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New Hafnium Oxide ALD Precursors

For many years there has been considerable interest in hafnium oxide based materials for high-k dielectric layers in both memory and logic applications. For logic applications there are many integration challenges still to be overcome before a new material and deposition techniques are accepted. However, for memory applications, Al_2O_3 dielectric layers are already being utilised in the capacitor structure with deposition via atomic layer deposition (ALD).
ALD has the ability to deposit uniform conformal layers on very aggressive three dimensional structures, making it the ideal deposition technique for current and future memory applications. ALD places specific demands on precursors, therefore SAFC Hitech has designed two new hafnium molecules specifically for ALD, HfD-02 and HfD-04, which are patent protected (Figure I).

HfD-02
Low melting solid
(~60°C)

HfD-04
Liquid

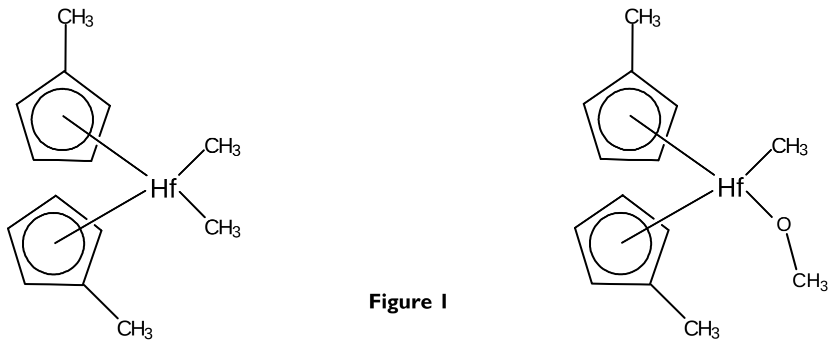

Figure I

HfD-02 Bis(methylcyclopentadienyl)dimethylhafnium(IV), $Hf[C_5H_4(CH_3)]_2(CH_3)_2$

HfD-04 Bis(methylcyclopentadienyl)methoxymethylhafnium(IV), $Hf[C_5H_4(CH_3)]_2(OCH_3)CH_3$

The current precursors of choice for the ALD of hafnium oxide based layers are hafnium amides, specifically, tetrakis (dimethylamino)hafnium, $Hf(NMe_2)_4$, and tetrakis(ethylmethylamino)hafnium, $Hf(NEtMe)_4$. These hafnium amides give "true" self limiting ALD at growth temperatures below ~275°C, above this temperature they thermally break down on the wafer surface destroying the self limiting growth mechanism. This gives poor step coverage, poor layer uniformity on single wafers and poor wafer to wafer uniformity on batch type processes, in addition to decomposition particles being created leading to loss of yield.
The new hafnium sources SAFC Hitech has designed demonstrate greater thermal stability than the hafnium amides allowing "true" self limiting ALD at higher deposition temperatures (Figure 2). To date ALD at 400°C has been demonstrated, but even higher temperatures may be accessible (Figure 3).

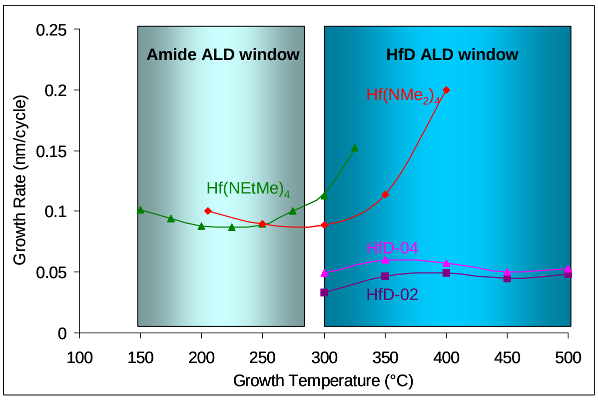

Figure 2: ALD comparison*

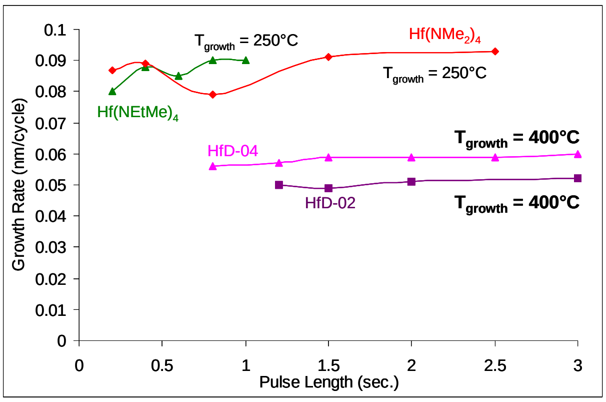

Figure 3: Precursor pulse length study*

*Kaupo Kukli, Tero Pilvi, Mikko Ritala, Timo Sajavaara, Jun Lu and Markku Leskelä, Thin Solid Films, 491, 328-338, 2005.
*Kaupo Kukli, Mikko Ritala, Timo Sajavaara, Juhari Keinonen and Markku Leskelä, Chem. Vap. Deposition, 8, No.5, 199-204, 2002.
*Jaakko Niinistö, Matti Putkonen and Lauri Niinistö, Helsinki University of Technology.

