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## ABSTRACT

Atomic/molecular layer deposition (ALD/MLD) is strongly emerging as the state-of-the-art gas-phase fabrication technique for novel functional inorganic-organic thin-film materials. In the actual ALD/MLD process development, selecting the proper sublimation temperatures for the inorganic and organic precursors is an important task. In particular, the latter ones tend to require higher sublimation temperatures. In this work, we systematically investigate a representative set of most common ALD/MLD organic precursors using low-pressure (4 mbar) thermogravimetric (TG) analysis. The onset temperature ( $T_{G_{onset}}$ ) where the weight loss starts is found to well foretell us the optimal precursor source temperature ( $T_{MLD}$ ) for ALD/MLD; typically, the  $T_{MLD}$  value used in a practical ALD/MLD experiment is lower by approximately 14% than the  $T_{G_{onset}}$  value. Moreover, we discuss the possibility to utilize the melting point of the compound as a starting point if such vacuum TG measurements are not available.

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## I. INTRODUCTION

Atomic/molecular layer deposition (ALD/MLD) is an attractive gas-phase route to fabricate new exciting inorganic-organic thin-film materials.<sup>1–7</sup> In this technique, ALD cycles for the inorganic constituent are combined with MLD cycles for the organic constituent. This, first of all, requires that the mutually reactive inorganic and organic precursors are vaporized and efficiently transported to the substrate surface one after the other in a highly controlled way. To avoid any unwanted gas-phase reactions, the precursor pulses are separated from each other by purging the reactor chamber with an inert gas pulse after each precursor pulse.

Like in the conventional ALD technology for inorganics, one of the major issues in ALD/MLD is the choice of the optimal precursors. To enable the mutual surface reactions and at the same time avoid the unwanted gas-phase side-reactions, precursor condensation or gas-phase decomposition, it is crucial to find an optimal combination of inorganic and organic precursors with similar thermal properties.<sup>8</sup> Here, in particular, the volatility, reactivity, and thermal stability of the precursors should be considered to ensure feasible film growth in the aimed hybrid inorganic-organic film deposition

temperature range.<sup>9–11</sup> In ALD/MLD, this often translates into issues related to the low vapor pressures of the organic precursors employed. These precursors are typically large organic molecules with high symmetry and strong intermolecular bonds and, hence, relatively low vapor pressures. To achieve enough precursor supply, these precursors must be heated to relatively high temperatures. Reaching the sublimation temperature is not absolutely necessary, as some vaporization occurs even below this temperature. However, at too low temperatures, the problem is slow vaporization kinetics.

Thermogravimetric (TG) analysis provides us with a simple and straightforward way to investigate the thermal properties of ALD/MLD precursors. In a TG experiment, a sample powder is heated with a fixed heating rate and its weight is constantly measured; from the start of the weight loss in the TG curve, the onset temperature ( $T_{G_{onset}}$ ) of precursor vaporization can be seen.<sup>12–14</sup> This is a highly valuable information as the  $T_{G_{onset}}$  provides us an easily obtained parameter to compare the volatilities of different (organic) precursor compounds and to establish the proper precursor source temperatures ( $T_{MLD}$ ) for them to be used in practice in ALD/MLD experiments.

One of the challenges with organic precursors is that extensive heating often required for their vaporization may also lead to their thermal decomposition before the high enough dosing level is reached.<sup>1,14</sup> In actual ALD/MLD conditions, this issue is often less serious,<sup>15</sup> as the ALD reactors typically operate under medium vacuum and utilize an inert carrier gas flow (typically nitrogen) in order to ensure comparable sublimation kinetics.<sup>16</sup> To mimic these practical conditions, the TG experiments for the determination of the onset temperatures should be carried out under vacuum using a constant inert gas flow. It should be emphasized that using a vacuum system is absolute necessity for many of the organics because they often decompose before they sublime under atmospheric pressure. This is vastly different from the behaviors of typical solid (inorganic) metal precursors for which atmospheric pressure measurements are often sufficient for estimating the precursor source temperatures in ALD.<sup>9</sup>

In this paper, we report vacuum TG analysis results for 15 representative organic precursors used in the ongoing ALD/MLD research. The results are discussed by comparing the obtained  $T_{\text{onset}}$  values with sublimation and/or melting temperatures reported in the literature for relevant organics and also with the  $T_{\text{MLD}}$  values used for these organic precursors in practice in reported ALD/MLD experiments.

