Optimizing the selection and supply of Hf precursor candidates for gate oxide


ABSTRACT
Selecting a precursor for gate oxide deposition requires extensive characterization of targeted molecules. Critical analytical parameters for MOCVD and ALD precursors, like vapor pressure, thermal stability, and metallic contamination are presented and results discussed herein for the most promising Hf precursors currently under investigation: Tetrakis(ethylmethylamino)hafnium (TEMAH), tetrakis(dimethylamino)hafnium (TDMAH), tetrakis(diethylyaminohafnium) (TDEAH), tetraakis(tertbutylox)hafnium (HTB) and hafnium tetrachloride (HfCl4). In this article, we show how these characterizations help in preventing precursors’ degradation, identifying gas-phase species and defining process windows and distribution parameters.

Introduction
Today there is considerable interest in the development and optimization of CVD films particularly in the search and evaluation of precursors for metal-organic chemical vapor deposition (MOCVD) and atomic layer deposition (ALD) of hafnium oxide films. Hafnium based oxides are being considered as promising candidates for high dielectric constant gate oxide for the 65nm node and beyond as well as for next-generation DRAM capacitors. For optimal handling, distribution and processing, the most important precursor selection criteria include physical state, vapor pressure, thermal stability at reasonable vaporization temperatures and purity. The optimal candidate needs to be reactive enough to enable non-reversible monolayer ALD, highest growth rate at reasonable process temperatures, and yet stable enough to enable proper handling, shelf-life and contamination-free delivery to the process reactor. Even though some of the promising precursors have been identified in the literature and compared in terms of deposition results [2–4], there is surprisingly very little comparative information on their thermal properties and purity requirements. In this work, these characterizations are assessed for a set of commonly considered Hf precursors.

HfCl4 is the most prominent member of the hafnium halide family – it is the most commonly used halogenated hafnium precursor. It is a moisture reactive white powder, with a high sublimation point of 320°C at atmospheric pressure and a vapor pressure of 1 torr at 190°C. HfCl4 is corrosive by-products, such as HCl, which may affect both the film quality and CVD chamber integrity, which can potentially limit its use. HfCl4 is, however, a strategic compound for chemical suppliers, as it is often the starting material to synthesize other metal-organic precursors. Its purity specifications are therefore of significant importance.

Hafnium complexes with amino ligands mainly consist of tetrakis(dimethylamido)hafnium (TDMAH), tetrakis(ethylmethylamido) hafnium (TEMAH) and tetrakis(diethylamido)hafnium (TDEAH). Successful ALD and CVD of HfO2 and HfN from such hafnium amides has been previously reported [5–7].

Hafnium complexes with alkoxo ligands notably consist of tetrakis(tert-butoxy) hafnium or Hf(OtBu)4 (HTB). Other possible alkoxo precursors are homoleptic and have bidentate ligands such as...
tetrakis(methoxymethylpropanoxy) hafnium (Hf(mmp)$_4$), tetrakis(acetyl acetionate)hafnium, Hf(acac)$_4$, and more recently tetra(2,2,7-trimethyl-3,5-octanedionato)hafnium (Hf(tod)$_4$). The use of bidentate ligands leads to a higher-order complexation between the metal and ligands that provides a shielding effect around the metal. It should lead to less reactivity to moisture. In addition, there are heteroleptic alkoxy precursors that incorporate mono- and bi-dentate ligands, such as bis (t-butoxy)bis(methoxymethyl propanoxy) hafnium (Hf(OtBu)$_2$)(mmp)$_2$ further called HTBMMP) which have also been reported [8]. Successful ALD and CVD of Hafnium oxides and silicates, for instance from HTB, have also been reported [2,4,10].

Precursor candidates that are both liquid and very volatile are most preferred, for easier delivery to the process chamber either by bubbling or by direct liquid injection. Solid precursors – such as those with bidentate ligands, would generally be transformed into liquid form by dissolution into a high-purity solvent media in order to help control a precise and regular flow of precursor, but this introduces additional risk of the solvent interferring with the process deposition chemistry particularly in CVD processes using oxidizing gases with hydrocarbon solvents. Optimal selection of a precursor and how it is used in high-volume semiconductor manufacturing requires detailed thermal property evaluation, which is not well documented today for many precursors.

