

# **THERMOGRAVIMETRIC STUDY OF VOLATILE PRECURSORS FOR CHEMICAL THIN FILM DEPOSITION**

## **Estimation of vapor pressures and source temperatures**

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### **Abstract**

Normal pressure thermogravimetry (TG) measurements were used to study the sublimation behavior of several volatile metal compounds, used as metal precursors in thin film fabrication by chemical vapor phase methods, like atomic layer deposition (ALD) and chemical vapor deposition (CVD). The results indicated that dynamic TG measurements may be used to find correct source temperatures to be used in an ALD reactor: a good correlation between the source temperatures used in ALD and temperatures corresponding to mass losses of 10 and 50% in TG was verified. It was also found that isothermal TG measurements offer a simple way for the vapor pressure measurements which otherwise are not trivial for solids with only moderate volatility.

**Keywords:** atomic layer deposition, chemical vapor deposition, evaporation, precursor, thermogravimetry, vapor pressure

### **Introduction**

Volatile precursors are needed in thin film fabrication by chemical vapor deposition (CVD) and atomic layer deposition (ALD) methods. In ALD the precursors are pulsed alternately one at the time onto the substrate and the growth proceeds via reactions between the adsorbed surface species and the incoming reactants. In CVD the precursors are introduced simultaneously onto the substrate and constant fluxes of precursors are required. Solid precursors are not desired in CVD because the sublimation rate of a solid may be inconstant due to particle sintering effects and therefore a homogeneous reactant flux may be difficult to maintain. In ALD the requirement is that during the reactant pulse the surface must be saturated but due to the self-limiting growth mechanism constant precursor flux is not required and therefore solid precursors are more easily adapted [1].

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Many kind of precursors have been utilized in CVD and ALD. The most important properties of precursors are volatility and reactivity. Volatility of a substance is best characterized by its vapor pressure. If vapor pressures of precursor compounds were known, it would be easy to compare their volatilities and find the right evaporation temperature for each precursor so that the precursor flux would be correct. However, vapor pressures of many possible precursor compounds are unknown due to the difficulty of measuring low vapor pressures of solid substances. Vapor pressure of a liquid is measured easily by observing the pressure and the temperature in which the liquid boils. Measurement of vapor pressure of a solid is much more complicated and is usually done with special equipment [2].

When a new precursor is tested in ALD or CVD, it would be important to know the right evaporation temperature so that the reactant flux and consumption could be tuned to an appropriate level already from the very beginning of the experiments. In general TG measurements have proven to be highly valuable when evaluating the properties of possible precursor compounds [3]. Dynamic measurements are used as a routine to evaluate the thermal stability and volatility of the compounds. Isothermal measurements give information about evaporation rates at certain temperatures. With TG measurements under reduced pressure, the low pressure ALD and CVD process conditions may be simulated.

In this paper we report thermogravimetric studies on several metal precursors and findings how the evaporation temperatures observed in TG correlate with the precursor evaporation temperature used in a one specific ALD reactor. It will be shown that while the ALD reactor operates at 5–10 mbar, normal atmospheric pressure TG measurements are well enough for determining the appropriate source temperatures. Investigations on possibilities of atmospheric pressure thermogravimetry in estimating vapor pressures are also reported.

## Experimental

A Mettler Toledo TA8000 system equipped with a TGA850 thermobalance was used for the thermal analyses of the samples under flowing nitrogen atmosphere. In dynamic experiments the heating rate was  $10^{\circ}\text{C min}^{-1}$  and the samples investigated were between 5 and 20 mg. The section area of the crucible was  $0.181\text{ cm}^2$ . Dynamic experiments were mainly performed in normal pressure. Under reduced pressure (ca 5 mbar) the equipment was leaking quite heavily and air got into the oven with the negative effect that the compounds could react with oxygen.

A special heating program was used for isothermal mass change determinations. The sample was heated to a desired temperature and then kept at this temperature for 20 min. Then the temperature was raised 20–40°C and the 20 min isothermal stage was repeated. At least 4 isothermal stages were measured. Sample sizes were about 30 mg.

The substances investigated were obtained from different sources. Simple halides and alkoxides were purchased from commercial chemical suppliers.  $\beta$ -diketonates were synthesized and thoroughly characterized in our laboratory [4, 5].

The quoted ALD source temperatures refer to a F-120 reactor (ASM Microchemistry, Espoo, Finland) [6] operated at 5–10 mbar.

