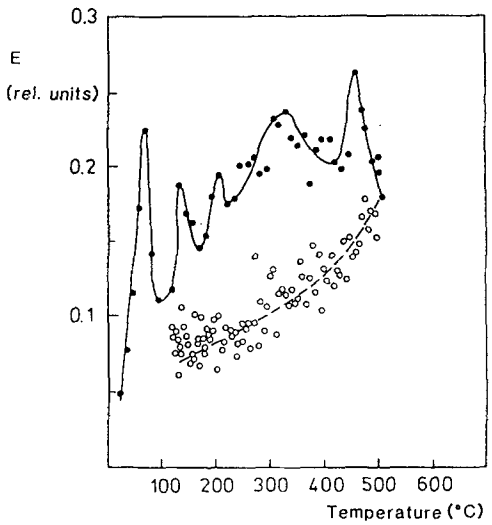

Fig. 4 ETA heating (–) and cooling (---) curves in flowing argon for a 650 nm thick ZnS film prepared from zinc acetate [58]

Structures and reactions of very thin films with thicknesses of a few nm can only be studied by transmission electron microscopy (TEM). Studies of thin films by TEM instruments with controlled heating rate are sparse, however. Instead rapid thermal annealing RTA-TEM systems are more commonly known and they are useful in the study of early stages in the solid-state reactions in multiphase layered thin films [59].

Materials studied by TA methods

TA studies of thin film materials removed from the substrate have been summarized by Sawada and Mizutani [1]. Table 1 presents a summary of studies

where thin films on substrate have been investigated. Glass transition and crystallization of electronic materials deposited on the thermocouple have most often been studied. In reaction studies isothermal TG has been applied. With small samples also, some kinetic studies have been carried out by DSC although the use of film samples removed from the substrate is more common in reaction studies with DSC [60].

Table 1 Examples of thin film/substrate materials studied by TA methods. The films have not been removed from the substrate

Film material/substrate	Property studied	Method	Reference
N-implanted Si/Si	Oxidation kinetics	TG	31
NbN/sapphire (quartz)	Oxidation kinetics	TG	35
Ga/thermocouple	Crystallization	DTA	36
As/thermocouple	Phase transition	DTA	37
Se/thermocouple	Glass transition/crystallization	DTA	39
As_2Se_3/thermocouple	Glass transition/crystallization	DTA	39
Ge_2Se_3/thermocouple	Glass transition/crystallization	DTA	39
In/thermocouple	Melting/crystallization	DTA	40
Se/thermocouple	Crystallization/melting	DTA	40
Se/thermocouple	Glass transition/crystallization	DTA	41
V_2O_5/thermocouple	Crystallization	DTA	42
Se/Al (kapton)	Glass transition/crystallization/melting	DTA	46
Se:Bi/Al (kapton)	Glass transition/crystallization/melting	DTA	49
$TaSi_2/SiO_2$	Crystallization kinetics	DSC	44
Al-Ti(Cr,Nb,Zr)/Al foil	Formation of aluminides	DSC	50
Al-Hf/Al foil	Reaction kinetics	DSC	51
IrO_2/Au	Crystallization	DSC/EGA	61
Co/sapphire (Si)	Oxidation/reduction	TM	52
CuO/Cu	Corrosion	MS-EGA	53
Au/GaAs	As evolution	MS-EGA	54
B_3N:H/Si	H_2 evolution	MS-EGA	55
ZnS	Structural transitions	ETA	58

Thin film precursors

Spray pyrolysis, dip-coating, spin-coating, the sol–gel method and the CVD technique are thin film preparation methods which are based on thermal decomposition (and reaction) of source materials (precursors). Thus, when these thin film deposition methods are used, the thermal decomposition, volatility and vapor

pressure of the precursors have to be known. TA methods and especially TG, are simple and useful ways to characterize the precursor properties.

The precursors may be elements, simple inorganic or organic molecules, metal complexes with inorganic or organic ligands, or metalorganic compounds. Thermal properties of elements and simple molecules are usually well known. On the other hand, properties of metal complexes and organometallics are often not well characterized and recent TA studies of precursors have concentrated on these compounds. The use of metal complexes and organometallics as source materials is necessary because transition metals have not many volatile compounds and because of the need to keep deposition temperatures as low as possible.

For liquid-phase deposition precursors the important aspects to be studied are the decomposition temperature and composition of the end-product. Examples for TA studies comprise spray pyrolysis ($SnHPO_4 \cdot H_2O$) [62], dip-coating ($Si(OC_4H_9)_4$) [63], spin-coating ($LiNb(OC_4H_9)_6$ [64], and sol–gel technique ($SiO_{1.5}(CH_2)_3NH(HClO_4)_{0.1}$ [8].