**Thermal properties of selected Hf precursors**

**Vapor pressure measurement**

One of the most critical thermal parameters of a precursor is its vapor pressure as a function of temperature. The latter needs to be known to optimize the delivery of precursor to the deposition chamber. Sufficient precursor vapor density is needed to allow adequate deposition rates and yet, care is needed not to overheat the precursor beyond its self-decomposition temperature. Thus, from knowledge of the thermal decomposition temperature of the precursor and its vapor pressure, one can assess its maximum permissible vapor density for the process.

The vapor pressure of a given precursor can be strongly influenced by any degradation that may have occurred. The three most common forms of degradation of these precursors would be (a) hydrolysis from trace moisture contamination, (b) thermal pyrolysis, and (c) oligomerization. Whereas partial oligomerization of product will not change its observed vapor pressure very much, degradation by trace hydrolysis or thermal decomposition will produce relatively high-volatility by-products that will significantly influence the observed vapor pressure. Therefore vapor pressure measurements require special attention. The description of a vapor pressure measurement setup at Air Liquide’s R&D centers is given below.

**Vapor pressure setup description**

A stainless steel precursor vessel is attached to a temperature-controlled manifold equipped with a capacitance manometer that is also temperature controlled. The precursor vessel can be cooled to as low as 77K using a liquid nitrogen bath or heated with a resistive band heater. Combination of both heating and cooling is necessary in order to induce freeze-pump-thaw cycles thereby discriminating between true precursor vapor pressure and artificially high vapor pressure from decomposition by-products that may potentially be present.

The precursor vessel is maintained at a lower temperature than all other portions of the manifold. This is done to ensure that precursor vapors cannot condense anywhere in the system other than the precursor vessel. The manifold is maintained at 120°C, while the pressure gauge is kept at 150°C. The pressure gauge is calibrated at an elevated temperature of 150°C.

Between measurements, a turbo pump helps achieve vacuum below 1 millitorr, which also determines the detection limit of the measurement. Vapor pressure curves are plotted and the data is fitted to the Clausius–Clapeyron equation in order to estimate its heat of vaporization, which is another important thermal property of the precursor.

**Vapor pressure measurements**

Samples are prepared and loaded into precursor vessel in a glove box under a nitrogen atmosphere. The nitrogen remaining in the vessel is removed by freeze-pump-thaw cycles on the sample vessel. These cycles are repeated until reproducible vapor pressures are observed.

Measurements are considered reliable only after the pressure in the manifold is stable over time, as there may be some passivation of the manifold upon addition of vapors of a new precursor. At each temperature, measurements are repeated to ensure that results are reproducible, indicating that decomposition by-products are not influencing vapor pressure measurements.

In Figure 3, measured values of TDEAH vapor pressure are given as a function of temperature along with the Clausius–Clapeyron plot indicating the heat of vaporization.

Table 1 lists a comparison of vapor pressure.

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**Table 1**

<table>
<thead>
<tr>
<th>Precursor</th>
<th>Vapor Pressure (mTorr)</th>
<th>Detection Limit (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hf(mmp)$_4$</td>
<td>1000</td>
<td>10</td>
</tr>
<tr>
<td>Hf(acac)$_4$</td>
<td>500</td>
<td>5</td>
</tr>
<tr>
<td>Hf(tod)$_4$</td>
<td>200</td>
<td>2</td>
</tr>
</tbody>
</table>

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**Figure 2**

Vapor pressure setup.
pressures for selected hafnium precursors.

TDEAH and TEMAH have relatively low vapor pressure, permitting less vapor density to be introduced into the deposition chamber. Thus, for a comparable vapor density as the other Hf precursors, higher vaporization temperatures will be required for TDEAH and TEMAH. However, an upper temperature limit will be imposed by thermal stability of the precursor and this is where complementary thermal characterization of the precursor is necessary.

