

Recent Developments in the MOCVD of Electronic Materials

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Chemical Vapour Deposition of the Oxides of Titanium, Zirconium and Hafnium for Use as High-k Materials in Microelectronic Devices. A Carbon-free Precursor for the Synthesis of Hafnium Dioxide

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A brief survey of the precursors used for the chemical vapour deposition of the dioxides of titanium, zirconium and hafnium is presented. The review covers precursors used for the closely related process known as atomic layer chemical vapour deposition (ALCVD or ALD). Precursors delivered by standard carrier gas transport and by direct liquid injection (DLI) methods are included. The complexes fall into four classes based upon the ligands: halides, alkoxides, acetylacetonates (acac) and nitrates. Compounds bearing a mixture of ligand types have also found application in this area. The impact of the ligand on the microstructure of the metal oxide film is greatest at lower temperatures where the deposition rate is limited by the surface reactivity. The first use of anhydrous hafnium nitrate, $Hf(NO_3)_4$, to deposit films of hafnium oxide on silicon is spectroscopy, X-ray diffraction and transmission electron microscopy. Copyright (© 2000 John Wiley & Sons, Ltd.

KEYWORDS CVD; metal nitrates; titanium; zirconium; hafnium dioxide; precursors

INTRODUCTION

As the gate length in field-effect transistors decreases, the thickness of the gate SiO_2 must also decrease. This trend faces an abrupt limit as the gate oxide thickness approaches ~ 2 nm, at which point direct tunnelling leads to unacceptably

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high leakage currents. One alternative involves replacing the ultra-thin SiO₂ films with a thicker film of a material having a higher dielectric constant. Materials of interest include the group IV metal oxides TiO₂, ZrO₂ and HfO₂. The chemical vapour deposition of these films is often carried out using metal alkoxides or β -diketonates as precursors. Recently, the deposition of highquality oxide films has been demonstrated using carbon- and hydrogen-free anhydrous metal nitrate precursors. In this article we give an overview of the compounds used as precursors in the CVD of group IV metal oxide films, discuss the effect of the precursor structures on the composition and

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microstructure of the resulting films, and describe the use of anhydrous hafnium(IV) nitrate to deposit thin HfO₂ films.

CVD PRECURSORS FOR GROUP IV METALOXIDES

Precursors used for group IV metal oxides are listed in Table 1. Metal chlorides were among the first compounds used in CVD processing.¹⁻⁷ Liquid TiCl₄ has a relatively low boiling point (136.4°C), while $ZrCl_4$ and $HfCl_4$ are solids that sublime near 300°C. Oxide films can be prepared from the chlorides either by hydrolysis, equation (1), or direct oxidation, equation (2). In the case of deposition from zirconium and hafnium chloride, temperatures greater than 800°C are often necessary and may lead to oxidation of the silicon substrate by the reactant gases.^{1,3-5} For these reasons interest in using group IV chlorides in the CVD of metal oxides for microelectronics applications is limited. Metal oxide films can also be obtained from the chlorides by the ALCVD method using the chemistry shown in equation (1).² Temperatures for these ALCVD processes are considerably lower than for the standard CVD methods.

$$\operatorname{TiCl}_4 + 2\operatorname{H}_2\operatorname{O} \xrightarrow{\Delta} \operatorname{TiO}_2 + 4\operatorname{HCl}$$
 1

$$\text{TiCl}_4 + \text{O}_2 \xrightarrow{\Delta} \text{TiO}_2 + 2\text{Cl}_2$$
 2

Metal alkoxides (Fig. 1) are attractive as precursors due to their high vapour pressures and lower deposition temperatures. Titanium isopropoxide, $Ti(O^i-Pr)_4$, has been the most widely used precursor for the deposition of titanium dioxide.⁸⁻¹⁵ High-quality films can be deposited from $Ti(O^i-Pr)_4$ either by direct thermolysis, equations (3 and 4), or by hydrolysis, equation (5). Similarly, $Zr(O^t-Bu)_4^{1,16-20}$ and $Hf(O^t-Bu)_4^{1,21}$ can be used to deposit zirconium and hafnium dioxide, respectively. Most metal alkoxides are sensitive to moisture and must be handled under inert atmosphere conditions. Recently, the stable, solid *neo*-pentoxides of titanium and zirconium were used to deposit the corresponding oxides in a MOCVD process.²²