In CVD deposition of III-V and II-VI compounds, metalorganic compounds are most often used. These are gases or volatile liquids and TA studies are not relevant. On the other hand, TA characterization of solid precursors is necessary. The volatility of metal complexes and their possible use in gas chromatography were intensively studied in the 1960s and 70s [65, 66]. Specifically, CVD deposition of high-temperature superconductors has increased interest in volatile compounds of alkaline earth and rare earth metals [67, 86]. These elements have very few volatile compounds and β-diketonates are the most promising among them (Fig. 5). β-diketonates are solid powders and relatively easy to prepare and handle. TA studies of CVD precursors for high-temperature superconductors have been reviewed comprehensively by Ozawa [68]. Recently, a series of new stable, volatile β-diketonates of Cu, Ca, Sr, Ba and Y have been characterized structurally and thermally [69]. Rare earth and alkaline earth β-diketonates have also been used in the preparation of electroluminescent thin film structures [70–72].

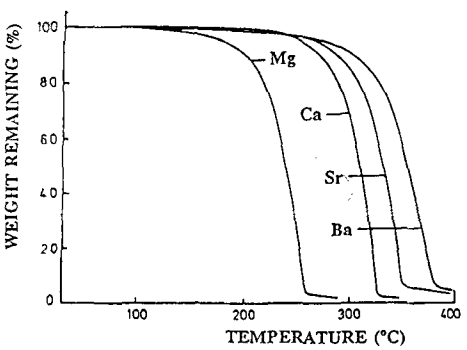

Fig. 5 TG curves for thd-chelates of alkaline earth metals (thd = 2, 2, 6, 6-tetramethyl-3, 5-heptanedione) [73]

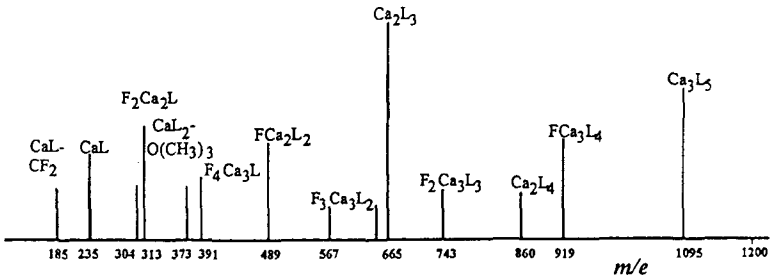

Fig. 6 Mass spectrum of calcium 1, 1, 1-trifluoro-5, 5-dimethylhexane-2, 4-dionate [85]

For gas phase deposition processes it is important to know which species exist in the gas phase and are participating in the film growth reaction. This has been studied by mass spectrometry [73]. The metal complexes may exit in the gas phase as clusters with high mass numbers and therefore UHV, high-resolution mass spectrometers with large mass range have been used (Fig. 6) [74, 75]. Conditions in MS and film processing reactors are not the same but, nevertheless, very useful data have been obtained by MS measurements [71, 76].

Besides rare earth and alkaline earth metal complexes the β-diketonates of most of the transition metals have been characterized by TA methods [77, 78]. Other volatile complexes and possible precursors for CVD processes are carboxylates [79], alkoxides [80, 81], thiocarbamates [82, 83] and some organometallics [84].

Conclusions

TA experiments using thin film samples are difficult to carry out mainly due to sample size requirements. However, due to the increasing importance of thin films for modern technology, it is expected that thin film TA techniques will develop and their use will increase since TA measurements can often provide information which can not be obtained by other techniques.

Supported thin films are the most difficult to study but, on the other hand, the results obtained are very useful for technical applications. Separation of film from substrate is tedious and during separation properties of the film may change. Many methods have been developed to overcome sensitivity problems encountered in the study of films on substrate. It appears that advanced techniques are needed where spectroscopical or microscopical measurements are combined with the TA techniques although such an instrumentation is often difficult to operate and expensive. Further increase in sensitivity of basic TA instrumentation would therefore be desirable but might be difficult to achieve.

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Zusammenfassung — Thermoanalytische Methoden werden relativ selten zur Beurteilung der physikalischen und chemischen Eigenschaften von Dünnschichten verwendet, können aber zur Untersuchung von Zusammensetzung, Phasenumwandlungen und Dünnschicht-Substrat-Wechselwirkungen eingesetzt werden. Es wird hier ein Überblick über die Möglichkeiten der TA-Methoden bei der Untersuchung von Dünnschichten gegeben. Die in Betracht gezogenen thermoanalytischen Methoden sind die klassischen Methoden TG und DTA/DSC, aber auch einige ergänzende Methoden werden kurz beschrieben. Das Schwergewicht liegt bei echten Dünnschichten. Es werden auch Details der Probenvorbereitung beschrieben. Eine wichtige Anwendung von TA-Methoden besteht in der Beschreibung von Präkursoren für das CVD-Wachstum von Dünnschichten und dies wird ebenfalls diskutiert.