Thermal analysis of metal organic precursors for functional oxide preparation: Thin films versus powders

P. Roura [a,*], J. Farjas [a], H. Eloussifi [a,c], L. Carreras [a,d], S. Ricart [b], T. Puig [b], X. Obradors [b]

[a] GRMT, Department of Physics, University of Girona, Campus Montilivi, Edif. PII, E17071 Girona, Catalonia, Spain
[b] Institut de Ciència de Materials de Barcelona, Consejo Superior de Investigaciones Científicas (ICMAB-CSIC), Campus de la UAB, 08193 Bellaterra, Catalonia, Spain
[c] Laboratoire de Chimie Inorganique, Faculté des Sciences de Sfax, Université de Sfax, BP 1171, 3000 Sfax, Tunisia[d]AMADE, Polytechnic School, University of Girona, Campus Montilivi, Edif. PII E17071, Girona, Catalonia, Spain
[d] AMADE, Polytechnic School, University of Girona, Campus Montilivi, Edif. PII E17071, Girona, Catalonia, Spain

A R T I C L E   I N F O

A B S T R A C T

The thermal decomposition of several metal organic precursors, used in the preparation of $YBa_2Cu_3O_{7-x}$ superconducting coated conductors (Cu acetate, Cu, Y and Ba trifluoroacetates and Ce propionate) is analyzed by means of several thermoanalytical techniques (TG/DTA, MS and DSC). In all cases, the metal organic precursors deposited as thin films decompose differently than powders from the same precursors. In thin films, decomposition is facilitated by the easier transport of reactive gas from the surrounding atmosphere and by the easier out-diffusion of volatile products. Consequently, films decompose at lower temperature and are more sensitive to the presence of any residual reactive gas in the furnace. Good thermal contact with the substrate is also shown to minimize overheating in films and avoid combustion processes that are otherwise often observed during the thermal decomposition of powders. Finally, the formation and stability of intermediate products towards the oxide formation, such as metal fluorides, differs in films because of the easier gas exchange. With respect to powders, these compounds are much less stable in films, where their decomposition temperature can be lowered by several hundreds of degrees Celsius. While in some cases the behaviour of films can be predicted by analyzing varying masses of precursor powders, this is not always the case. Therefore, thermal analysis carried out on films is recommended to avoid erroneous conclusions about materials preparation drawn from powders.

1. Introduction

Thermal decomposition of metal organic precursors is a current route for the synthesis of metal oxides in the form of powders, thin films or nanostructures [1–5]. Films can be obtained by chemical solution deposition (CSD) techniques. A solution containing the precursor is spread over a substrate and, after solvent evaporation, the film is pyrolyzed. By controlling the precursor concentration and spreading conditions, film thickness can vary from tens of nanometres to several microns. These techniques allow fabrication of low-cost oxide single or multilayers that find application in microelectronics [6], high-temperature superconductors [7–9], photovoltaic energy conversion [10], optical layers [11], ferroelectric devices [12], etc.

The oxide quality critically depends on the pyrolysis conditions (heating rate to the isothermal stage, temperature and furnace atmosphere) when metal organic decomposition takes place. At this point, thermoanalytical techniques (notably thermogravimetry (TG) coupled with mass spectrometry (MS) or infrared spectroscopy) are very useful because they give information about the decomposition temperature, decomposition mechanism and kinetics and allow prediction of the evolution of the reaction when the material is submitted to a particular temperature programme [13]. Since the signal delivered by any technique is proportional to the sample mass, m_i, thermal analysis experiments are usually done with the precursor in the form of powders (typically, $m_i > 5$ mg) [6], whereas experiments on films are very scarce (typically, $m_i < 1$ mg/cm^2). This is so because, for the low masses of films, the TG baseline instability impedes the accurate analysis of the decomposition mass-loss curve. Consequently, the question arises: "Is the information delivered by powders (e.g. decomposition temperature, final or intermediate products and their dependence on the atmosphere) valid for films?"

In this paper, we will show that, in general, one should expect a negative answer whenever the decomposition kinetics is controlled by a transport step. To be more specific, films are expected

to decompose differently than powders when the decomposition is controlled by: (a) transport of reactive gas (usually O_2 or H_2O); (b) evolution of gaseous species (reaction products or solvents) or (c) heat transport out of the sample (see the summary given in Fig. 1). All these aspects are not exclusive of decomposition processes but are intrinsic to most solid–gas reactions [14]. The fact is that, for most precursors we have analyzed to date, significant differences have been observed between powders and films. So, it is clear that optimization of the pyrolysis step can be hardly achieved with thermal analyses on powders. It is necessary to develop experimental procedures for measuring the decomposition directly on films or, alternatively, to establish criteria that would help to deduce the behaviour of films from that of powders.

Substrates can also have a catalytic effect on decomposition reactions through their chemical terminations (e.g. H^+ terminations on the surface of glass substrates enhance the decomposition of $Y(TFA)_3$ [15]) or by promoting epitaxial growth of the oxide. Film deposition requires the preparation of a solution that may in turn modify the molecular structure of the precursor. However, such an effect is absent in this present study because of the chemical similarity between solvents and salts (e.g. acetic acid and acetates). Furthermore, a surface energy difference between films and powders may also exist. Nevertheless, as these effects are not related to any transport mechanism they will not be analysed here.