TDMAH and HTB have higher vapor pressures than the other two organometallic precursors examined in this study. From vapor pressure data, these precursors may be better candidates to meet the step-coverage requirements for DRAM deep-trench structures with high aspect ratios since it requires pulse times lasting several seconds of residence time to enable the molecules to reach the bottom of deep trenches. For TDMAH, the downside is in the difficulties associated with handling and storage (low melting point solid that requires freezer storage).

**Thermal behavior of selected Hf precursors**

Thermal behavior of metal-organic precursor is best assessed with an advanced TGA/DSC/DT setup that can enable by-product and evaporation-product monitoring. When using the setup under ramping temperature (typically at 10°C/min), 1) the thermal transition points of the precursor (glass transition, melting, evaporation, decomposition) can be determined, 2) the remaining non-volatile residues are a good indicator of the thermal degradation of the precursor before evaporation. The latter is also an indicator of precursor purity. Independent of their vapor pressure, precursors with higher non-volatile residues amount may entail more elaborate distribution systems and reactor clogging. Also, when using the TGA under isothermal conditions, one can assess if at a given temperature, the precursor preferably evaporates or decomposes. This can be accomplished both by monitoring the exhaust by-products and measuring the non-volatile residue content.

In the following section, such thermal behavior assessment is performed for HTB, TDEAH, TEMAH and TDMAH, notably under isothermal conditions (80°C, 120°C and 150°C to simulate usual distribution temperatures).

**Thermal behavior analysis setup**

The thermal behavior analysis setup composed of a thermal gravimetric analyzer (TGA), used with a differential thermal analysis (DTA) or differential scanning calorimetry (DSC) system and coupled with a Fourier transform infra red spectrometer (FTIR). A QMS spectrometer is also coupled in parallel with the FTIR for relevant studies. The TGA setup is placed in an argon-purged glove-box and can operate both at atmospheric pressure and under vacuum.

**TGA/DSC characterization of selected precursors**

HTB, TDEAH, TDMAH and TEMAH mass loss during TGA runs at atmospheric pressure under open crucible conditions and 10°C/min temperature ramp are represented as a function of temperature in Figure 4. The non-volatile residues for HTB, TDEAH, TEMAH and TDMAH are 2.0%, 7.3%, 2.1% and 3.4% respectively. This may indicate that for increasing temperature and atmospheric pressure, TDEAH has the highest decomposition that occurs before evaporation and may, as a result, entail clogging issues. TDMAH has the lowest 50% mass loss temperature (148°C), but its non-volatile residue was slightly higher than that of HTB and TEMAH, indicative of some partial decomposition even before 148°C.

Thermal transition points are assessed using DSC. For TDMAH, it reveals a melting point at about 40°C. Non-volatile residue amounts using DSC (closed crucible) are higher, e.g. 17% for TDEAH and 10% for TEMAH, as a result of longer evaporation time, allowing the precursor to reach a higher temperature that can lead to decomposition. HTB has much lower non-volatile residue even with a closed crucible (<2%) due to its much higher volatility that enables evaporation before decomposition. Figure 5 displays the DSC analysis of HTB and HTBMMP. HTBMMP is a hexa-coordinated bidendate heteroleptic precursor, which has been claimed as less reactive towards water. Figure 5 shows that two thermal transitions are observed for HTBMMP (melting around 107°C and then simultaneous evaporation and/or decomposition), while a clean sharp evaporation peak is only detected at 234°C for HTB.

![Figure 3. VP curve for TDEAH (left), Clausius–Clapeyron VP curve for TDEAH (right).](image-url)
of HTB is confirmed by its low non-volatile residue content and by its good thermal behavior as discussed later. For the heteroleptic precursor HTBMMP, FT-IR exhaust analysis confirmed that several organic by-products are released during various steps, showing again a more complex thermal behavior for this precursor.

Evaporation vs. decomposition of Hf precursors at typical distribution temperatures

Combining mass spectroscopy or FTIR exhaust analysis with TGA at constant temperatures significantly increases the information content of a thermoanalytical run and therefore helps to better interpret mechanisms of thermal decomposition reactions if they occur. The studied temperatures are 80°C and 150°C for HTB, 120°C and 150°C for TEMAH and TDEAH, 150°C for TDMAH.

