Designing Suitable Metal Amidinate Sources for TiN and Ba/Sr-containing Thin Films

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Selection of Suitable Platforms for ALD

Metal Amidinates

- **Bidentate “chelating” effects** → Improved thermal stability
- **$R^{1,2,3}$ tuning in amidinate** → Volatility and reactivity control
- **No direct M-C bonds** → Less carbon incorporation in films
- **Amidinates** of La, Cu, Co, Ru, Ni, Er, Gd, Zr, Hf, Y are used efficiently in ALD.
New Amidinate Sources for Ba, Sr and Ti

- TiN is an excellent barrier and also a good electrode material.
- The current titanium sources (TDMATi and TDEATi)
  - lack thermal stability and decompose at elevated temperatures
  - may lead to inferior quality TiN films.
- New Ti (III) Amidinate is designed to overcome these limitations
- STO, BTO and BST find applications in
  - NVFeRAM, microwave, DRAM, MEMs.
- Ba and Sr amidinates are also developed as alternative sources.
New Ti, Sr, and Ba Sources from Rohm and Haas

Ti-FAMD

Sr-AMD

Ba-AMD
**Ti-FAMD** offers:

- highly volatile liquid Ti (III) precursor
- Clean evaporation with negligible residues
- VP = 0.1 Torr at 80 °C, suitable for ALD
TiN Thin Film Processing from Ti (III) FAMD

Source Temp: 85 °C

ALD TiN: 280 < T < 310 °C

CVD TiN: 310 < T < 335 °C

CVD TiCN: T > 335 °C

ALD process window is 280 < T < 310 °C
TEM of ALD TiN

Real space image

Diffraction pattern

Plane view

Cross-section

Amorphous with some tiny nanocrystalline regions
Smooth films (with RMS = 0.46nm) were obtained.
TiN ALD: Step Coverage by TEM

Conformal in 80:1 aspect ratio hole, ALD at 335 °C with ammonia
No C in the films at < 335 °C by XPS

Ti-FAMD
Vapor Pressure of Sr AMD

$$\log P(\text{Torr}) = 10.41 - \frac{3887}{T (K)}$$

Temperature Centigrade

Vapor Pressure (Torr)
Using Me$_3$N as a carrier gas increases the TG vapor transport rate of Sr(thd)$_2$ and Sr(amd)$_2$

- >3 x faster for Sr(thd)$_2$
- >6 x faster for Sr(amd)$_2$
- Sr(amd)$_2$/Me$_3$N >20 x faster than Sr(thd)$_2$/N$_2$
High Thermal Stability of Sr/Ba-AMD

Stable up to 250° C

Stable up to 220° C

Thermal stability studies by Accelerated Rate Calorimetry analysis (ARC)
## Properties of the New Ti, Sr, and Ba Precursors

<table>
<thead>
<tr>
<th>Name</th>
<th>M. W. (g/mol)</th>
<th>Appearance</th>
<th>M. P. (ºC)</th>
<th>Density (g/mL)</th>
<th>Vapor Pressure</th>
<th>Thermal Stability</th>
<th>¹H NMR</th>
<th>Solubility</th>
<th>Shelf life</th>
<th>TGA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-FAMD</td>
<td>283.37</td>
<td>Deep Brown liquid</td>
<td>N/A</td>
<td>0.90</td>
<td>Data collection in progress</td>
<td>Stable to 250 ºC by ARC</td>
<td>Organic impurity N.D.</td>
<td>Soluble in hydrocarbon solvents (&gt; 0.1 M)</td>
<td>Stable over 3 months</td>
<td>Clean evaporation</td>
</tr>
<tr>
<td>Sr-AMD</td>
<td>852.38</td>
<td>White solid</td>
<td>&gt; 200 ºC</td>
<td>0.50</td>
<td>log (P (\text{Torr}) = 7.872 - 3129/T(\text{K}))</td>
<td>Stable to 220 ºC by ARC</td>
<td>Organic impurity N.D.</td>
<td>Soluble in hydrocarbon solvents (0.1 M)</td>
<td>Stable over 6 months</td>
<td>Clean evaporation</td>
</tr>
<tr>
<td>Ba-AMD</td>
<td>961.79</td>
<td>White solid</td>
<td>&gt; 200 ºC</td>
<td>0.54</td>
<td>Data collection in progress</td>
<td>Stable to 220 ºC by ARC</td>
<td>Organic impurity N.D.</td>
<td>Stable in hydrocarbon solvents (0.1 M)</td>
<td>Stable over 4 months</td>
<td>Clean evaporation</td>
</tr>
</tbody>
</table>
Summary

- New sources of Ti, Sr and Ba are needed for TiN, STO and BST applications.

- Ti-FAMD, Sr-AMD and Ba-AMD with greater thermal stability are developed.

- Preliminary ALD results for TiN using liquid Ti (III) source are reported.

- Further growth studies on BST and STO are to be conducted.