The examples given below correspond to metal organic precursors used for the fabrication of $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting tapes. These tapes consist in the active superconductor layer (1–2 μm thick) separated from the metallic substrate by one or several oxide thin buffer layers such as ceria (CeO_2) or other oxides [16,17]. Additional examples published in a shorter format can be found in Ref. [18].

2. Experimental

Most precursors were used in their commercial form of powders: anhydrous $Y(TFA)_3$ was supplied by Aldrich, and $CuAc_2$ and $Cu(TFA)_2$ hydrate, by Alfa-Aesar. Ce propionate was synthesised from Ce acetate (see details in Ref. [19]) and $Ba(TFA)_2$ from Ba carbonate [20]. The powders were analysed inside alumina pans without cover to facilitate gases exchange (crucible section area, 0.2 cm^2). To obtain thin films, the precursor salts were dissolved in acetic or propionic acid and, then, a microdrop was spread on an appropriate substrate and dried below 100 °C or, alternatively, a spin coater was used. Thin glass discs, platinum foils or silicon and (001)LaAlO$_3$ single crystalline substrates were used depending on the experiment (typical area of one substrate side was 1 cm^2). To increase the mass of the samples, films were deposited on both

Fig. 1. Scheme showing several transport processes that can have some influence on the formation and microstructural development of oxide powders and films.

substrate sides and several (usually two) substrates were kept some mm apart inside the TG furnace, to allow gas exchange with the furnace atmosphere. The quoted thickness of the films is their "nominal thickness", i.e. the thickness the film would have if transformed into a dense oxide. In our studies we have found two kinds of films: (a) aggregates of particles [15] and (b) dense films [21]. However, the different behaviour between powders and films does not depend on this structural feature but on the fact that gas and heat transport is easier in films (see Section 3).

TG analyses were done with a SDTA851eLF apparatus from Mettler Toledo and a Setsys Evolution apparatus from Setaram under continuous flow of high-purity gases (usually 40 mL/min). The TG curves were corrected by the apparatus baseline, measured during a consecutive measurement under the same conditions. Additionally, the final mass of the sample was always measured and compared with that deduced from the TG curve. Significant discrepancies led us to discard experiments. These precautions were essential for the experiments on films. These apparatus simultaneously delivered the differential thermal analysis signal (DTA). For the differential scanning calorimetry (DSC) measurements, the DSC822 from Mettler Toledo was used. And finally, mass spectroscopy (MS) measurements were taken simultaneously to the TG curves with an MKS Spectra Quadrupole (Micro Vision Plus), which detects molecular fragments with $m/z < 300$ amu.

Several apparatus were used for the X-ray diffraction experiments (XRD): (a) Smart Apex diffractometer of Bruker AXS (with Mo X-ray source) where collection of the diffracted photons was done with a CCD detector that increases the experimental sensitivity at the expense of resolution; (b) conventional D8 Advance diffractometer from Bruker AXS in the $\theta - 2\theta$ configuration (Cu X-ray source); and (c) thin film diffractometer PANalytical model X'pert PRO MRD (Cu X-ray source). XRD spectra were analyzed using EVA software from SOCABIM and the JCPDS database from the International Centre of Diffraction Data.

3. Results and discussion

3.1. Transport of reactive gas: decomposition of Ce propionate

The dependence on m_i is easily understood due to the reactive gas consumption at the sample surface. Higher m_i implies faster gas consumption and, consequently, a less reactive atmosphere near the sample because of the higher concentration gradient between the sample surface (at the bottom of the crucible) and the free atmosphere (at the top of the crucible). Thus, T_{dec} must move towards the value for inert conditions when m_i increases. In the case of films, a higher mass corresponds to a thicker film. Consequently, the reactive gas must diffuse over a greater distance through the solid precursor and as a result decomposition will be slower (higher T_{dec}) for thicker films. Finally and given the same precursor mass for powders and films, because the crucible section is usually much smaller than the substrate area, the reactive gas will reach the film surface more easily than the powder and thus T_{dec} will be minimal for thin films.

These predictions are aptly illustrated by the TG curves corresponding to the decomposition of Ce propionate in air and N_2 (Figs. 2 and 3) [11,19]. Notice that powders decompose in air at a lower temperature when m_i diminishes, and that decomposition begins at the same temperature as in the inert atmosphere when m_i is high enough (see asymptotic behaviour in Fig. 3). Similarly and as to be expected, films decompose in air at a lower temperature when they become thinner (Fig. 2). The most interesting fact for our discussion is that, for the same initial mass T_{dec} is lower for thin films than for powders (Fig. 3). This behaviour is mainly due to the lower mass per unit area (substrate area for films and crucible se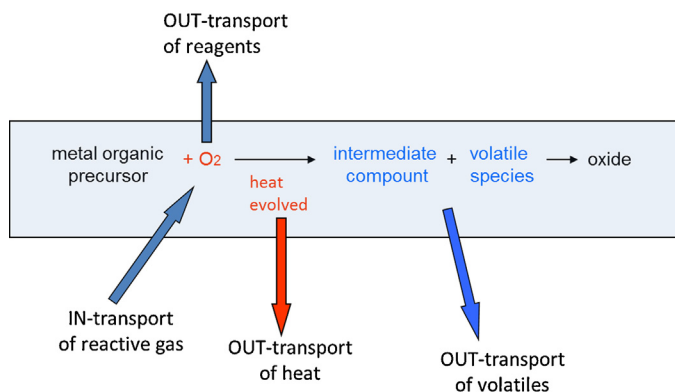ction for powders) of films. The