## Results and discussion

### *Estimation of source temperatures from dynamic TG measurements*

Dynamic TG measurements under normal pressure were performed for the compounds presented in Table 1 which also reports some of the TG results. Most of the compounds studied evaporated in a single step without any significant decomposition, the residues were less than 10% at 600°C. Some of the compounds had small steps in their TG curves before or after the main evaporation step. The early steps before were usually assigned to an evaporation of coordinated solvent, free ligand or water. Some of the studied compounds evaporated or decomposed releasing volatile species in more than one step. It is generally considered that compounds which evaporate in one or two steps, the first one being associated with an evaporation of coordinated solvent, and leave only a small amount of residue, meaning minimal decomposition, are the most suitable precursors. However, some precursors show a TG curve with many steps but are still suitable precursors. In these cases the precursor compound is evaporated in the thin film deposition process at a temperature below the decomposition temperature while in TG it has not yet fully evaporated when the decomposition temperature is reached. Under reduced pressure TG, the evaporation takes place at lower temperature and hence decomposition may not be observed. In the case of air and moisture sensitive chemicals TG-curve showing decomposition may also be due to exposure to air during loading the sample. Anyhow a rejection of a compound just because it shows a TG curve with multiple steps and/or large residue may sometimes be a mistake.

Some experiments were also made under reduced pressure of ca 5 mbar which is about the pressure in our ALD reactor. However, because the TG equipment clearly was not properly designed to work under reduced pressures, significant leakage was present and air getting in destroyed some of the air sensitive samples during the measurements. From the curves measured under reduced and normal pressure for  $\text{Al}_2\text{Cl}_6$  (Fig. 1) it is seen that, as expected, lowering the pressure makes the compounds to evaporate at lower temperature. Because of the leakage problem, no further experiments were performed under reduced pressure.

When the source temperature found appropriate in the ALD reactor is plotted vs. the temperature at which the mass loss in the main evaporation step is 10% (Fig. 2), a pretty good correlation between different precursors is seen. Same kind of a correlation is found also when the ALD source temperature is plotted vs. temperature where 50% of the sample mass is lost. Using the curve in Fig. 2 it is possible to estimate with a reasonable accuracy a source temperature for a new ALD precursor from its dynamic TG curve. One reason for the scatter in Fig. 2 is that the evaporation temperatures used in ALD correspond to a quite wide range of vapor pressures from 0.01 to 0.9 mbar. It must also be emphasized that, because of instrumental factors, the curve

in Fig. 2 is valid only for this specific thermobalance–ALD-reactor combination. Table 1 reports  $T(m10\%)$ ,  $T(m50\%)$  and  $T(\text{ALD})$  for the precursors studied.