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The new sources show good vaporisation characteristics (Figure 4) and give low residues by thermal gravimetric analysis, TGA, (Figure 5) making these sources suitable for bubbling or direct liquid injection precursor delivery options. The higher thermal stability of the new sources also gives a wider ALD temperature window when compared to the hafnium amides; therefore, there have been no uniformity or particle issues during precursor testing. Simple capacitor structures have been fabricated using layers deposited from each source and capacitance-voltage graphs are included (Figures 6 and 7).

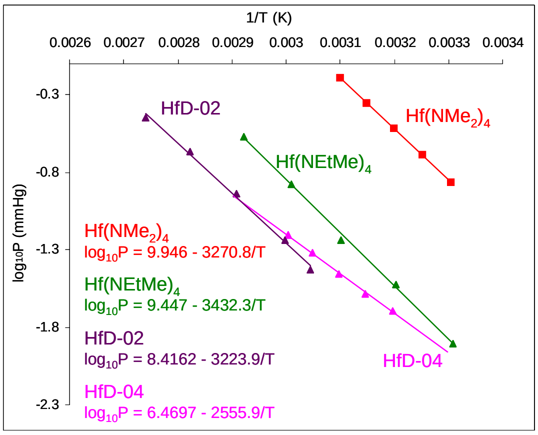

Figure 4: Vapour pressure data for Hf sources measured in house

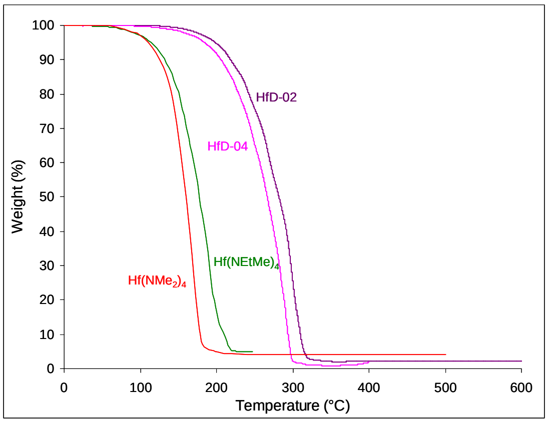

Figure 5: TGA comparison under N_2 at atmospheric pressure

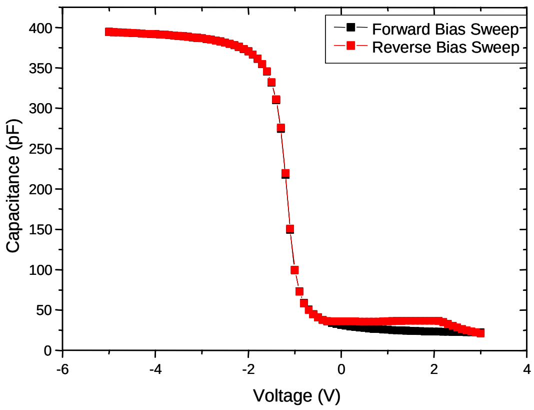

Figure 6: CV data for 54nm thick annealed HfO_2 layer deposited from HfD-02 after annealing at 850°C for 30min, N_2 Al/HfO_2/(SiO_2)/p-Si(100)/Al

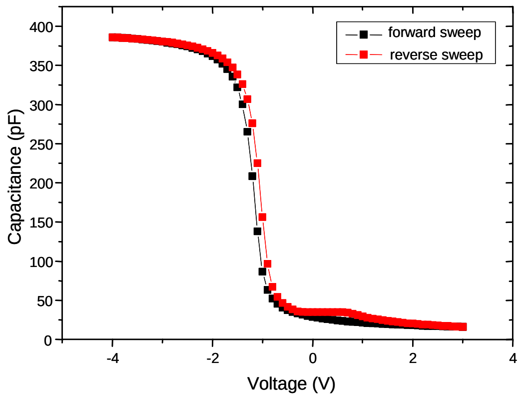

Figure 7: CV data for 64nm thick annealed HfO_2 layer deposited from HfD-04. after annealing at 850°C for 30min, N_2 Al/HfO_2/(SiO_2)/p-Si(100)/Al