## II. EXPERIMENT

All the thermogravimetric analyses were carried out on a modified Perkin Elmer TGA 7 thermobalance under a low pressure (4 mbar) and controlled nitrogen gas flow. The  $\text{N}_2$  gas flow was vertical in respect to the sample holder. A sample powder of 5–10 mg was placed in a steel crucible of  $\sim 12.6 \text{ mm}^2$  in section

area such that the bottom of the crucible was always covered with the powder to ensure the similar sublimation area. In each TG run, the sample was heated with a rate of  $2 \text{ }^\circ\text{C}/\text{min}$ ; this slow heating rate was chosen to guarantee uniform heating across the sample.

The substances investigated were purchased from different commercial chemical suppliers, mainly Sigma-Aldrich and TCI Chemicals; similar precursor powders from the same suppliers had also been previously employed in our practical ALD/MLD works based on a commercial hot wall F-120 reactor (ASM Micro-chemistry, Espoo, Finland) operated at 2–4 mbar. It should be emphasized that the other quoted  $T_{\text{MLD}}$  precursor source temperatures from the literature (other than our works) are not necessarily based on this specific ALD reactor type; this is important, as there are likely to be some (systematic) differences in the required/used precursor source temperatures depending on the reactor configuration.

## III. RESULTS AND DISCUSSION

If we investigated altogether 15 solid organic compounds through a similar vacuum ( $\sim 4$  mbar) TG analysis; examples of the TG curves are displayed in Fig. 1. The 15 organic compounds investigated are listed in Table I. We also include in this table 54 other organic precursor compounds used in practical ALD/MLD experiments in the literature, together with the precursor source temperatures used in these experiments. When considering the  $T_{\text{MLD}}$  values listed, it should be emphasized that the optimal precursor source temperature depends on the precursor delivery system/reactor configuration. In Table I, we also give for each precursor compound the following parameters collected from literature: melting point ( $T_m$ ), possible decomposition temperature ( $T_{\text{decomp}}$ ), and sublimation ( $T_{\text{sub}}$ ) or vaporization ( $T_{\text{vap}}$ )