**Table 1** Results from dynamic TG measurements and  $T(\text{ALD})$

| Compound                  | $T_f/^\circ\text{C}$ | Mass remaining/% | $T(m10\%)/^\circ\text{C}$ | $T(m50\%)/^\circ\text{C}$ | $T(\text{ALD})/^\circ\text{C}$ |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|---------------------------|----------------------|------------------|---------------------------|---------------------------|--------------------------------|---------------------------|-----|-------|-----|-----|-------|-----|-------|---------------------------|------|---------------------|-----|-------|-----|--------------------------|-------|---------------------------|-------|------------------|------|---------------------|------|--------------------------|------|-----------------|-------|---------------------------|------|-------|------|-------|-------|----------------|-------|---------------------------|------|-----------------|-----------------|-------|---------------------|------|-----------------|---------------------------|------|-------|------|---------------------|-------|-------|------|---------------------------|-------|------------------|-------|---------------------|----------------|-------|------|---------------------------|-------|---------------------------|------|-------|------|-----|------|---------------------------|-----------------|---------------------------|-------|------|-----|-------|-------|-----|-------|-----|-------|---------------------------|------|------------------|-----|------|-----|-----|-------|-----|-------|---------------------------|------|-------|------|------------------|-----|------|------|---------------------------|-----|
| $\text{Al}_2\text{Cl}_6$  | 190                  | 4.10             | 138                       | 163                       | 70–100                         |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 2.40             |                           |                           |                                | $\text{ZnCl}_2$           | 600 | 1.44  | 471 | 554 | 360   | 600 | 1.44  | $\text{ZrCl}_4$           | 363  | 8.25                | 241 | 282   | 165 | 600                      | 5.50  | $\text{NbCl}_5$           | 206   | 25.40            | 157  | 183                 | 90   | 285                      | 2.20 | 600             | 1.48  | $\text{In}_2\text{Cl}_6$  | 220  | 83.25 | 387  | 432   | 285   | 463            | 2.86  | 600                       | 1.48 | $\text{TaCl}_5$ | 220             | 13.97 | 155                 | 178  | 90              | 397                       | 8.69 | 600   | 6.95 | Ti(IV) isopropoxide | 59    | 97.13 | 102  | 149                       | 40–50 | 187              | 8.69  | 248                 | 6.19           | 318   | 3.37 | Ta(V) ethoxide            | 285   | 5.43                      | 199  | 242   | 105  | 600 | 4.74 | $\text{MoCl}_5$           | 108             | 94.78                     | 147   | 169  | 130 | 194   | 42.02 | 244 | 13.53 | 531 | 3.20  | 600                       | 1.07 | Al(III) ethoxide | 316 | 3.83 | 205 | 251 | 135   | 600 | 0.32  | $\text{Mg}(\text{thd})_2$ | 126  | 96.49 | 252  | 291              | 110 | 320  | 0.25 | $\text{Sr}(\text{thd})_2$ | 414 |
| $\text{ZnCl}_2$           | 600                  | 1.44             | 471                       | 554                       | 360                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 1.44             |                           |                           |                                | $\text{ZrCl}_4$           | 363 | 8.25  | 241 | 282 | 165   | 600 | 5.50  | $\text{NbCl}_5$           | 206  | 25.40               | 157 | 183   | 90  | 285                      | 2.20  |                           | 600   | 1.48             |      |                     |      | $\text{In}_2\text{Cl}_6$ | 220  | 83.25           | 387   |                           | 432  | 285   |      |       |       | 463            | 2.86  | 600                       | 1.48 |                 | $\text{TaCl}_5$ | 220   |                     |      |                 | 13.97                     | 155  | 178   | 90   |                     | 397   | 8.69  |      |                           |       | 600              | 6.95  | Ti(IV) isopropoxide | 59             | 97.13 | 102  | 149                       | 40–50 | 187                       | 8.69 | 248   | 6.19 | 318 | 3.37 |                           | Ta(V) ethoxide  | 285                       |       |      |     | 5.43  | 199   | 242 | 105   | 600 | 4.74  | $\text{MoCl}_5$           | 108  | 94.78            | 147 | 169  | 130 | 194 | 42.02 | 244 | 13.53 | 531                       | 3.20 | 600   | 1.07 | Al(III) ethoxide | 316 | 3.83 | 205  | 251                       | 135 |
| $\text{ZrCl}_4$           | 363                  | 8.25             | 241                       | 282                       | 165                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 5.50             |                           |                           |                                | $\text{NbCl}_5$           | 206 | 25.40 | 157 | 183 | 90    | 285 | 2.20  |                           | 600  | 1.48                |     |       |     | $\text{In}_2\text{Cl}_6$ | 220   | 83.25                     | 387   | 432              | 285  | 463                 | 2.86 |                          | 600  | 1.48            |       | $\text{TaCl}_5$           |      |       | 220  | 13.97 | 155   | 178            | 90    | 397                       | 8.69 | 600             |                 | 6.95  | Ti(IV) isopropoxide | 59   | 97.13           | 102                       |      |       |      | 149                 | 40–50 | 187   | 8.69 | 248                       | 6.19  | 318              | 3.37  |                     | Ta(V) ethoxide | 285   |      |                           |       | 5.43                      | 199  | 242   | 105  | 600 | 4.74 |                           | $\text{MoCl}_5$ | 108                       |       |      |     | 94.78 | 147   | 169 | 130   | 194 | 42.02 |                           | 244  | 13.53            |     |      |     | 531 | 3.20  | 600 | 1.07  | Al(III) ethoxide          | 316  | 3.83  | 205  | 251              | 135 | 600  | 0.32 | $\text{Mg}(\text{thd})_2$ | 126 |
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|                           | 285                  | 2.20             |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 1.48             |                           |                           |                                | $\text{In}_2\text{Cl}_6$  | 220 | 83.25 | 387 | 432 | 285   | 463 | 2.86  | 600                       | 1.48 | $\text{TaCl}_5$     | 220 | 13.97 | 155 | 178                      | 90    | 397                       | 8.69  | 600              | 6.95 | Ti(IV) isopropoxide | 59   | 97.13                    | 102  | 149             | 40–50 | 187                       | 8.69 | 248   | 6.19 | 318   | 3.37  | Ta(V) ethoxide | 285   | 5.43                      | 199  | 242             | 105             | 600   |                     | 4.74 | $\text{MoCl}_5$ |                           | 108  | 94.78 | 147  |                     |       | 169   | 130  | 194                       | 42.02 | 244              | 13.53 | 531                 | 3.20           | 600   | 1.07 | Al(III) ethoxide          | 316   | 3.83                      | 205  | 251   | 135  | 600 | 0.32 | $\text{Mg}(\text{thd})_2$ |                 | 126                       | 96.49 | 252  | 291 | 110   |       |     |       | 320 | 0.25  | $\text{Sr}(\text{thd})_2$ | 414  | 2.71             | 323 | 382  | 210 |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| $\text{In}_2\text{Cl}_6$  | 220                  | 83.25            | 387                       | 432                       | 285                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 463                  | 2.86             |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 