This work encompasses precursor development for the fabrication of metal oxide thin films of titanium and zirconium. It is well known that precursor chemistry is central to the process development of thin film deposition techniques such as MOCVD and ALD. The main principle behind precursor development is the variation of the ligand skeleton to obtain easily vaporizable compound that decomposes under optimum conditions. The peripheral organic groups have an effect on the intermolecular interaction of the complexes. This in turn, can modify the physicochemical properties of the complex. Therefore, in this work, new precursors were developed and were characterized for their thermal and chemical properties. The most promising precursors were then applied in MOCVD, ALD and spin coating film deposition techniques. The films were evaluated in detail for their crystallinity, morphology and composition. Furthermore, functional properties of the films, in terms of optical and electrical properties, were also studied.

1. Guanidinate precursor chemistry for Zr(IV) and MOCVD of ZrO₂ thin films

A series of novel heteroleptic compounds of zirconium amide based guanidinate compounds (G₁–G₄) were successfully developed as precursors for MOCVD of ZrO₂ thin films exhibiting improved physicochemical properties compared to their respective parent amides (Chapter 3). Mono– and bis–guanidinate complexes were synthesized by a facile insertion reaction using diisopropylcarbodiimide (Scheme 1). While compounds G₁–G₃ were monomeric solids with a monoclinic or orthorhombic crystal lattice at room temperature, G₄ was a liquid precursor. All the compounds were less sensitive to air and moisture compared to the parent alkylamides. The fluxional properties of the compounds were confirmed by variable temperature NMR experiments in the temperature range –20 to 80 °C. Mass fragmentation studied by EI–MS showed that G₁ undergoes facile cleavage of the ligands to yield simple species which was encouraging in terms of precursor application in MOCVD technique. Thermal evaluation revealed that the compounds were thermally stable compared to their parent amides although their volatility was almost unaffected. The compound can be sublimed in quantitative yields without decomposition under optimum thermal conditions (100–120 °C). The physicochemical properties indicated that these compounds can act as potential MOCVD and ALD precursors.
Thin films of ZrO$_2$ were successfully deposited from G1 over the temperature range 400–700 °C on Si(100) (Chapter 6).\textsuperscript{1} Moderate growth rates of the order of 20 nm/min were obtained under optimized CVD process conditions. XRD revealed that films grown at lower temperature were amorphous (400 °C) and began to crystallize above 450 °C. Monoclinic phase was obtained for the films grown in the temperature range 500–700 °C (Figure 1). Morphology of the thin films was studied by SEM where the as–deposited films were uniform, dense and stoichiometric. The composition of the films was analyzed by RBS/NRA and XPS. The amount of carbon and nitrogen impurities was found to be low. Optical studies showed comparatively high transmission values (~80%) and the band gap was found to be in the range 5.5–5.7 eV for the thin films grown in the temperature range 400–700 °C.

The improved thermal stability of the guanidinate based compounds compared to the parent amides makes them very appealing for ALD applications. This was confirmed when compound G2 was applied successfully in a simple water assisted ALD process to deposit thin films of high permittivity cubic phase of ZrO$_2$ in the absence of any additional dopant or heat treatment. This is a significant contribution towards high-k ZrO$_2$ film deposition by ALD. The films revealed low root–mean–square (rms) roughness (below 5% of the film thickness) and an excellent step coverage and conformality (30:1 aspect ratio). Dielectric properties studied on ZrO$_2$ metal–insulator–metal (MIM) capacitors and showed high permittivity and low leakage currents.$^2$

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2. Ketoiminate class of precursors for Zr and solution based processing of ZrO₂ thin films