Table 1. P	recursors for	chemical	vapour	deposition	of	group IV of	xides
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Precursor	b.p. (°C)	$T_{\rm b}$ (°C)	Minimum T_{d} (°C)	References
TiCl	136.4	n.r.	200	6, 7
$Ti(O^{i}-Pr)$	232	80-120	250	8-15
[Ti(u-ONep)(ONep)]	n.r.	120	300	22
$Ti(NO_3)$	40 (subl.)/0.2 mm	22-40	230	42, 44
ZrCl.	331 (subl.)	158-200	800	3-5
$Zr(O^{i}-Bu)$	81/3 mm	50-70	300	1, 16-20
$[Zr(\mu-ONep)(ONep)_2]_2$	n.r.	170	300	22
Zr(acac),	171–173 (m.p.)	150-220	350	23-26
Zr(tfac),	130 (subl.)/0.005 mm	130-180	300	23, 24, 27, 29, 30
Zr(thd),	180 (subl.)/0.1 mm	200-230	500	26, 31-34
Zr(acac) ₂ (hfip) ₂	dist. $80^{\circ}/10^{-3}$ mm	77.5	350	38, 39
$Zr(O^{i}-Pr)_{2}(thd)_{2}$	110–111 (m.p.)	195	350	40
$Zr(O'-Bu)_{2}(thd)_{2}$	261-263 (m.p.)	195	350	· 40
$Zr_2(O^i - Pr)_2(thd)_2$	160–163 (m.p.)	200	350	35, 36
$Zr(NO_2)$	95 (subl.)/0.2 mm	75-85	285	41, 43
HfCl.	320 (subl.)	n.r.	n.r.	1
$Hf(O^{t}-Bu)$.	90/5 mm	n.r.	n.r.	1, 21
Hf(tfac).	n.r.	190	300	24, 28, 29
$Hf(NO_3)_4$	95 (subl.)/0.2 mm	75	250	41

 $T_{\rm b}$ =bubbler temperature, $T_{\rm d}$ =deposition temperature, n.r.=not reported.

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Fig. 1. Schematic drawing of group IV alkoxide precursors: $M(O'-Bu)_4$, $Ti(O'-Pr)_4$, and $[M(\mu-ONep)(ONep)]_2$

$$Ti[OCH(CH_3)_2]_4 \xrightarrow{\Delta} TiO_2 + 2CH_3CHCH_2 + 2(CH_3)_2CHOH$$

$$Ti[OCH(CH_3)_2]_4 \xrightarrow{\Delta} TiO_2 + 4CH_3CHCH_2 + 2H_2O$$

$$Ti[OCH(CH_3)_2]_4 + 2H_2O \xrightarrow{\Delta} TiO_2 + 4(CH_3)_2CHOH$$

In β -diketonate complexes (Fig. 2) the metal centre is surrounded by eight oxygen atoms making them generally more stable towards

hydrolysis than alkoxides. The zirconium and hafnium acetylacetonates, $Zr(acac)_4$ and $Hf(acac)_4$, decompose to give ZrO₂ and HfO₂ at 350°C but require source temperatures around 200°C for sufficient vaporization.23-26 The trifluorinated analogues, $Zr(tfac)_4$ and $Hf(tfac)_4$, are more volatile but the increased risk of fluorine contamination is undesirable.23,24,26-30 Tetramethylheptanedionato zirconium, Zr(thd)₄, (this precursor is also abbreviated Zr(dpm)₄ where dpm stands for dipivaloylmethanato) is especially stable, can be handled in air, and has been shown to deposit high-quality films.^{26,31-34} Unfortunately, Zr(thd)₄ requires source temperatures between 200-230°C and substrate temperatures greater than 500°C. Reduction of carbon in β -diketonate-deposited films requires the addition of O_2 during deposition.