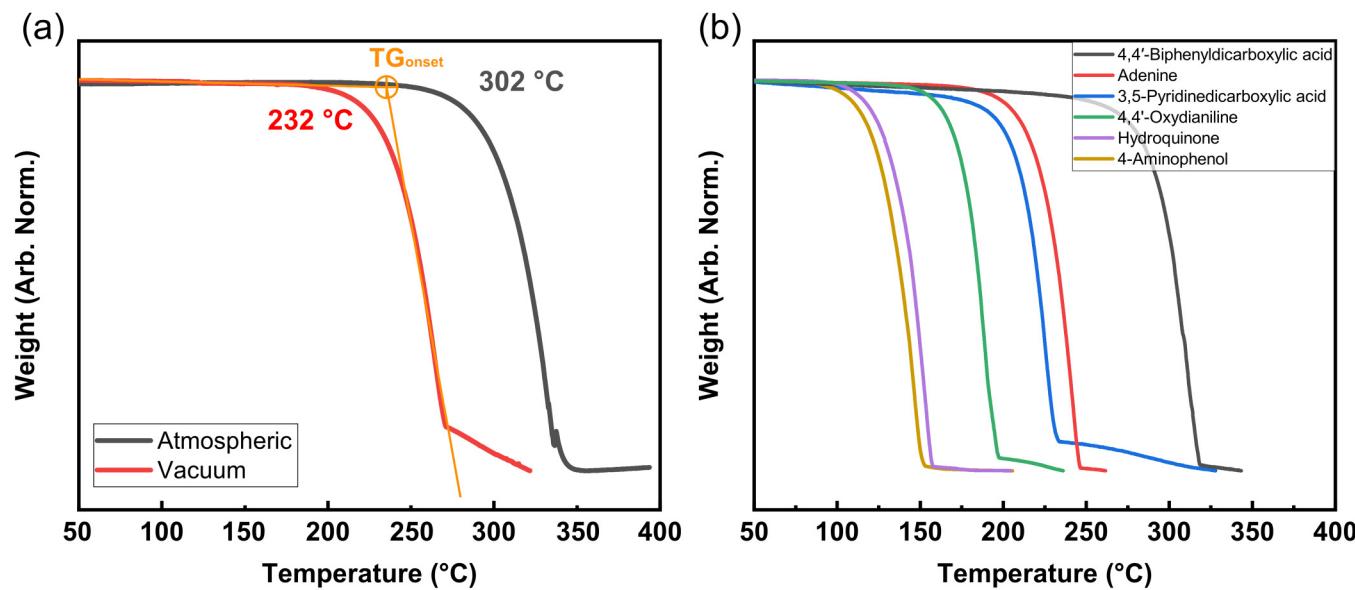


FIG. 1. TG curves recorded (a) for terephthalic acid under vacuum ( $\sim 4$  mbar) and atmospheric pressure (corresponding  $T_{\text{onset}}$  values and their definition are also indicated) and (b) for other selected organics under vacuum (the weight scale is normalized).

**TABLE I.** Precursor source temperatures ( $T_{MLD}$ ) used for organic precursors in ALD/MLD, together with the present vacuum  $TG_{onset}$  temperatures and the phase-change temperatures ( $T_m$ ,  $T_{sub}$ ,  $T_{vap}$ , and  $T_{decomp}$ ) collected from literature. For phase-change type: M is for melting, D is for decomposition, V is for vaporization, and S is for sublimation.

Precursor	No	Molecule	$T_{MLD}$ (°C)	$TG_{onset}$ (°C)	$T_{phase\text{-}change}$ (°C)	Phase-change type
Propargyl alcohol	1		Not given in Refs. 17 and 18		-53	M
Ethylenediamine	2		RT <sup>7,19,20</sup>	8		M
2-Aminoethanol	3		80 <sup>21</sup>		10	M
Ethylene glycol	4		~30 <sup>22-24</sup>		-13	M
Glycidol	5		~60 <sup>25,26</sup>		-54	M
Glycine	6		~200 <sup>27,28</sup>		240	D
1,4-Butynediol	7		50 <sup>29</sup>		53	M
Oxalic acid	8		100 <sup>30</sup>		185	D
Lactic acid	9		115 <sup>31</sup>		18	M
1,4-Butanediol	10		~80 <sup>29,32,33</sup>		19	M
Glycerin	11		~60 <sup>24,34,35</sup>		18	M
Phenol	12		~80 <sup>36,37</sup>		41	M
1,2-Ethanedithiol	13		RT <sup>38</sup>		-41	M
Maleic anhydride	14		~80 <sup>21,39,40</sup>		53	M
Malonic acid	15		125 <sup>41</sup>		136	D
Diethylene glycol	16		100 <sup>42</sup>		-10	M
1,4-Benzenediamine	17		~70 <sup>43-45</sup>		142	M
4-Aminophenol	18		~111 <sup>2,46-48</sup>	122	189	M
Hydroquinone	19		~90 <sup>7,22,43,46,49-66</sup>	132	172	M
Diacetylene glycol	20		~80 <sup>67-69</sup>		112	M

TABLE I. (Continued.)

