

# technical bulletin

## New Zirconium Oxide Precursor for ALD

As the size of memory devices continues to be reduced the traditional materials used for the dielectric layer are becoming unsuitable.  $\text{Al}_2\text{O}_3$ , grown by atomic layer deposition (ALD), is already being used commercially to replace  $\text{SiO}_2$  but to meet future demands materials with even higher dielectric constant are required. Hafnium oxide based materials have been investigated for some time and several precursors for ALD are available to high purity in large volume, including two new sources designed by SAFC Hitech to provide optimum performance.

For the next generation memory devices there has been renewed interest in zirconium oxide based dielectric layers and particular attention to deposition via ALD. SAFC Hitech has therefore designed a new zirconium precursor specifically for ALD based on its highly successful  $\text{HfO}_2$  ALD work. Figure 1 illustrates the structure of the new source ZrD-04 **Bis(methylcyclopentadienyl)methoxymethylzirconium(IV)**. The physical properties of this source (high thermal stability, excellent reactivity, liquid) are such that it offers significant advantages over conventional zirconium sources i.e. Zr amides.

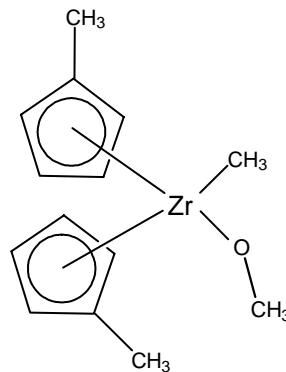


Figure 1: ZrD-04 structure

In detail the ZrD-04 shows good vaporisation characteristics and low residues in thermogravimetric analysis (TGA) and its vapour pressure is such that bubbling or direct liquid injection precursor delivery methods are equally suited. Figures 2 and 3 highlight the beneficial physical properties of ZrD-04 by comparison with the current precursor of choice  $\text{Zr}(\text{NEtMe})_4$ .

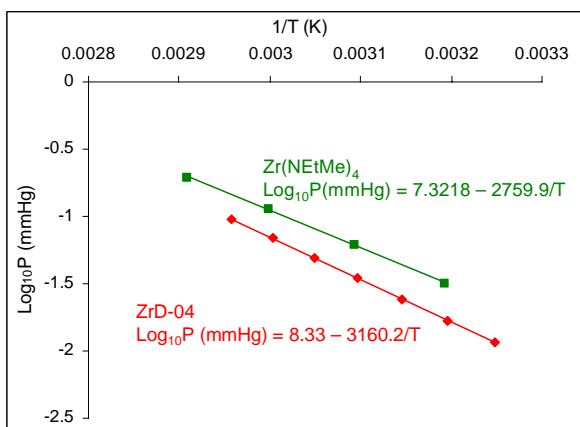


Figure 2: Vapour pressure data for ZrD-04 and TEMAZ recorded by SAFC Hitech

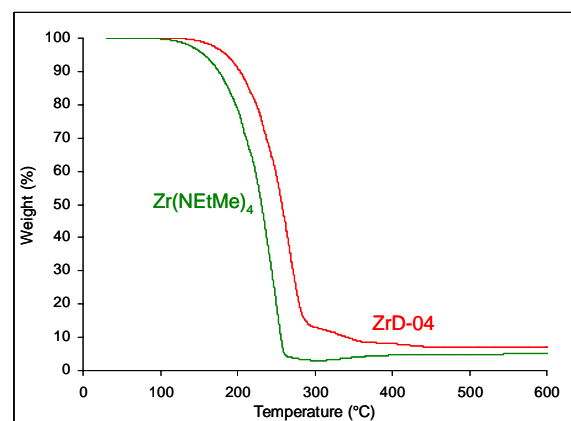


Figure 3: TGA data for ZrD-04 and  $\text{Zr}(\text{NEtMe})_4$

# technical bulletin

The long term stability of the source was also examined and compared to a conventional Zr amide source. Figures 4 and 5 highlight the differences observed when holding samples at 160°C for prolonged periods. A total absence of any decomposition in the ZrD-04 case contrasted with degradation of the conventional amide source after 6 hours. The ZrD-04 source can therefore be operated at higher temperatures without transport variation over time.

