Inexpensive set-up for determination of decomposition temperature for volatile compounds

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Abstract

The utility of precursors for atomic layer chemical vapour deposition (ALCVD) growth is limited by the sublimation and decomposition temperatures. Sublimation temperatures are conveniently obtained by thermogravimetry (TG) under vacuum. We present here a relatively inexpensive method to obtain information about the decomposition temperature for a precursor candidate for ALCVD. This approach requires an oven with a controlled temperature gradient and a long ampoule for each precursor. The precursors tested in this work comprise the thd complexes (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, La, and Ca.
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1. Introduction

Atomic layer chemical vapour deposition (ALCVD, also named atomic layer epitaxy (ALE) or atomic layer deposition (ALD)) [1] is a thin-film growth process where the film is systematically manufactured by sequential gas pulses of two or more precursors, each pulse being followed by a purge of an inert gas. The precursor will for each pulse react with all surfaces in the reaction chamber and produce a chemically adsorbed layer. This layer will, in turn, function as a reactant for the following pulse in the precursor sequence. The growth will be limited to one monolayer of precursor per pulse, and is a self-limited growth process. Thermal decomposition of the precursors is highly unwanted since this will produce uncontrolled growth, and reliable information about decomposition temperatures for precursors is accordingly of great importance.

There are other criteria that apply for precursors used in ALCVD processes than for those in ordinary CVD growth. These have been surveyed thoroughly in [1,2], and among the many factors involved special attention has been focused on: volatility, stability, reactivity, etching, and purity. The most critical factors in this respect are that the precursors have to be volatile and thermally stable during the entire growth step they are involved in. The concern for the latter factors usually limits the lower and upper temperature windows for ALCVD growth. To select a precursor for ALCVD growth one therefore needs information about the sublimation as well as decomposition temperature.

The main criterion for precursors used in ordinary CVD growth is that they should be easily volatilised and that the precursor mixtures should not be too

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reactive so that undesirable gas-phase reactions are limited. Thermal decomposition of a precursor is not a problem here as long as the unwanted decomposition products are volatile and chemically stable under the conditions in the reaction chamber. Many CVD growth processes are based on thermal surface decomposition of one or more precursors.

In ALCVD growth, the precursors are used in a different way. The precursors are brought into the gas phase in more or less the same way as with normal CVD, but they should be reactive enough to react with all surfaces in the reaction chamber. In fact the precursors used for ALCVD may just as well be highly reactive since gas-phase reactions and associated problems are eliminated, but they should not decompose on any surface or in the gas phase. Decomposition hampers self-limiting growth and hence the control with, and quality of, the film diminishes. However, films may be formed with a tolerable thickness inhomogeneity even though a small part of a precursor is decomposing, but it should be recalled that the decomposition rate increases exponentially with temperature.

Information about sublimation temperature may conveniently be obtained by thermogravimetric (TG) analysis under vacuum. Vacuum should be used to mimic the conditions during the growth process, viz. in order to ensure comparable sublimation kinetics during the TG testing and the actual film growth. A simple method for determination of the decomposition temperature for a compound in the gas phase is apparently not described in the literature. Differential thermal analysis (DTA) or differential scanning calorimetry (DSC) can not be used since the precursors per definition are volatile. Attempts have been made to use mass spectrometry to determine the decomposition temperature for different precursors [3–5], but this method is cumbersome. Moreover, although mass spectrometry may give invaluable information about decomposition paths and products, it is an expensive technique and not even vaguely accurate enough when it comes to temperature control and determination unless precautions as mentioned in [3–5] are taken. A part of the problem stems from the fact that it is difficult to establish whether the precursor decomposes in the gas phase before it enters the mass spectrometer, or decomposes by the bombardment of electrons in the ion chamber. It would, of course, be possible to use softer ionisation, e.g., chemical ionisation with

$CH_5{}^+$, but such an approach is not often used for the purpose. Mass spectrometric analyses may, with rather large rebuilding of the units concerned, be integrated into the ALCVD growth chamber [6–8] and in this way give instant information about whether decomposition of a given precursor takes place during the deposition step. Another approach is to use IR analysis in different geometries [9], but this still requires rather sophisticated equipment and analyses.

This report concerns an inexpensive method that may be used to obtain information about the decomposition temperature of volatile compounds.

2. Equipment and procedures

A furnace with a well defined and controllable temperature gradient is needed. The present furnace (Fig. 1(a)) has an overall length of 1 m and includes eight separate zones. However, this turned out to be more zones than actually necessary. In the present equipment, the temperature was set by applying a constant voltage to each zone. This was supplied from one common voltage source that in turn was subjected to the variations in the current flow from the in-house outlet. This gave some variation in power to the eight-zone oven, and a resulting temperature fluctuation of ca. ±1% on the Celsius scale over a period of 1 day. It is of course possible to increase the temperature precision by applying separate temperature controllers for each zone, but this increases the cost of the system appreciably without improving the results noticeably.