The recent development of mixed ligand precursors (Fig. 3) attempts to combine the



Fig. 2. Schematic drawing of group IV β -diketonate precursors: Zr(thd)₄ and M(acac)₄

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Fig. 3. Schematic drawing of group IV mixed ligand precursors: cis-Zr(acac)₂(hfip)₂ and M₂(Oⁱ-Pr)₆(thd)₂

favourable properties of alkoxides and β -diketonate complexes.^{35–39} The liquid compound $Zr(acac)_2(hfip)_2$, where $hfip=OCH(CF_3)_2$, has been used to deposit ZrO₂ as low as 350°C.^{38,39} The compound is reported to be more stable towards hydrolysis than $Zr(O'-Bu)_A$ and the vapour pressure lies between the zirconium β -diketonates and *tert*-butoxide. The mixed tetramethylheptanedionato-alcoholato $Zr(O^{i}-Pr)_{2}(thd)_{2}$ complexes, and $[Zr(O^{i} -$ Pr)₃(thd)]₂, have been used in direct liquid injection CVD.^{35,36,40} The volatilities of Zr(Oⁱ- $Pr_{2}(thd)_{2}$ and $[Zr(O^{i}-Pr)_{3}(thd)]_{2}$ do not appear to be a significant improvement over the acetylacetonates, as evaporator temperatures for the depositions were 195°C. Zirconium dioxide films could be deposited, however, between 300 and 600°C from 0.1 M THF solutions of the compounds. $[Zr(O^{i}-Pr)_{3}(thd)]_{2}$ and $Ti(O^{i} Pr_{2}(thd)_{2}$ have also been used to deposit lead zirconate titanate using direct liquid injection CVD.36

The anhydrous metal nitrates are the only precursors that are completely carbon-, hydrogenand halogen-free.^{41–44} The volatility of the anhydrous nitrates arises from the covalent nature of the interaction between the metal centre and the oxygen atoms of the chelating nitrato groups (Fig. 4). Typical source temperatures range from 40° C for titanium nitrate to 80° C for zirconium and hafnium nitrate. No additional oxygen is required for deposition, and high-quality films of TiO₂, ZrO₂ and HfO₂ have been grown at substrate temperatures below 250°C. Because the nitrate ligands themselves are strongly oxidizing, the

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anhydrous group IV metal nitrates should not be mixed with liquid or solid organic compounds or other readily oxidized materials. In pure form, however, we have seen no evidence that anhydrous metal nitrates are shock sensitive or subject to violent decomposition upon heating. There have been no reports of using anhydrous metal nitrates in a direct liquid injection CVD process.

THE CRITICAL SILICON-MO₂ INTERFACE

In the studies of devices produced with high κ oxides in direct contact with the silicon substrate, a 1–2 nm interfacial layer has been observed by



Fig. 4. Schematic drawing of group IV anhydrous metal nitrate precursors

cross-sectional transmission electron microscopy.^{11,15,42–48} As even very thin interfacial layers of a low κ material will seriously decrease the capacitance of the stack, the existence of this layer may significantly impact the electrical properties of the device. The effective permittivity for multiple layers is given by

$$\varepsilon_{\text{eff}} = (d_1 + d_2)\varepsilon_1\varepsilon_2/(d_1\varepsilon_2 + d_2\varepsilon_1) \qquad 6$$

where d and ε are the thickness and permittivity of the layers. Also, for a gate oxide of a given thickness, an increase in the interfacial thickness effectively decreases the thickness of the high κ layer, which may lead to higher leakage currents. Therefore, to benefit from the high permittivity replacement, the thickness of any interfacial layer must be limited.