1.48             |                           |                           |                                | $\text{TaCl}_5$           | 220 | 13.97 | 155 | 178 | 90    | 397 | 8.69  | 600                       | 6.95 | Ti(IV) isopropoxide | 59  | 97.13 | 102 | 149                      | 40–50 | 187                       | 8.69  | 248              | 6.19 |                     | 318  | 3.37                     |      |                 |       | Ta(V) ethoxide            | 285  | 5.43  | 199  | 242   | 105   | 600            | 4.74  | $\text{MoCl}_5$           | 108  | 94.78           | 147             | 169   | 130                 | 194  |                 | 42.02                     | 244  | 13.53 |      | 531                 | 3.20  |       |      | 600                       | 1.07  | Al(III) ethoxide | 316   | 3.83                | 205            | 251   | 135  | 600                       | 0.32  | $\text{Mg}(\text{thd})_2$ | 126  | 96.49 | 252  | 291 | 110  | 320                       | 0.25            | $\text{Sr}(\text{thd})_2$ | 414   | 2.71 | 323 | 382   | 210   |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| $\text{TaCl}_5$           | 220                  | 13.97            | 155                       | 178                       | 90                             |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 397                  | 8.69             |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 6.95             |                           |                           |                                | Ti(IV) isopropoxide       | 59  | 97.13 | 102 | 149 | 40–50 | 187 | 8.69  | 248                       | 6.19 |                     | 318 | 3.37  |     |                          |       | Ta(V) ethoxide            | 285   | 5.43             | 199  | 242                 | 105  | 600                      | 4.74 | $\text{MoCl}_5$ | 108   | 94.78                     | 147  | 169   | 130  | 194   | 42.02 | 244            | 13.53 |                           | 531  | 3.20            |                 |       |                     | 600  | 1.07            | Al(III) ethoxide          | 316  | 3.83  | 205  | 251                 | 135   | 600   | 0.32 | $\text{Mg}(\text{thd})_2$ | 126   | 96.49            | 252   | 291                 | 110            | 320   | 0.25 | $\text{Sr}(\text{thd})_2$ | 414   | 2.71                      | 323  | 382   | 210  |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| Ti(IV) isopropoxide       | 59                   | 97.13            | 102                       | 149                       | 40–50                          |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 187                  | 8.69             |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 248                  | 6.19             |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 318                  | 3.37             |                           |                           |                                | Ta(V) ethoxide            | 285 | 5.43  | 199 | 242 | 105   | 600 | 4.74  | $\text{MoCl}_5$           | 108  | 94.78               | 147 | 169   | 130 | 194                      | 42.02 | 244                       | 13.53 | 531              | 3.20 | 600                 | 1.07 | Al(III) ethoxide         | 316  |                 | 3.83  | 205                       |      |       |      | 251   | 135   | 600            | 0.32  | $\text{Mg}(\text{thd})_2$ | 126  | 96.49           | 252             | 291   | 110                 | 320  | 0.25            | $\text{Sr}(\text{thd})_2$ | 414  | 2.71  | 323  | 382                 | 210   |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| Ta(V) ethoxide            | 285                  | 5.43             | 199                       | 242                       | 105                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 4.74             |                           |                           |                                | $\text{MoCl}_5$           | 108 | 94.78 | 147 | 169 | 130   | 194 | 42.02 |                           | 244  | 13.53               |     |       |     | 531                      | 3.20  | 600                       | 1.07  | Al(III) ethoxide | 316  | 3.83                | 205  | 251                      | 135  | 600             | 0.32  | $\text{Mg}(\text{thd})_2$ | 126  | 96.49 | 252  | 291   | 110   | 320            | 0.25  | $\text{Sr}(\text{thd})_2$ | 414  | 2.71            | 323             | 382   | 210                 |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| $\text{MoCl}_5$           | 108                  | 94.78            | 147                       | 169                       | 130                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 194                  | 42.02            |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 244                  | 13.53            |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 531                  | 3.20             |                           |                           |                                |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 1.07             |                           |                           |                                | Al(III) ethoxide          | 316 | 3.83  | 205 | 251 | 135   | 600 | 0.32  | $\text{Mg}(\text{thd})_2$ | 126  | 96.49               | 252 | 291   | 110 | 320                      | 0.25  | $\text{Sr}(\text{thd})_2$ | 414   | 2.71             | 323  | 382                 | 210  |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| Al(III) ethoxide          | 316                  | 3.83             | 205                       | 251                       | 135                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 600                  | 0.32             |                           |                           |                                | $\text{Mg}(\text{thd})_2$ | 126 | 96.49 | 252 | 291 | 110   | 320 | 0.25  | $\text{Sr}(\text{thd})_2$ | 414  | 2.71                | 323 | 382   | 210 |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| $\text{Mg}(\text{thd})_2$ | 126                  | 96.49            | 252                       | 291                       | 110                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
|                           | 320                  | 0.25             |                           |                           |                                | $\text{Sr}(\text{thd})_2$ | 414 | 2.71  | 323 | 382 | 210   |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |
| $\text{Sr}(\text{thd})_2$ | 414                  | 2.71             | 323                       | 382                       | 210                            |                           |     |       |     |     |       |     |       |                           |      |                     |     |       |     |                          |       |                           |       |                  |      |                     |      |                          |      |                 |       |                           |      |       |      |       |       |                |       |                           |      |                 |                 |       |                     |      |                 |                           |      |       |      |                     |       |       |      |                           |       |                  |       |                     |                |       |      |                           |       |                           |      |       |      |     |      |                           |                 |                           |       |      |     |       |       |     |       |     |       |                           |      |                  |     |      |     |     |       |     |       |                           |      |       |      |                  |     |      |      |                           |     |