FT-IR exhaust monitoring along with non-volatile residue analysis shows that HTB fully evaporates without decomposition and does not decompose in the transfer lines of the FT-IR, even at 150°C. Even though highly reactive towards moisture, HTB is consequently a precursor that can be delivered at high vapor densities without decomposition. Conversely, alkyl amino precursors, TDEAH, TEMAH and TDMAH, exhibit longer transfer time in the TGA after their evaporation, and show indications of decomposition such as significant amount of free ligand in the exhaust. TDEAH and TEMAH were both partly decomposed at 120°C and 150°C. This decomposition likely occurs after evaporation during the transfer time to the FT-IR, and possibly not during the evaporation process. Figure 6 illustrates that TEMAH decomposition largely increases between 120°C and 150°C (decrease of FT-IR peaks absorbance at 875 cm⁻¹ and at 978 cm⁻¹) even though its vapor pressure is higher at 150°C. TEMAH should consequently be preferably distributed at temperatures lower than 120°C even if it results in lower vapor density. Note that at 120°C EMA is significantly present (N–C stretch at 717 cm⁻¹), suggesting non-negligible decomposition even at 120°C. Similarly, TDMAH partly decomposes at 150°C.

The properties of HTB, TDEAH, TEMAH and TDMAH are summarized in Table 2. The observed by-products mainly consist of ligand moieties and synthesis impurities. HTB was found to be stable in the gas phase up to at least 150°C. TEMAH, TDEAH and TDMAH were partly decomposed at 120°C and much more at 150°C, suggesting that one should avoid or minimize the duration of exposure of the precursors to elevated temperatures during the distribution process even though their vapor pressures are lower, as discussed earlier.

Shelf-life assessment by NMR analysis: Case of TEMAH and TDEAH

Another means of monitoring thermal degradation of precursors in the liquid phase is by NMR. In one of our studies, two hafnium precursors, TDEAH and TEMAH, were heated at 120°C for several weeks and the degradation by-products monitored by NMR. The heating of precursors was done by placing small amounts of precursor into sealed stainless steel vessels that were submerged in a heated oil bath maintained at 120°C. After heating, the precursor samples were diluted in deuterated cyclohexane solvent and analyzed by a ¹H NMR (500 MHz Varian). Figure 7 shows the NMR analysis from non-heated and heated samples of these two precursors.

In all cases, the dominant peaks observed are the ethyl and methyl alkyl groups of the amino ligands in these two precursors. However several weaker impurity peaks are observed to increase as the precursors are heated for longer periods of time. These impurity peaks are indicated in the lower portion of the figure where the vertical scaling of NMR spectra has been expanded (see Figure 7). After 2 weeks of heating, both TDEAH and TEMAH show several peaks associated with formation of free ligand. In the case of TDEAH, the free ligand is diethylamine (DEA) and in the case of TEMAH, the free ligand is...
ethylmethylamine (EMA). The splittings and number of peaks observed for these alkyl amines are complicated by the tendency of amines to complex to the metal in the precursor. In fact, the NMR peaks observed indicate both DEA and EMA are present in the samples in both complexed and non-complexed forms. Whereas the non-complexed DEA or EMA are quite similar to reference spectra of the amines by themselves, the complexed form of the amines show a splitting effect from N-H that is not present in the non-complexed form and coincidentally this splitting is approximately the same as that observed in adjacent carbon splitting seen in ethyl groups. So in effect, the quartet seen for –CH$_2$ in DEA is split into two quartets spaced apart by equivalent amount as within the quartet that yields a quintet nmr peak overall. In the case of EMA, the singlet observed from the lone –CH$_3$ group in EMA seen in non-complexed EMA is split into a doublet upon complexation.

Another notable change in NMR spectra upon heating the precursors is the broadening of the base in the main alkyl group peaks. This is most likely an effect of oligomerization of the molecules where they complex to one another via N-bridging bonds.