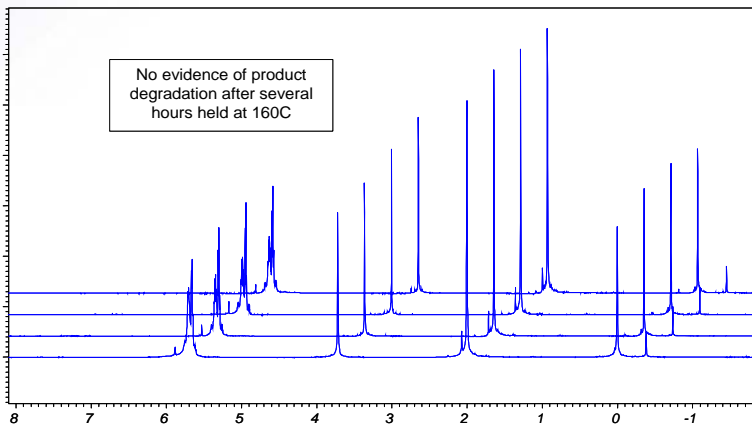


Figure 4 ZrD-04 at 160°C NMR stability data after 0hr, 1hr, 3hr and 6hr

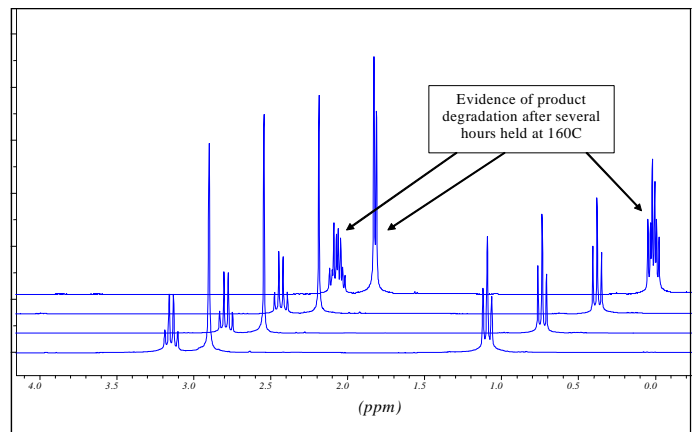


Figure 5 Zr(EtMe)<sub>4</sub> at 160°C NMR stability data after 0hr, 1hr, 3hr and 6hr

Another particular advantage attributable to the increased thermal stability of ZrD-04 is access to higher deposition regimes that should make process integration easier. To assess the true benefits of the source a series of ALD growth studies have been performed at a number of test sites with remarkable results to demonstrate 'true' self limiting ALD at deposition temperatures of 300°C. Deposition at even higher temperatures is also reasonably controllable thus the deposition growth window has been enlarged to give a highly robust process that is not as temperature dependant as current ZrO<sub>2</sub> ALD processes.

The data recorded using ZrD-04 and H<sub>2</sub>O with a source temperature of 68°C and reactor pressure of 2-3 mbar is shown in figures 6 and 7. Evidence for thermal decomposition of the source is not observed until 375°C with temperatures over 400°C necessary to move fully to the kinetic regime of the growth curve.

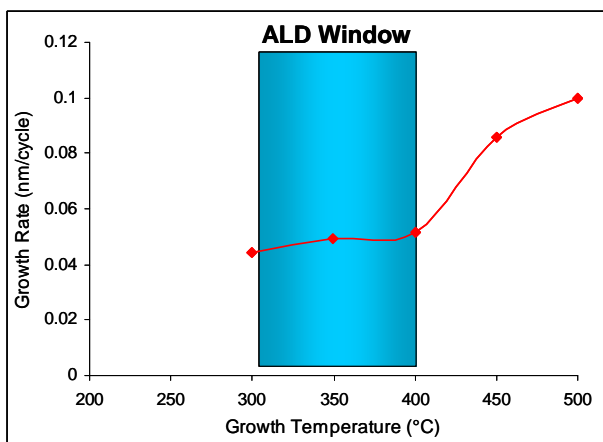


Figure 6 ZrD-04/H<sub>2</sub>O growth rate vs temperature data

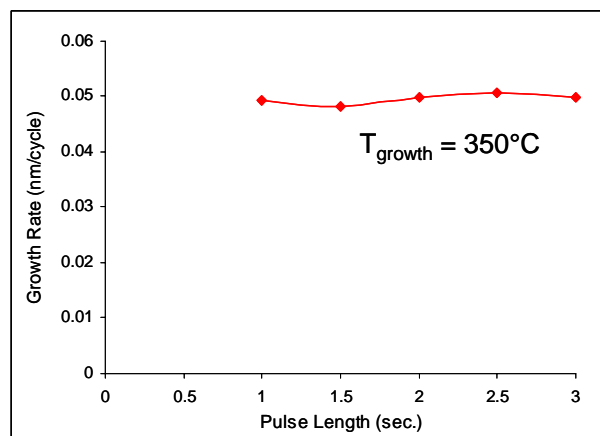


Figure 7 ZrD-04/H<sub>2</sub>O growth rate vs pulse length data