#### *Vapor pressure determination from isothermal TG measurements*

In the sublimation process of a compound in a TG measurement three main steps are involved: (1) desorption of the molecules from the solid, (2) diffusion of the molecules in the sample cup from the solid surface into buffer gas flow on the top of the cup, (3) transportation of the molecules by the buffer gas into the outlet. Under normal pressure conditions, the gas phase diffusion (step 2) may be assumed to be the rate-limiting step. Therefore, the desorption step of the compound is at equilibrium

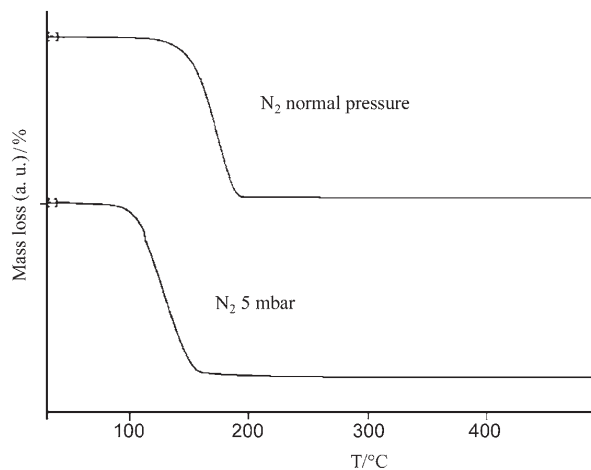


Fig. 1 TG curves of  $\text{Al}_2\text{Cl}_6$  under normal and reduced 5 mbar pressure

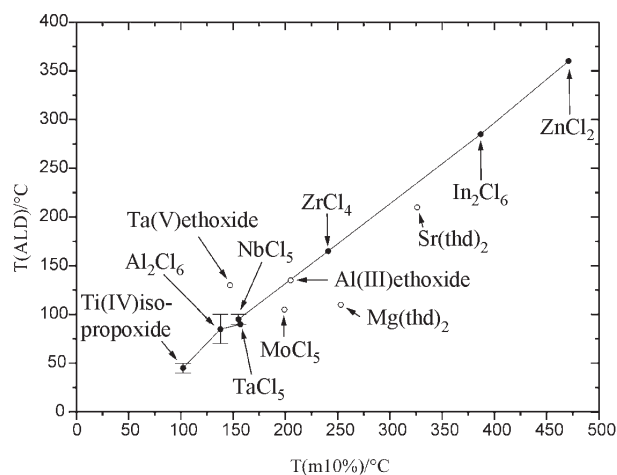


Fig. 2 Actual evaporation temperatures used in ALD ( $T(\text{ALD})$ ) as a function of measured  $T(m10\%)$

and, considering ideal gas behaviour, the vapor pressure of the compound at the gas–solid interface is equal to the saturation vapor pressure, i.e.

$$P_0 = \exp[-(\Delta H/RT) + (\Delta S/R)] \quad (1)$$

where  $R$  is the ideal gas constant and  $T$  is the sublimation temperature;  $\Delta H$  and  $\Delta S$  are the standard enthalpy and entropy of the sublimation of the compound, respectively.

With typical buffer gas flow rates the transportation of the molecules in the main flow stream is efficient and hence the vapor pressure may be considered to approach zero at a certain height ( $L$ ) above the sample cup.

When the diffusion is the rate limiting step, the sublimation rate is independent of the specific surface area of the compound. Only the area through which the diffusion takes place, i.e., the section area of the crucible, has meaning. Pauleau and Fasasi [7] have shown by using gas laws that under these conditions the sublimation rate may be expressed by an equation

$$S_R = \frac{dn_1}{dt} = k\sqrt{RT} \frac{P_0}{P} \quad P \gg P_0 \quad (2)$$

where  $dn_1$  is the number of moles of precursor molecules per  $\text{cm}^2$  leaving the gas-solid interface during the time  $dt$ ,  $P$  is the total pressure,  $T$  is the sublimation temperature and  $P_0$  is saturation vapor pressure. Factor  $k$  is

$$k = \frac{1}{L(\sigma_{12})^2} \sqrt{\frac{2M_2}{\pi^3(M_1^2 + M_1M_2)}} \quad (3)$$

where  $M_1$  is the molar mass of the evaporated species,  $M_2$  molar mass of the buffer gas and  $\sigma_{12}$  the average collision diameter ( $\sigma_{12} = (\sigma_1 + \sigma_2)/2$ ),  $\sigma_1$  is the collision diameter of the sublimed molecule and  $\sigma_2$  that of the buffer gas).