In the cases of TiO_2 and Ta_2O_5 , the interfacial layer, as evaluated by medium energy ion scattering and secondary ion mass spectrometry, exhibits a compositional gradient from pure SiO_2 to pure metal oxide.^{11,15,45–47} Thermodynamics predicts that the silicon interface with both these oxides will be unstable with respect to silicon oxidation



Fig. 5. Plot showing the temperature dependence of the growth rate. The individual data points are from the experimental measurements and the solid lines are derived from the model discussed in the text

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and/or metal silicidation around 700°C.⁴⁹ Similar thermodynamic considerations suggest the interface to be stable between silicon and ZrO₂, Al₂O₃ or HfO₂.⁴⁹ Interfacial layers are observed for these oxides as well.^{43,48} In contrast to the case of TiO₂, however, MEIS studies suggest that the interface formed between zirconium dioxide and silicon is pure SiO₂.⁴³

Processes leading to the formation of interfacial layers include (1) reaction between the metal oxide film and the silicon substrate, (2) oxidation of the silicon surface prior to or during the deposition of the oxide film by the precursor or a contaminant, and (3) oxygen diffusion through the thin metal oxide membrane during or after deposition. Several approaches to eliminating these pathways are being considered. A barrier layer of SiO_xN_y or Si₃N₄ can be deposited onto the silicon prior to the oxide growth. Ideally, such a layer would separate the metal oxide and the silicon, thus preventing direct reaction. Also, the nitride layer can serve as a barrier to the diffusion of oxidants into the silicon. An alternative approach towards improving the interface characteristics involves incorporating silicon oxide into the high κ film. Though these materials are expected to have dielectric constants lower than the pure metal oxides, studies on Zr-Si-O and Hf-Si-O mixtures indicate that they may be a promising substitute.^{50,51} Additionally, the presence of silicon also inhibits the crystallization of the metal oxide, thus reducing grain boundaries and surface roughness that can lead to dielectric breakdown and higher leakage currents. Finally, atomic layer CVD techniques could potentially be used to control the composition of the oxide films at the atomic level. Recently, ALCVD using metal alkoxides as the oxygen source (in place of O₃, H₂O or H_2O_2) in conjunction with metal chlorides was reported.52 The interfacial layer thickness was reduced.

IMPACT OF PRECURSOR STRUCTURE AND KINETICS ON FILM MICROSTRUCTURE

The performance of metal oxide films as dielectrics depends on composition (stoichiometry and purity) and microstructure. One might reasonably

ask whether variation in precursor structure exerts any influence on the composition and microstructure of the resulting film. Especially among precursors that deposit compositionally correct films, does the variation of the ligand change the microstructure?

In an attempt to answer this question, a side-byside comparison of the TiO_2 deposition kinetics and the corresponding microstructures was studied using titanium(IV) isopropoxide and anhydrous titanium(IV) nitrate.⁴⁴ All depositions were conducted at low pressures (<10⁻⁴ Torr) in an ultrahigh vacuum chemical vapour deposition reactor.

Deposition Kinetics

From the data in Fig. 5, we identify three regimes of CVD growth: (i) a low temperature regime (<250°C for TN and <400°C for TTIP) in which the TiO₂ deposition rate increases rapidly with temperature, (ii) an intermediate regime (250-600 and 400-700°C for TN and TTIP, respectively) in which the deposition rate is roughly independent of temperature, and (iii) a high temperature regime, for which the deposition rate decreases with increasing temperature. Similar growth rate trends have been reported for many other CVD systems. The low temperature regime is usually attributed to reaction-limited deposition, i.e., to CVD growth, which is limited by the rate of precursor decomposition. The growth rate increases with temperature due to Arrhenius dependence on thermal energy. At intermediate temperatures, growth becomes limited by the precursor-substrate collision rate. In this regime, growth is said to be *flux-limited*, and the growth rate is independent of temperature.

The TiO₂ growth rate trends for both TTIP and TN can be rationalized by invoking rapid precursor desorption at high substrate temperatures. Scheme 1 summarizes the generic events involved in an UHV-CVD process. We analyse the growth kinetics in terms of a two step model. The first step is reversible adsorption of the precursor (**P**) on the growth surface, and the second is irreversible reaction of adsorbed **P** to form solid TiO₂:

$$\mathbf{P}_{(g)} \underset{k_{dar}}{\overset{\kappa_{ad}}{\rightleftharpoons}} \mathbf{P}_{(ad)}$$

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$$\mathbf{P}_{(ad)} \xrightarrow{\kappa_r} \mathrm{TiO}_{2(s)} + \mathrm{by-products}_{(g)}$$

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where k_{ad} , k_{des} , and k_r are the rate constants for adsorption, desorption and reaction, respectively. The precise nature of the chemisorbed precursor, $\mathbf{P}_{(ad)}$, is unknown.