Two other degradation by-products observed in vapor-phase FTIR are C$_2$H$_4$ and CH$_4$, however both of them are too volatile to be observed by liquid-phase NMR in these experiments. Plus, CH$_4$ would only be formed at much higher temperatures. In addition to the free ligands, the expanded spectra also show

**TABLE 2: VAPORIZATION KINETICS AND GAS-PHASE DECOMPOSITION SUMMARY**

<table>
<thead>
<tr>
<th>HF Precursor</th>
<th>Isotherm T (°C)</th>
<th>Rate of mass loss (mg/s)</th>
<th>Detected decomposition</th>
<th>Detected by-products</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTB</td>
<td>80°C</td>
<td>0.0028</td>
<td>No</td>
<td>C$_2$H$_6$, tBuOH (traces)</td>
</tr>
<tr>
<td></td>
<td>150°C</td>
<td>0.0645</td>
<td>No</td>
<td>C$_2$H$_6$, tBuOH (traces)</td>
</tr>
<tr>
<td>TEMAH</td>
<td>120°C</td>
<td>0.0042</td>
<td>Partly EMA</td>
<td>EMA</td>
</tr>
<tr>
<td></td>
<td>150°C</td>
<td>0.0159</td>
<td>Partly EMA</td>
<td>EMA</td>
</tr>
<tr>
<td>TDEAH</td>
<td>120°C</td>
<td>0.0008</td>
<td>Partly DEA</td>
<td>DEA, C$_2$H$_4$</td>
</tr>
<tr>
<td></td>
<td>150°C</td>
<td>0.0038</td>
<td>Partly DEA, C$_2$H$_4$</td>
<td>DMA</td>
</tr>
</tbody>
</table>

Figure 6. Degradation of TEMAH during isothermal TGA (120°C and 150°C).

Figure 7. 1H NMR spectra of TDEAH (left) and of TEMAH (right).
1\(^1\)C sidebands and the isotopic solvent impurity, C\(_6\)D\(_4\)H as one would expect. This study shows that elevated storage temperature of either TDEAH or TEMAH yields degradation observable by \(^1\)H NMR in comparable amounts. In both cases, the degradation observed by NMR shows formation of protonated ligands – some of which are bound to the metal site of the precursor.

### Precursor purity

All contamination analyses were performed at Air Liquide Balazs Laboratories. Metal analyses were performed initially on two sources of HfCl\(_4\). Initial sample preparation was completed by taking 0.1–1.0 g of Hf precursor material followed by dilution in a HF/HNO\(_3\)/H\(_2\)O solution. Material handling was performed in an N\(_2\) glove box, and all reagents and deionized water were semiconductor grade or better. Analyses were performed via inductively coupled plasma mass spectrometry (ICP-MS) for the elements with part-per-trillion (ppt) to part-per-billion (ppb) type detection limits (<DL simply reported in Table 3). ICP optical emission spectroscopy (ICP-OES) was utilized for elements at higher concentrations, most notably zirconium. Additional metal analyses were conducted on the four complexes, TDMAH, TDEAH, TEMAH and HTB. Using a similar analysis scheme with ICP-MS and ICP-OES (Table 3).

Spikes and spike recoveries were also performed to ensure method validity and all recoveries were found in the 70–115% range. As these Hf complexes are likely purified from a starting HfCl\(_4\) source, much of the contamination seen in the complexes in Table 3 is indeed removed. The only elements observed for these compounds were aluminum, titanium, and iron at varying concentrations. Aluminum and titanium results in TDMAH, TDEAH, and TEMAH were analyzed both by two different ICP mass spectrometers, dynamic reaction cell ICP-MS and high-resolution ICP-MS with similar results.

An important note to make here is that sample preparation for these materials can make a significant difference in the final measured results. Although simple dilution was used for all results reported here, sample evaporation is another widely used technique. For these materials, however, extreme care should be taken when using the evaporation technique. In the case of the aluminum and titanium analogs of these hafnium complexes, for example Al(DEA)\(_3\) and Ti(DEA)\(_4\), the boiling point can be quite low; approximately 50 and 112°C, respectively. These compounds would be lost in an evaporation step, and in fact upon analysis following evaporation we measured much lower concentrations for Al and Ti; reflecting that the artificially low concentrations are not representative of the actual amounts in the hafnium compound.