When isothermal measurements are carried out for a compound, all the factors in Eq. (2) except the sublimation temperature  $T$  and the saturation vapor pressure  $P_0$  may be considered constant. The terms of Eq. (2) may be rearranged so that it will take a form

$$P_0 = \frac{S_R}{\sqrt{T}} LP(\sigma_{12})^2 \left( \sqrt{\frac{2M_2R}{\pi^3(M_1^2 + M_1M_2)}} \right)^{-1} \quad (4)$$

Thus, the saturation vapor pressure  $P_0$  may be determined when the terms on the right side of the equation are known. As a limitation for using this method it is assumed that only one kind of species of the compound being studied is present in the gas phase and no decomposition occurs. Problems also arise from determining the collision diameter.

The only constant term depending straight on the TG equipment is  $L$  which, however, is a bit ill-determined parameter as it is hard to say at which height the pressure reaches zero. Therefore, the system was calibrated by measuring sublimation rates in different temperatures for compounds ( $\text{Al}_2\text{Cl}_6$ ,  $\text{In}_2\text{Cl}_6$ ,  $\text{ZnCl}_2$  and  $\text{TaCl}_5$ ) whose vapor pressures and other terms in the Eq. (4) are known. The vapor pressures for these compounds were obtained from literature [8]. Collision diameters for the compounds were estimated using the bond length and angle data reported in literature [9, 10] or by measuring the average diameter of the molecule from a molecular model. Table 2 presents calculated and literature data for the compounds.

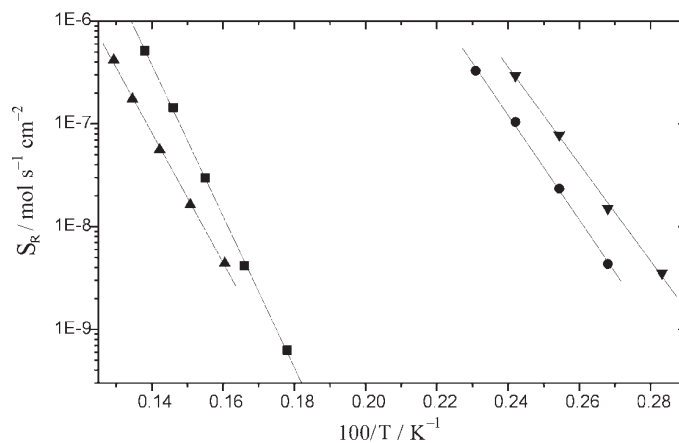
The outcome of the isothermal measurements was a well behaving mass vs. time curve where at each temperature a linear mass decrease was observed. A slope of each linear section gives the sublimation rate at this temperature. In Fig. 3 there is an Arrhenius diagram which presents the temperature dependence of the sublimation

rates of these four compounds. Sublimation processes comply with the Arrhenius law. The apparent activation energies of the sublimation processes may be deduced from the slopes of the straight lines in Fig. 3. Because vapor pressure and sublimation rate are proportional, from the Eq. (1) we see that the slope of the straight lines is  $\Delta H/2.3R$ . The measured average  $\Delta H$  values for compounds studied are presented in Table 2. The literature values are reasonably close.

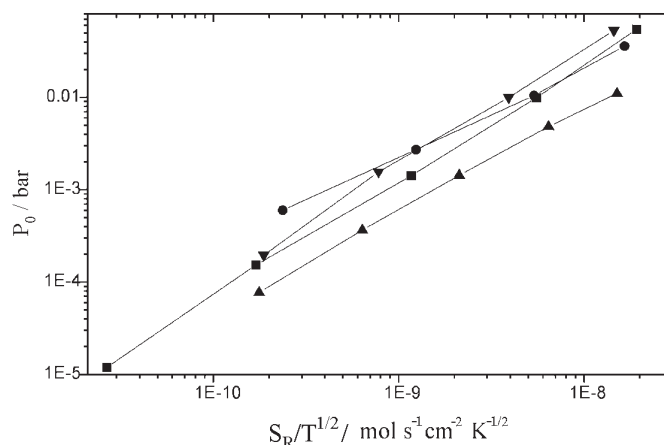
**Table 2** Results from isothermal measurements, calculated vapor pressures and literature values