Precursor	No	Molecule	T <sub>MLD</sub> (°C)	TG <sub>onset</sub> (°C)	T <sub>phase-change</sub> (°C)	Phase-change type
Uracil	21		~207 <sup>28,70–73</sup>	209	330	M
1,6-Hexanolide	22		60 <sup>74</sup>		-2	M
Fumaric acid	23		Not given in Ref. 7		299	S
Maleic acid	24		~172 <sup>75,76</sup>		132	M
1,6-Diaminohexane	25		40 <sup>77</sup>		39	M
Succinic acid	26		140 <sup>27</sup>		186	M
1,6-Hexanediol	27		85 <sup>78</sup>		40	M
1,3,5-Benzenetriol	28		Not given in Ref. 7		218	M
Thymine	29		~207 <sup>28,73</sup>		316	M
Tetracyanoethylene	30		RT <sup>79,80</sup>		198	M
Glutaric acid	31		199 <sup>81</sup>		97	M
L-(+)-aspartic acid	32		225 <sup>27</sup>		230	D
Adenine	33		~210 <sup>28,70,73</sup>	220	360	D
4-Aminobenzoic acid	34		Not given in Ref. 7		188	D
Malonyl chloride	35		Not given in Ref. 82		54	V
trans,trans-Muconic acid	36		Not given in Ref. 7		290	M
1,4-Benzenedithiol	37		35 <sup>43</sup>		97	M
8-Hydroxyquinoline	38		~100 <sup>7,83–85</sup>		75	M

TABLE I. (Continued.)

Precursor	No	Molecule	T <sub>MLD</sub> (°C)	TG <sub>onset</sub> (°C)	T <sub>phase-change</sub> (°C)	Phase-change type
L-(+)-glutamic acid	39		165 <sup>86</sup>		201	D
Triethanolamine	40		~148 <sup>87,88</sup>		20	M
1,4-Diisocyanatobenzene	41		90 <sup>89</sup>		94	M
Pimelic acid	42		139 <sup>41</sup>		104	M
3-(Trifluoromethyl)phenol	43		~80 <sup>36,37</sup>		-2	M
Phthalic acid	44		177 <sup>90</sup>		210	D
Terephthalic acid	45		~185 <sup>43,49,91-98</sup>	232	402	S
Isophthalic acid	46		212 <sup>90</sup>		342	S
2,3-Pyridinedicarboxylic acid	47		150 (unpublished work)	186	188	D
2,6-Pyridinedicarboxylic acid	48		235 <sup>97</sup>	188	245	D
3,5-Pyridinedicarboxylic acid	49		~190 <sup>5,97,99</sup>	203	325	D
2,3-Pyrazinedicarboxylic acid	50		145 <sup>100</sup>		188	D
2-(2,2,4-Trimethyl-1,2-azasilolidin-1-yl) ethanamine	51		55 <sup>39</sup>		54	V
(E)-Aconitic acid	52		114 <sup>86</sup>		190	D
Suberic acid	53		139 <sup>41</sup>		143	M
DL-arginine	54		200 <sup>28</sup>		230	D
Acetonedicarboxylic acid	55		135 <sup>86,90</sup>		132	M
2-Aminoterephthalic acid	56		225 <sup>101</sup> and 185 <sup>102</sup>	223	324	D

TABLE I. (Continued.)