In addition to metal analysis, the chloride content was also measured in each of the amino and alkoxo ligand compounds to help gauge purity. As the starting material is the HfCl\(_4\) compound, inefficient purification can potentially lead to large amounts of chloride in the final product. Sample preparation was performed by extracting the chloride from the hafnium complex followed by analysis via ion chromatography (IC). As with metal analysis, a spike was performed to ensure good recovery and an appropriate IC method; the response in this case is 78%. The results in Table 3 indicate the different levels of chloride in some Hf compounds.

By carefully performing metal analysis of precursors, the impurities that may contaminate the deposition can be forecasted. As illustrated here, Ti but also Zr, since they have the same chemistry compared to Hf, may be a recurrent contaminant for any Hf precursors. It is also demonstrated that different precursors or the same ones provided by different manufacturers, may have similar high levels of Zr since they are synthesized with the starting HfCl\(_4\) of the same purity. Another source (source 2 in Table 3) should be identified to solve the problem. These results also show the difference in the level of Cl depending on the molecule. Robust analytical capability

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**TABLE 3: METALLIC AND CHLORIDE CONTAMINATION IN HF PRECURSORS**

<table>
<thead>
<tr>
<th>Element</th>
<th>HfCl(_4) SOURCE 1 (ppb)</th>
<th>HfCl(_4) SOURCE 2 (ppb)</th>
<th>TDMAH (ppb)</th>
<th>TDEAH (ppb)</th>
<th>TEMAH (ppb)</th>
<th>HTB (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>B</td>
<td>388ppm</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Na</td>
<td>290ppm</td>
<td>530</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Mg</td>
<td>365</td>
<td>100</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
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<td>&lt;DL</td>
</tr>
<tr>
<td>Al</td>
<td>126ppm</td>
<td>500</td>
<td>&lt;DL</td>
<td>800</td>
<td>590</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>K</td>
<td>2290</td>
<td>220</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Ca</td>
<td>810</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Ti</td>
<td>2,150</td>
<td>1,100</td>
<td>3,310</td>
<td>2,865</td>
<td>3,790</td>
<td>1,100</td>
</tr>
<tr>
<td>Cr</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Mn</td>
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<td>&lt;DL</td>
</tr>
<tr>
<td>Fe</td>
<td>1220</td>
<td>480</td>
<td>&lt;DL</td>
<td>650</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Ni</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
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<td>&lt;DL</td>
</tr>
<tr>
<td>Cu</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Ba</td>
<td>500</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
<td>&lt;DL</td>
</tr>
<tr>
<td>Zr (ICP-OES)</td>
<td>1,490 ppm</td>
<td>390 ppm</td>
<td>1,610 ppm</td>
<td>1,860 ppm</td>
<td>1,650 ppm</td>
<td>1,350 ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>–</td>
<td>–</td>
<td>710</td>
<td>500</td>
<td>235</td>
<td>86</td>
</tr>
</tbody>
</table>

**Note:** ppm stands for parts per million, ppb stands for parts per billion, and DL stands for detection limit.
is critical not only in the screening process of new molecules but also for troubleshooting any contamination excursions once these new materials go into high-volume production in fabs.

Conclusion

Reliable handling, supply and distribution of Hf metal-organic precursors requires a good knowledge of fundamental properties such as volatility, degradation kinetics and purity. Incomplete understanding of these properties can lead to unacceptable process performance (growth rates, clogging of the tubing, etc.) and film quality (surface roughness, composition, etc.).

In this study, Air Liquide provides an overview of its precursor characterization capabilities necessary for full evaluation of MOCVD and ALD precursors. Vapor pressure measurements for thermal properties determination, degradation by-products identification and trace metallic impurity analysis have shown significant differentiation between the most promising hafnium precursors. By developing existing techniques and customizing analyzers, Air Liquide intends to improve characterization in order to better identify future promising candidates for high dielectric constant gate oxide deposition.

ACKNOWLEDGEMENTS

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REFERENCES

[10] K. Kubli et al., Chemical Vapor Deposition (2003), “ALD of HfO2 films using Hf(OtBu)2(mmp)2 and water”.
[12] Inorgtech Epichem Database.
[16] Kojundo Database.