|                           | $\Delta H(\text{calc.})/$ | $\Delta H(\text{lit})/$ | $T/\text{K}$ | $S_R/$   | $P_0(\text{calc.})/$               | $P_0(\text{lit})/$ | $P_0(\text{calc.})/$ |
|---------------------------|---------------------------|-------------------------|--------------|----------|------------------------------------|--------------------|----------------------|
|                           | $\text{kJ mol}^{-1}$      |                         |              |          | $\text{mol s}^{-1} \text{cm}^{-2}$ | bar                | $P_0(\text{lit})$    |
| $\text{Al}_2\text{Cl}_6$  | -90.4±2.9                 | 114.1                   | 353.15       | 3.52E-09 | 2.53E-04                           | 1.95E-04           | 1.30                 |
|                           |                           | 113.6                   | 373.15       | 1.50E-08 | 1.34E-03                           | 1.56E-03           | 0.86                 |
|                           |                           | 113.0                   | 393.15       | 7.77E-08 | 8.87E-03                           | 9.97E-03           | 0.89                 |
|                           |                           | 112.4                   | 413.15       | 2.94E-07 | 4.09E-02                           | 5.29E-02           | 0.77                 |
| $\text{ZnCl}_2$           | -121.1±2.4                | 133.8                   | 623.15       | 4.41E-09 | 5.89E-05                           | 7.72E-05           | 0.76                 |
|                           |                           | 133.0                   | 663.15       | 1.64E-08 | 2.64E-04                           | 3.65E-04           | 0.72                 |
|                           |                           | 132.2                   | 703.15       | 5.62E-08 | 1.08E-03                           | 1.43E-03           | 0.75                 |
|                           |                           | 131.4                   | 743.15       | 1.75E-07 | 3.95E-03                           | 4.83E-03           | 0.82                 |
| $\text{In}_2\text{Cl}_6$  | -141.0±1.9                | 130.7                   | 773.15       | 4.19E-07 | 1.07E-02                           | 1.10E-02           | 0.97                 |
|                           |                           | 181.8                   | 563.15       | 6.31E-10 | 2.05E-05                           | 1.19E-05           | 1.73                 |
|                           |                           | 180.1                   | 603.15       | 4.18E-09 | 1.80E-04                           | 1.54E-04           | 1.17                 |
|                           |                           | 178.2                   | 643.15       | 2.96E-08 | 1.71E-03                           | 1.42E-03           | 1.21                 |
| $\text{TaCl}_5$           | -97.5±2.8                 | 176.2                   | 683.15       | 1.44E-07 | 1.05E-02                           | 9.89E-03           | 1.07                 |
|                           |                           | 173.9                   | 723.15       | 5.17E-07 | 4.53E-02                           | 5.44E-02           | 0.83                 |
|                           |                           | 92.2                    | 373.15       | 4.34E-09 | 4.14E-04                           | 6.01E-04           | 0.69                 |
|                           |                           | 91.8                    | 393.15       | 2.34E-08 | 2.87E-03                           | 2.72E-03           | 1.06                 |
| $\text{Mg}(\text{thd})_2$ | -79.3±1.9                 | 91.3                    | 413.15       | 1.04E-07 | 1.60E-02                           | 1.05E-02           | 1.51                 |
|                           |                           | 90.9                    | 433.15       | 3.29E-07 | 5.95E-02                           | 3.59E-02           | 1.66                 |
|                           |                           | 433.15                  | 2.08E-09     | 8.54E-04 |                                    |                    |                      |
|                           |                           | 473.15                  | 1.14E-08     | 5.93E-03 |                                    |                    |                      |
| $\text{Sr}(\text{thd})_2$ | -105.1±4.9                | 493.15                  | 2.92E-08     | 1.75E-02 |                                    |                    |                      |
|                           |                           | 513.15                  | 6.48E-08     | 4.33E-02 |                                    |                    |                      |
|                           |                           | 533.15                  | 1.23E-07     | 8.92E-02 |                                    |                    |                      |
|                           |                           | 513.15                  | 2.28E-09     | 1.11E-03 |                                    |                    |                      |
|                           |                           | 553.15                  | 1.18E-08     | 7.23E-03 |                                    |                    |                      |
|                           |                           | 593.15                  | 6.15E-08     | 4.79E-02 |                                    |                    |                      |

Figure 4 shows the correlation between vapor pressures ( $P_0$ ) and the sublimation rates ( $S_R$ ) divided by  $T^{1/2}$  (Eq. (4)). The axes are logarithmic. The four compounds



**Fig. 3** Arrhenius diagram for sublimation of  $\text{Al}_2\text{Cl}_6$  ( $\blacktriangledown$ ),  $\text{ZnCl}_2$  ( $\blacktriangle$ ),  $\text{In}_2\text{Cl}_6$  ( $\blacksquare$ ) and  $\text{TaCl}_5$  ( $\bullet$ ) under normal pressure of  $\text{N}_2$



**Fig. 4** Sublimation rate of  $\text{Al}_2\text{Cl}_6$  ( $\blacktriangledown$ ),  $\text{ZnCl}_2$  ( $\blacktriangle$ ),  $\text{In}_2\text{Cl}_6$  ( $\blacksquare$ ) and  $\text{TaCl}_5$  ( $\bullet$ ) divided by  $T^{1/2}$  ( $\text{mol s}^{-1} \text{cm}^{-2} \text{K}^{-1/2}$ ) as a function of literature vapor pressure values

give lines with slightly different slopes and places. Anyhow, already this simple procedure which has the molecular mass (i.e. the form of the subliming species) as the only assumed parameter in addition to the primary isothermal TG data gives a reasonably good, order-of-magnitude estimation of the vapor pressure.