A central design criterion for the equipment has been that the precursors should be exposed to the same type of environment as in the ALCVD reactor. This has been accomplished by making an ampoule of silica glass and loading it with a small amount of precursor, conveniently placed in an open container. The loaded ampoule is sealed under a pressure resembling that in the reactor during film growth, and inserted into the gradient oven with the precursor at a position where the temperature is close to the sublimation temperature. The precursor will then sublime and diffuse into the warmer parts of the ampoule where it decomposes at an appropriate temperature.

The thermal gradient in the oven is set so that the temperature profile give high resolution (low temper-
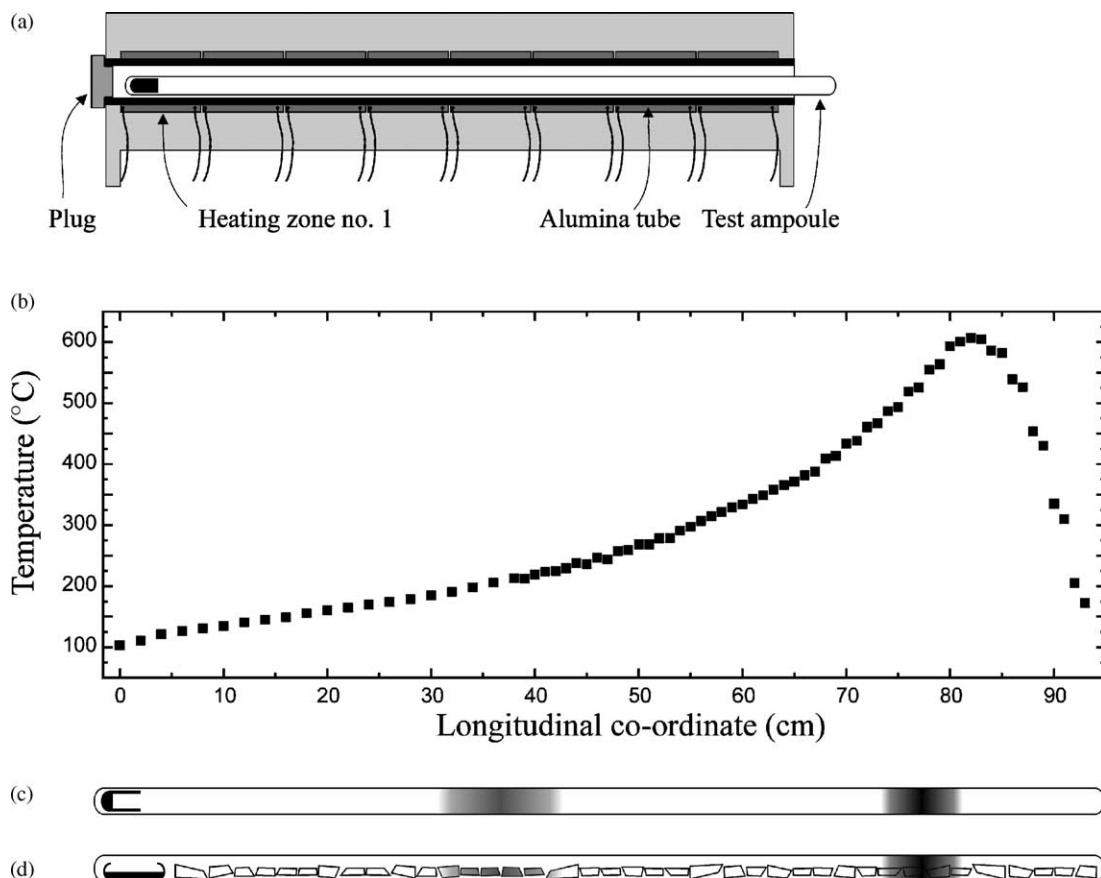
Fig. 1. (a) Gradient oven with decomposition test ampoule inserted. Separate power supplies for individual zones are indicated. (b) Typical temperature profile. (c) Schematic illustration of detection of decomposition deposits for complexes with coloured products. (d) Means to detect decomposition deposits for complexes with transparent or non-coloured products.

ature gradient) where needed and a low resolution (steep temperature gradient) otherwise. The thermal profile used during the tests described in this report is shown in Fig. 1(b). This gave a good resolution at the lower temperatures, where identification of possible thermal decomposition is most important for the selection of ALCVD-process parameters, and a sharp gradient at higher temperatures, where fragments from the first decomposition step degrade further. The occurrence of the latter residue also serves to prove that sublimation transport of the precursor material actually has taken part.