Precursor	No	Molecule	T <sub>MLD</sub> (°C)	TG <sub>onset</sub> (°C)	T <sub>phase-change</sub> (°C)	Phase-change type
2,3,5,6-Tetrafluoro-1,4-benzenediol	57		Not given in Ref. 22		169	M
2-Fluoro-4-(trifluoromethyl) benzaldehyde	58		~60 <sup>36,37</sup>		182	V
2,5-Dihydroxyterephthalic acid	59		190 (unpublished work)	230	281	D
4,4'-Oxydianiline	60		~140 <sup>43,46,103–109</sup>	168	191	M
Sebacic acid	61		147 <sup>41</sup>		220	M
Terephthaloyl chloride	62		90 <sup>110</sup>		81	M
Trimesic acid	63		245 <sup>98</sup>	252	375	M
2,6-Naphthalenedicarboxylic acid	64		250 <sup>111</sup> and 225 <sup>112</sup>	275	>300 <sup>a</sup>	M
PMDA	65		150 <sup>77</sup>		283	M
4,4'-Biphenyldicarboxylic acid	66		250 <sup>112</sup>	287	>300 <sup>a</sup>	M
7-Octenyltrichlorosilane	67		~100 <sup>69,113,114</sup>		223	V
1,2,4,5-Benzene tetracarboxylic acid	68		~190 <sup>7,90</sup>		281	M
4,4'-Azodibenzoic acid	69		~310 <sup>115,116</sup>	325	330	D

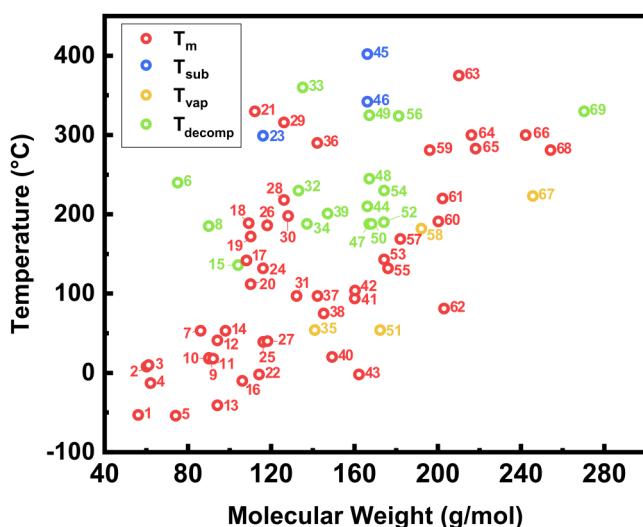
<sup>a</sup>The reported melting points for 64 (2,6-naphthalenedicarboxylic acid) and 66 (4,4'-biphenyldicarboxylic acid) are both just >300 °C, which is just a rough estimate.

temperature; the T<sub>m</sub> data are mostly from Jean-Claude Bradley Open melting dataset<sup>117</sup> and cross-checked with manufacturers' catalogs such as Sigma-Aldrich's (in case of significant deviation, the manufacturer's value was used).

Optimally, an organic compound used as a precursor should show in our (vacuum) TG run a single sharp weight-loss step due to sublimation. This was essentially the case for all the compounds investigated (c.f., the examples shown in Fig. 1). For our further discussion, we analyzed the TG data by determining the TG<sub>onset</sub>

temperature from the weight-loss step as demonstrated in Fig. 1(a) for terephthalic acid (TPA).

For TPA, we carried out the TG analysis also under normal pressure. From the two TG curves recorded in vacuum (4 mbar) and normal pressure, it can be seen that the TG<sub>onset</sub> value is—as expected—considerably lower for the vacuum run. In the case of TPA, the difference between the two TG<sub>onset</sub> values, 302 and 232 °C, is as large as 70 °C. According to previous literature data for TPA, the onset temperature is as high as 330 °C; however, this TG analysis was



**FIG. 2.** Relation between the molecular weight and selected thermal properties ( $T_m$ ,  $T_{\text{sub}}$ ,  $T_{\text{vap}}$ , and  $T_{\text{decomp}}$ ) for the 69 organic compounds listed in Table I.

carried out in 1 atm  $\text{N}_2$  atmosphere with a much higher heating rate (10  $^{\circ}\text{C}/\text{min}$ ).<sup>118</sup> It is important to note that for TPA, the atmospheric pressure TG run is feasible; this is, however, not the case for many of the organics as many of them tend to decompose before sublimation when heated under normal pressure. From Table I, it can be seen that for many organic compounds used as precursors in ALD/MLD, the decomposition temperature is relatively low.