To further improve the vapor pressure determination accuracy, all the terms in Eq. (4) except  $L$  were taken into account by multiplying  $S_R/T^{1/2}$  with  $c$ :

$$P_0 = cL \frac{S_R}{\sqrt{T}} \quad (5)$$



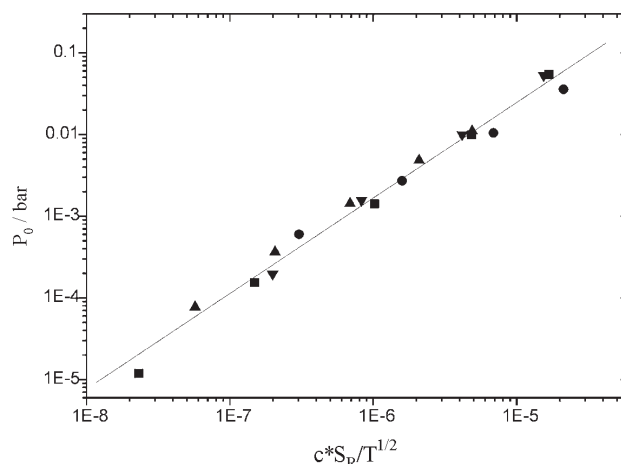
where

$$c = P(\sigma_{12})^2 \left( \sqrt{\frac{2M_2R}{\pi^3(M_1^2 + M_1M_2)}} \right)^{-1} \quad (6)$$

As a result, the data points of the four compounds settled close to a single line (Fig. 5). When a straight line is fitted to all the measured points it gets the form

$$\log P_0 = 1.170 \pm 0.036 \log \frac{cS_R}{\sqrt{T}} + 4.24 \pm 0.22 \quad (7)$$

Using the curve in Fig. 5 which is described by Eq. (7) unknown vapor pressures may be estimated by measuring the sublimation rates at different temperatures, assuming a certain form for the subliming species ( $M_1$ ) and estimating its collision diameter ( $\sigma_1$ ). The equation is of course valid only for the thermobalance that we used because it contains a parameter ( $L$ ) depending on the system itself. For other thermobalances similar measurements to form the calibration curve must be done.



**Fig. 5**  $c^*S_R/T^{1/2}$  of  $\text{Al}_2\text{Cl}_6$  ( $\blacktriangledown$ ),  $\text{ZnCl}_2$  ( $\blacktriangle$ ),  $\text{In}_2\text{Cl}_6$  ( $\blacksquare$ ) and  $\text{TaCl}_5$  ( $\bullet$ ) as a function of literature vapor pressure values

The four compounds used for setting up the calibration line were chosen to cover a broad range of volatility, corresponding for example in our ALD reactor a source temperature range of 70–360°C. Still the data fits nicely to the single line. To estimate the precision of the method among this data set, the vapor pressures from the literature ( $P_0(\text{lit})$ ) were compared to those ( $P_0(\text{calc.})$ ) calculated from the measured data using the calibration line (Eq. (7)). The ratios  $P_0(\text{calc.})/P_0(\text{lit})$  varied from 0.7 to 1.7 which suggests that vapor pressures obtained with this method should be accurate within a factor of two. Such an accuracy is considered encouraging recognising the simplicity of the procedure and the problems of accurate vapor pressure measure-

ments of low volatility solids. In ALD and CVD research vapor pressures known within a certainty of 50–200% are already appreciated as they allow a comparison of alternative compounds and give a good starting point for choosing a source temperature for a new compound. In addition, as the present method gives also the temperature dependence of the vapor pressure, a readjustment of the source temperature after the first experiment becomes straightforward.

Table 2 reports also the vapor pressures estimated for two metal–organic precursors, namely  $\text{Mg}(\text{thd})_2$  and  $\text{Sr}(\text{thd})_2$  (*thd*=2,2,6,6-tetramethyl-3,5-heptanedionato). Vapor pressure data for these complexes have not been reported earlier. While calculating the vapor pressures, the subliming species were assumed to be monomers.

## Conclusions

The results indicate that a good correlation is found for the ALD source temperatures and the temperatures measured in TG. The temperatures corresponding to both 10 and 50% evaporation can be used for estimating source temperatures for new precursors. Isothermal TG measurements offer a simple way for the vapor pressure measurements which otherwise are not trivial.

\* \* \*

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