600 nm

Fig. 6. Scanning electron micrographs comparing TiO_2 grown using $Ti(O^i-Pr)_4$ (TTIP) and $Ti(NO_3)_4$ (TN)



Scheme 1. Summary of the kinetic events involved in the TiO₂ UHV-CVD

Fig. 6 shows the scanning electron micrographs of films deposited under similar conditions. The vital result reflected in this figure is that below 500°C the microstructures depend on the nature of the precursor, whereas above this temperature the microstructures are indistinguishable.

From the above kinetic analysis, we begin to see how the microstructure of a TiO₂ CVD film might be temperature- and precursor-specific. At low temperatures, the adsorbed precursors will sample a wide range of surface sites before reacting, as the characteristic reaction time is quite long. The diffusional path explored by an adsorbed molecule is a strong function of the adsorbate-surface potential energy surface. For TN and TTIP, which have very different structures, one might expect analogously different diffusional paths. For example, the nitrate ligands on TN have lone electron pairs that could participate in specific donor-acceptor interactions with the TiO₂ surface, whereas the hydrocarbon nature of the TTIP ligands precludes such interactions. If the structure of the TiO₂ surface were highly anisotropic (as is the case for anatase and rutile), TN surface migration could be more rapid in some directions than in others, while TTIP migration could be isotropic. Under such conditions, one might predict equiaxed microcrystallites from TTIP and more unusually shaped crystallites from TN.

As temperature increases, the adsorbed precursors undergo fewer and fewer diffusional hops before reacting. Eventually, the characteristic migration length will become so short that

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the precursor will react at or desorb from the site on which it adsorbs. One would expect no influence of the precursor on film microstructure under such conditions, which is just what is observed for flux-limited TiO_2 deposition from TN and TTIP. At these higher temperatures diffusion of titanium and/or oxygen atoms (or ions) on a clean TiO₂ surface or along grain boundaries, represented by k'_{diff} in Scheme 1, will alter the microstructure.

In summary, comparison of the microstructures of films deposited at similar temperatures for TTIP and TN revealed significant differences in the reaction rate limited regime. As the growth rates of the two precursors converged in the flux-limited regime, the respective microstructures became indistinguishable. In the reaction rate limited regime the differences in microstructures were attributed to differences in the precursor lifetime on the surface, its characteristic diffusion length and its selectivity. These effects also explain why the grain size of the TiO₂ decreased with increasing temperature for both precursors. At higher temperatures in the flux-limited regime and beyond, grain size increases with increasing temperature. In this regime, microstructure is dominated by diffusion of titanium and/or oxygen atoms on the surface or along grain boundaries. This work suggests that the search for a dependence of film microstructure and properties on the structure of the molecular precursor should focus on the reaction rate limited kinetic regime.

CVD OF HAFNIUM DIOXIDE USING $HF(NO_3)_4$

Thin films of HfO_2 were grown using anhydrous hafnium (IV) nitrate, HN, which was synthesized from $HfCl_4$ and N_2O_5 using literature procedures and purified by sublimation.^{53,54} The HN was stored and precursor vessels were loaded under an inert atmosphere.

All depositions were performed in a stainless steel low-pressure reactor which consists of a six-way cross equipped with 4.5-inch diameter Conflat flanges. Using only the mechanical pump the base pressure of the reactor was <1 mTorr. Two of the flanges were unused. One

flange was equipped with a viton O-ring sealed door for wafer loading. The precursor line enters the chamber through the top flange and the bottom flange is capped with a 1/4-inch fused silica window sealed to the flange knifeedge with a viton O-ring. The Si(100) substrates were cleaned by standard procedures and placed onto a circular molybdenum susceptor (1/8-inch thick) situated at the centre of the reactor. The Mo susceptor was heated with a Variac-controlled, 1000 W, quartz halogen lamp located in a parabolic aluminium reflector and directed through the fused silica window. The temperature of the susceptor was measured with a Ktype thermocouple embedded 1 cm into the side of the susceptor. The final flange was connected to a Lindberg tube furnace set to 500°C. A thermocouple gauge located between the six-way cross and the cracking furnace measured the reactor pressure.