To gain an overview, we plot in Fig. 2 the  $T_m$ ,  $T_{\text{sub}}$ ,  $T_{\text{vap}}$ , and  $T_{\text{decomp}}$  values collected from literature for all the chosen 69 organic compounds against their molecular weight ( $M$ ); in general, an increasing trend is seen for all these values with increasing  $M$ . There is naturally considerable scattering in the data, presumably due to specific chemical bonding effects on lattice energy and thereby sublimation characteristics. Sublimation enthalpy ( $\Delta H_{\text{sub}}$ ) depends on factors such as atomic weights, hybridization states and bonding

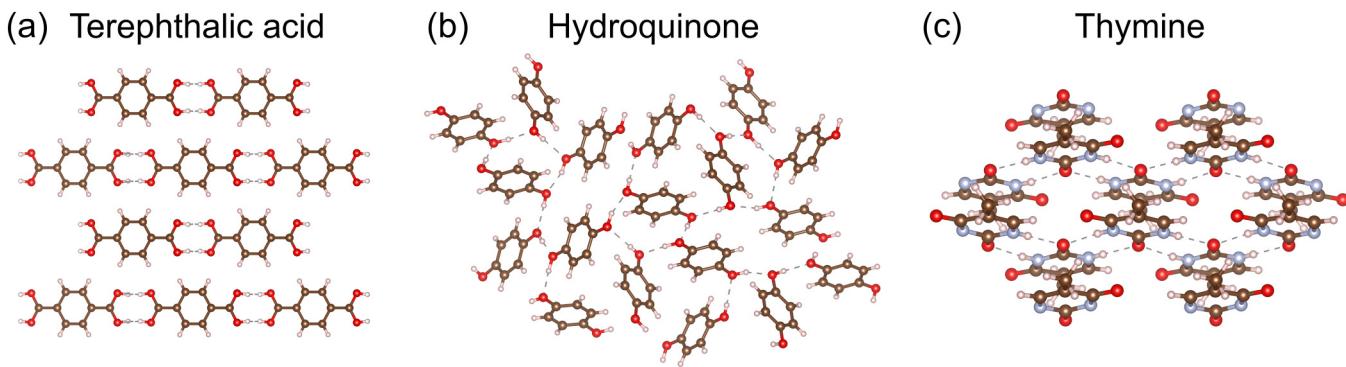
environments of the component atoms, as well as the nature and the number of hydrogen bonds occurring in the crystal structure.<sup>119</sup>

As a general trend of organics,  $\Delta H_{\text{sub}}$  increases with increasing number of carbon atoms; however, aliphatic and aromatic compounds follow somewhat separate trends. Slight difference is also seen between linear and branched molecules; branched molecules are often sterically hindered and show, therefore, weaker interactions and lower  $T_m$  values.<sup>119</sup> Molecular symmetry has also a distinct effect on  $T_m$  of organic compounds, such that the more symmetric molecules in the crystalline form tend to have higher melting temperatures in comparison to similar molecules with lower symmetry.<sup>120</sup>

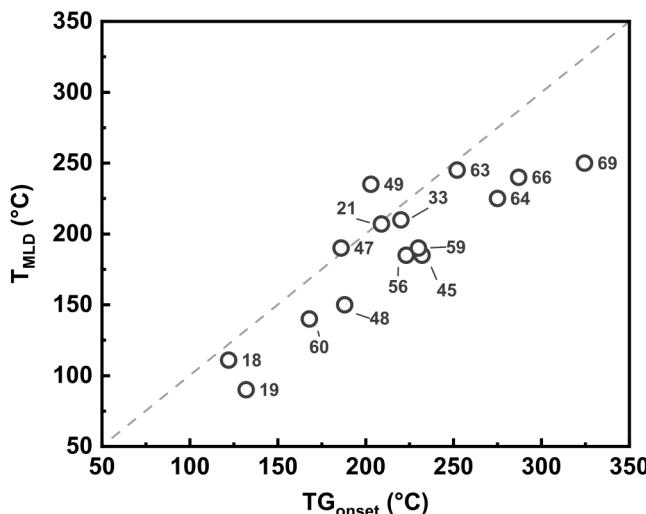
From Fig. 2, the “higher-than-expected” temperature values for the compounds 6 (glycine), 21 (uracil), 23 (fumaric acid), 29 (thymine), 36 [(2E,4E)-hexa-2,2-dienedioic acid], 45 (TPA), 46 (isophthalic acid), and 63 (trimesic acid) are well explained by the strong hydrogen bonding (SHB) effect.