A convenient experimental procedure is: the gradient oven is preheated to establish a gradient with a desired temperature profile. The loaded ampoule is,

after evacuation and sealing, inserted into the gradient oven with the precursor located in the colder zone at a temperature close to the sublimation temperature established by TG. The ampoule is left in the oven until most of the precursor has sublimed and diffused lengthwise along the ampoule (usually 1–2 days). The heat treatment is concluded by removing the ampoule from the furnace and leaving it to cool in air. The ampoule is then subjected to visual inspection, which in the successful case will show that most of the precursor has been sublimed from the cold end and decomposed in the warmer parts (Fig. 1(c)). Data are extracted by noting the positions of the deposits on the ampoule wall and comparing these positions with the temperature profile of the gradient oven.

The estimated precision in thus determined decomposition temperatures depends on the temperature gradient at the location of the deposit and the fluctuations of the supplied voltage. In the set-up used, the temperature precision is estimated to be some $\pm 4\,^\circ$C for up to 300 $^\circ$C, $\pm 6\,^\circ$C in the range of 300–400 $^\circ$C, and $\pm 8\,^\circ$C above 400 $^\circ$C.

The procedure works best for precursors who produce coloured deposition products. The present test series was performed on thd (Hthd = 2,2,6,6-tetramethylheptane-3,5-dione) complexes of the 3d metals. The decomposition products of most of these precursors are usually the corresponding metal or metal oxide(s) with distinct colours. In cases where one expects colourless decomposition products it may turn out to be difficult or impossible to detect decomposition products on the ampoule wall by visual inspection. A remedy in such cases is to insert pieces of a non-transparent material with a polished surface in the ampoule (Fig. 1(d)). Changes in the reflectivity of the polished pieces can then be used to establish that deposition has taken place. Care must be taken to ensure that heat transport along the inserted material is minimised in order not to alter the temperature profile along the ampoule. One venture is to cut the insert material in small irregular chips so that heat conduction from chip to chip becomes limited. Small spheres may also be used. The use of longer pieces of metal wires may change the temperature profile in the ampoule significantly and should accordingly be avoided. Pieces of polished single crystals of silicon were used in the present case.

The described procedure is intended for solid precursors that do not melt during the sublimation process. However, liquid and gaseous precursors may be used in the same set-up after minor modifications. A liquid precursor may simply be inserted into the ampoule in a suitable container to avoid that the precursor floats along the entire ampoule. Alternatively, small floating barriers may be made during the forming of the ampoule. The gradient oven may also be given an inclined position when liquid precursors are involved. For a gaseous precursor the ampoule may be replaced by an open tube, where a slow stream of precursor gas is fed in at a cool end of the tube. Reduced pressures may be achieved by connecting a pump at the other end of the tube.

3. Experimental

We have studied the decomposition of $VO(thd)_2$, $Cr(thd)_3$, $Mn(thd)_3$, $Fe(thd)_3$, $Co(thd)_2$, $Ni(thd)_2$, $Cu(thd)_2$, $Zn(thd)_2$, $La(thd)_3$ ($La_2(thd)_6$ [10]), and $Ca(thd)_2$ ($Ca_3(thd)_6$ [11]) according to the above procedure. The precursors have been made in-house according to a modified procedure of the one described in [12].

TG analysis under ca. 1 mbar of flowing N_2 and with a heating rate of 1 $^\circ$C/min was performed with a Perkin-Elmer TGA 7 system to establish the sublimation temperature for these precursors. The onset temperature for a detectable TG mass loss was chosen as the sublimation temperature (Table 1). The ampoules used for the decomposition experiments were made of silica glass and had an inner diameter of 5 mm and a length of ca. 1 m. A small silica-glass container (volume: ca. 0.06 ml) charged with the precursor to be tested was inserted into the ampoule prior to evacuation. The $Zn(thd)_2$, $La(thd)_3$, and $Ca(thd)_2$ complexes produce colourless decomposition products, and chips of the polished silicon were in these cases accordingly inserted lengthwise along the ampoule prior to evacuation. The experiments and their evaluations followed the procedure described earlier.

4. Results and discussion

The TG analyses show that all tested complexes undergo a simple one-step sublimation process. The degradation experiments show that the decomposition mainly occurs in two steps. The first step occurs in the lower-temperature region where the deposition product has the same colour as the metal or metal oxide under study, the next at higher temperatures where black coloured products are seen. $Fe(thd)_3$ shows in addition also deposition in an intermediate temperature range where the product has the same colour as in the first range. For $Ca(thd)_2$ and $Ni(thd)_2$, it seems that the two decomposition stages overlap.