A series of new β–ketoiminato complexes of Zr(IV) (K₁–K₆) were synthesized by the convenient route of substitution reaction starting from [Zr(NEt₂)₄] (K₁–K₅) (Scheme 2) and [Zr(OPr)₄.iPrOH] (K₆). The yields were reasonably good and the purity of the complexes was confirmed by ¹H NMR study. The solid state structures determined by single crystal XRD revealed that complexes K₁–K₄ were monomeric while complex K₆ was dimeric in the solid state. ¹H NMR indicated fluxional behavior of the compounds in solution. The heteroleptic complexes K₁–K₃ were found to be thermally fragile compared to the homoleptic complexes K₄ and K₅ as indicated by TG/DTA study. Among the homoleptic ketoiminates, K₅ showed enhanced stability than K₄. TG/DTA study showed that the compounds had a narrow temperature window between volatilization and decomposition. The chemical stability and thermal fragility of the homoleptic ketoiminates make them less suitable for thermal MOCVD but rather more suitable for application in solution based techniques like LI–MOCVD or spin–coating to fabricate ZrO₂ thin films.
Based on the promising chemical properties and thermal characteristics, the homoleptic β–ketoiminato complex K5, was employed in a spin coating method to deposit thin films of ZrO2 (Figure 2). The films after deposition were annealed in the temperature range 350–700 °C for 1 h. The films showed a gradual transition from amorphous to crystalline structure with the rise in annealing temperature (350–700 °C) as revealed by XRD while SEM showed the formation of dense and uniform films. This study shows that introduction of chelating β–ketoiminato ligands with mixed N,O–coordination in the complex can make it suitable as precursors for application in solution based process such as spin coating. The low annealing temperature adopted for crystalline film preparation is an added advantage. This is the first example of a detailed study on functionalized β–ketoiminato of Zr(IV) aimed at application for solution based processing of thin films. The films also showed high transmission (~ 90%) in the visible region with optical band gap in the range 5.57–5.79 eV and thus have potential for use in optical or optoelectronic devices especially for low cost electronics.
3. Aminoalkoxide based precursor for Ti(IV) and MOCVD of TiO₂

[Ti(dmap)₂(NMe₂)₂] (Hdmap= 1–dimethylamino–2–propanol) (D1) was synthesized by the elimination reaction (Scheme 3) of Hdmap on [Ti(NMe₂)₄] resulting in a red oily compound that could be distilled at moderate temperature (90–100 °C). The yield of this reaction is high, could be easily purified and scale up to large batches was straightforward and simple. [Ti(dmap)₂(NMe₂)₂] also showed a enhanced shelf–life which is an important figure of merit for a CVD/ALD precursor. This compound was thoroughly characterized by NMR, MS and elemental analysis. The fluxionality of the compound was studied by variable–temperature NMR experiment in toluene–d₈. The molecular fragmentation was studied by EI–MS study which showed the cleavage of labile groups under the adopted conditions. The presence of labile organic moieties helps in the convenient dissociation of the precursor under MOCVD conditions. The thermal characterization revealed that [Ti(dmap)₂(NMe₂)₂] was volatile with sufficient temperature window and with low residual mass in TGA. Isothermal study at different temperatures (60, 80 and 100 °C) revealed that this compound could be sublimed over.

Figure 2: Summary of the solution based processing of ZrO₂ thin films with K5.
a long period of time without decomposition. These factors make it convenient for application in MOCVD of TiO$_2$ thin films.

Scheme 3: Reaction scheme showing the synthesis route for the [Ti(dmap)$_2$(NMe$_2$)$_2$] (D1).

Consequently [Ti(dmap)$_2$(NMe$_2$)$_2$] was employed in a MOCVD process to deposit thin films of titanium dioxide on Si(100) in the temperature range 500–800 °C (Figure 3) using oxygen as the oxidant. The presence of oxygen and nitrogen ligation to the metal in the precursor helps in maintaining a balance between stability and reactivity. Very high growth rates of the order of 320 nm/min was observed at deposition temperature of 700 °C. The films were polycrystalline with anatase phase appearing at lower deposition temperature (600 °C) while a mixed phase (anatase and rutile) was obtained at 700 °C. Further rise in deposition temperature to 800 °C resulted in the dominance of anatase phase in the films. SEM showed the formation of a dense film with long columnar structures (in the crystalline films). RBS/NRA analysis proved the presence of almost stoichiometric TiO$_2$ thin films with very low amount of nitrogen (<1%) or carbon (~5%) in the films. The films were hydrophilic with contact angle as low as 30° and it decreased with rise in deposition temperature. High absorbance was observed for the films deposited on ITO substrates and the optical band gap calculated from Tauc's plot varied in the range 2.8–3.3 eV. Thin films of TiO$_2$ were deposited on ITO substrates to study the photoelectrochemical properties of the films. Thin films grown at 700 °C showed a high photocurrent response (~550 μA/cm$^2$ at 1.5 V vs. Ag/AgCl). The TiO$_2$ films also showed high IPCE values which makes them suitable for photocatalytic applications.
Figure 3: Summary of the MOCVD of TiO$_2$ thin films with D1.