Namely, compounds that contain larger numbers of hydrogen-bond acceptor/donor groups are typically rigid, relatively symmetric and tightly packed, and show higher sublimation enthalpies.<sup>121</sup> Most evidently, the SHB effect is seen for TPA; it has eight strong H-bonds from four different points of the molecule (Fig. 3). In the case of compounds 23 and 36, the *trans*-position and tight crystallographic packing place them even higher in the Fig. 2 plot. Among the hydrogen-bonded systems, also the specific H-bond arrangement affects the sublimation characteristics (Fig. 3). For example, dicarboxylic acids behave differently from the corresponding monofunctional molecules.<sup>119</sup> On the other hand, e.g., for the compound 43 (3-(trifluoromethyl) phenol), the “lower-than-expected” position in Fig. 2 is presumably due to the trifluoro group and steric hindrance.

Now, to discuss the relevance of our vacuum TG analysis, we plot in Fig. 4 the obtained  $\text{TG}_{\text{onset}}$  values against the  $T_{\text{MLD}}$  values used in practical ALD/MLD experiments. Interestingly, the  $T_{\text{MLD}}$  values are typically lower by approximately 14% (standard deviation 8%) than the  $\text{TG}_{\text{onset}}$  values. We believe this observation could serve as a rough guiding rule when setting the source temperature for the organic precursor during the course of a new ALD/MLD process development. Naturally, the specific reactor configuration and the selected pulsing and purging times naturally play a certain role as well; for example, in the case of ethylene glycol (molecule 4),



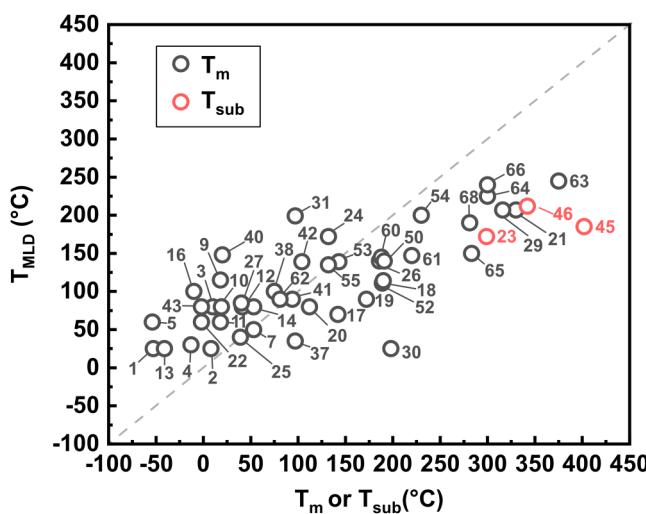
**FIG. 3.** Examples of different H-bonding schemes: (a) TPA has eight H-bonds from four different points of the molecule, (b) hydroquinone has only four H-bonds from two different spots ( $-\text{OH}$ ), and (c) thymine has four H-bonds from three different spots, with much more tight molecular packing.