The estimated decomposition temperatures for the tested complexes (Table 1) appear to show some correlation with the electron count (EC) for the central metal atom of the complex (all counts referring to mononuclear species). The complexes with EC = 18 (Cr and Ni) have the highest thermal stability. The

Table 1
Temperatures (°C) for onset (t_{ons}) of sublimation of complex (uncertainty ± 3 °C), onset and end (t_{end}) of decomposition of complex (uncertainty in parentheses), onset and end of degradation of organic fragment (uncertainty ± 8 °C), and electron count (EC) for the central metal atom of the complex (assuming mononuclear species)

Complex	Sublimation t_{ons}	Decomposition		Degradation of organic fragments		EC
		t_{ons}	t_{end}	t_{ons}	t_{end}	
VO(thd)$_2$	129	368 (6)	494 (8)	591	600	15
Cr(thd)$_3$	127	435 (8)	463 (8)	594	600	18
Mn(thd)$_3$	124	240 (4)	260 (4)	590	600	19
Fe(thd)$_3$	124	210 (4)	264 (4)	–	–	–
		274 (4)	311 (6)	445	600	20
Co(thd)$_2$	118	311 (6)	440 (8)	512	600	17
Ni(thd)$_2$	138	330 (20)	465 (20)	Not detected	Not detected	18
Cu(thd)$_2$	127	173 (4)	225 (15)	593	600	19
Zn(thd)$_2$	121	349 (6)	415 (8)	556	593	20
La(thd)$_3$	184	451 (8)	507 (8)	574	590	15
Ca(thd)$_2$	190	Not detected	Not detected	590	600	10

Temperatures refer to measurements at an estimated pressure of ca. 1 mbar.

thermal stability decreases with both larger and smaller EC, but the decrease in decomposition temperature is more pronounced for the complexes with the higher ECs. VO(thd)$_2$ (and possibly La$_2$(thd)$_6$ and Ca$_3$(thd)$_6$) should perhaps be neglected from such comparisons because of the special composition and structure, and the possibility that some of the complexes are subjected to dimerisation or de-polymerisation should be kept open.

Decomposition of complexes like these may be homogeneous (viz. occur in the gas phase) and/or heterogeneous (viz. take place on a surface). The present type of experiment is not able to differentiate between the two types of decomposition courses. However, both types of decomposition incidents are unwanted in ALCVD growth.

When metalorganic complexes decompose at low temperatures, the products will most likely be the metal or its oxide and volatile organic fragments. The organic fragment(s) will in turn diffuse further into the warmer parts of the apparatus and in the end decompose to a carbon-like residue. Bykov et al. [5] have studied the decomposition of the residues that form when thd complexes decompose, and found that these decompose at ca. 600 °C, which is consistent with our findings of black deposits in the same temperature region (Table 1). The decomposition of Ni(thd)$_2$ represents an exception to this pattern in that the dark deposit at around 600 °C was absent,

whereas the lower-temperature deposition region was extended. Our working hypothesis is that the first decomposition product of Ni(thd)$_2$ here acts as a catalyst for the decomposition of the organic fragments. In this way, the latter species never reach the higher-temperature region. When Ni(thd)$_2$ decomposition experiments were run for 3 days it was indeed also possible to observe a grey area stretching all the way from 185 °C and into the organic-fragment degradation zone specified in Table 1. Throughout the entire deposition region there were also seen randomly distributed darker spots signalising regions with more extensive decomposition. A satisfactory explanation is not found, but in close association with this behaviour it is recorded that the reproducibility of the decomposition temperatures for Ni(thd)$_2$ (some ± 20 °C between repeated runs) are somewhat poorer than for the other precursors (ca. ± 5 °C) studied.

The decomposition of Ni(thd)$_2$ and Cu(thd)$_2$ have also been studied by MS which gave decomposition temperatures of 362 [3] and 330 °C [5], respectively. This is consistent with our findings for Ni(thd)$_2$ (330–465 °C), but significantly higher than our decomposition temperature for Cu(thd)$_2$ (173–225 °C; repeatedly obtained in several runs).

Even though thermal decomposition of one precursor may give uncontrolled growth in mono-component ALCVD growth, the same will not necessarily be true for multi-component growth. For example, Mn(thd)$_3$

decomposes already at $240\,^\circ$C and the depositions of MnO_x above this temperature reflects uncontrolled ALCVD growth [13]. Nevertheless, it is possible to use $Mn(thd)_3$ as precursor in combination with $La(thd)_3$ at higher temperatures to obtain controlled growth of lanthanum manganite [13,14]. The reason for this important distinction is most probably that when $Mn(thd)_3$ decomposes on an MnO_2 surface, the thd ligands simply desorb, whereas when $Mn(thd)_3$ breaks down on a surface where La is present, the thd ligands are swapped from Mn to La. A surface-controlled growth is, therefore, still possible since the thd ligands now adsorbed at the La atoms block further $Mn(thd)_3$ ligands from being adsorbed and subsequently decomposed. Such an effect works only if the decomposition of the precursor is surface activated. The ALCVD growth will in such a case again become uncontrollable above the decomposition temperature for $La(thd)_3$.

Acknowledgements

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