**FIG. 4.** Present TG<sub>onset</sub> values plotted against the T<sub>MLD</sub> values used as the precursor source temperature in practical ALD/MLD experiments in literature; the dashed line represents the situation for TG<sub>onset</sub> = T<sub>MLD</sub>.

the T<sub>MLD</sub> values vary from 30 °C (F-120 ASM reactor)<sup>122</sup> even up to 80 °C (when the ethylene glycol was stored in an external container and the flow to the reactor was controlled with a valve).<sup>35</sup>

We, moreover, investigated how well the normal-pressure T<sub>m</sub> or T<sub>sub</sub> value could be utilized for the proper T<sub>MLD</sub> value search. These values are well tabulated in basic literature for most of the relevant organic precursors. Like in the case of our TG<sub>onset</sub> values, a clear correlation between T<sub>m</sub>/T<sub>sub</sub> and T<sub>MLD</sub> is seen in Fig. 5.



**FIG. 5.** Reported normal-pressure T<sub>m</sub> and T<sub>sub</sub> values plotted against the T<sub>MLD</sub> values used as the precursor source temperature in practical ALD/MLD experiments in literature; the dashed line represents the situation for T<sub>m</sub>/T<sub>sub</sub> = T<sub>MLD</sub>.

Nevertheless, in this plot, much more “random” variation is seen compared to the TG<sub>onset</sub> versus T<sub>MLD</sub> plot shown in Fig. 4. In particular, the proper T<sub>MLD</sub> seems to be higher than T<sub>m</sub>/T<sub>sub</sub> at low temperatures and vice versa at high temperatures. The reason behind this observation is not fully understood; however, the “too high” T<sub>MLD</sub> values for the precursors with the lowest T<sub>m</sub>/T<sub>sub</sub> values are apparently due to the fact that in ALD/MLD the precursors are not commonly cooled below room temperature.

Finally, we like to turn back to terephthalic acid as an illustrative example. For TPA, Alfa Aesar catalog reports T<sub>sub</sub> at 402 °C; this is determined in a sealed glass tube as a point where the vapor pressure of TPA reaches 1 atm. Other chemical manufacturers typically report only the T<sub>m</sub> value, which is higher than 300 °C. As discussed earlier in this work, the normal-pressure TG measurements (in N<sub>2</sub>) revealed the onset temperature between 300 and 330 °C depending on the heating rate. Our vacuum TG<sub>onset</sub> value of 232 °C is, thus, clearly closest to the T<sub>MLD</sub> value of 185 °C typically used in practical ALD/MLD experiments.<sup>123</sup>

#### IV. SUMMARY AND CONCLUSIONS

In the present work, we measured the TG<sub>onset</sub> temperatures for 15 representative organic compounds commonly employed as precursors in ALD/MLD. The measurement conditions (vacuum, slow heating rate) were chosen so that the TG<sub>onset</sub> values obtained could provide us with useful estimates for the source temperatures required for these organic precursors in the practical ALD/MLD growth of inorganic-organic thin films. Indeed, a clear correlation between the thus far reported T<sub>MLD</sub> values and our TG<sub>onset</sub> values was seen, the former being by approximately 14% lower (standard deviation of 8%).

Since the vacuum TG technique is not always available, we also considered the possibility to estimate the T<sub>MLD</sub> temperatures based on the melting points T<sub>m</sub>, commonly found in literature for the relevant organic compounds. For this purpose, we collected thermal data for altogether 69 organic compounds (including the 15 compounds experimentally investigated in the present work) so far employed in ALD/MLD. It was found that the T<sub>m</sub> values, in general, reflect relatively well the TG<sub>onset</sub> and T<sub>MLD</sub> values. However, particularly challenging are the materials with strong hydrogen bonds as these tend to considerably increase the melting point but not necessarily the required T<sub>MLD</sub> temperature.

Being able to choose the precursor source temperatures properly allows faster process optimizing. Too low source temperatures require longer pulse lengths, thus elongating deposition times and possibly also leading to larger fluctuations in the temperature profile along the reactor chamber. In contrary, too high source temperatures may lead to decomposition of the precursor and uncontrollable film growth.

#### Authors' Contributions

J.M., A.K., and J.H. contributed equally to this work.

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