The HN precursor vessel was heated to 82°C by Variac-controlled heating tape. High purity nitrogen was used as the carrier gas. The flow of carrier gas was maintained at 20 sccm using a mass flow controller. The chamber pressure during deposition was 0.20 Torr. The films in this study were deposited at susceptor temperatures between 300 and 500°C. Under these conditions the observed growth rates ranged from 2.5 to 10.0 nm per minute.

Film crystallinity was studied using a Siemans D-5005 X-ray diffractometer and showed that films grown at 450°C were polycrystalline, monoclinic



Fig. 7. Cross-sectional TEM of HfO₂ deposited on Si(100)

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HfO₂. The observed preferential orientation was difficult to determine because of the close d-spacing and broadening of many of the reflections. The four strongest reflections occurred at 24.5, 28.6, 31.6 and 35.0° . The low-angle peak could be attributed to either the 011 or 110 reflections, and the high angle peak could be due to the 002 or 200 reflections. The peaks at 28.6° and 31.6° could be uniquely assigned to the 111 and 111 reflections, respectively.

Cross-sectional, high resolution transmission electron microscopy (Fig. 7), using a Philips CM200 field emission electron microscope operated at an accelerating voltage of 200 kV, suggested the films were polycrystalline and provided evidence that an amorphous interfacial layer, 1.1-1.5nm thick, was present between the silicon substrate and the HfO₂.

The Rutherford backscattering spectrum was obtained on a spectrometer purchased from NEC that was equipped with an MAS 1700 end station. The He⁺ beam had an energy of 2.0 MeV, and the charge collected was typically 10 µC using a beam current of 15 nA. Medium energy ion scattering data using a He⁺ beam suggest that the ratio of O to metal in such high permittivity films is high by approximately 10% (M. Copel, personal communication, 2000). After adjusting the RBS data, the stoichiometry of the as-deposited films ranged from HfO_{2,2} to HfO_{2,4}. The observed ratio of O to Hf was higher for films that were deposited at lower temperatures. Other metal oxides deposited using anhydrous metal nitrates were reported to contain excess oxygen, which could be removed by heating the films under an inert atmosphere.

Three hafnium dioxide films were studied by Xray photoelectron spectroscopy on a Phi 5802 Multitechnique Electron Spectrometer using 350 W monochromatic Al K_{α} X-rays. Carbon was present at the surface of all the films and was essentially removed by sputtering away the top 20 Å. Angular resolved XPS, obtained at 15, 25 and 45° take-off angles, probed the composition at increasing film depths. At 45° no nitrogen was detected in the films. Zirconium was found in all the films and varied between 0.5 and 5.28 at. %. The observed Zr comes from zirconium impurities in the HfCl₄ used to synthesize the HN precursor. The variation in Zr concentration is likely to be due to a heterogeneous distribution of Zr(NO₃)₄ in the

 $Hf(NO_3)_4$ precursor vessel. Correct evaluation of the film stoichiometry requires that we examine O/ (Hf+Zr). For 45° data these values were 2.29, 2.06 and 2.31, respectively, in agreement with the values obtained by RBS.

SUMMARY

Anhydrous hafnium nitrate was found to be an effective precursor for the chemical vapour deposition of HfO₂. The conditions probed in this study included growth temperatures as low as 300°C, and no additional oxygen source was necessary to promote deposition. Under all conditions, RBS and XPS indicated that the films contained 10-20% approximately excess oxygen. Zirconium, present in the HfCl₄ used to synthesize $Hf(NO_3)_4$, was the major impurity detected by XPS in the bulk of the film. Nitrogen concentrations were at or below the detection limits of XPS (~ 0.2 at. %).

Each group IV metal dioxide has been successfully deposited using the corresponding anhydrous metal nitrate. Thus, these precursors join the metal chlorides, β -diketonates and alkoxides as a general class of precursor useful for depositing metal oxide films. The decision to use a particular precursor will depend on the application. Especially during depositions conducted at lower temperatures where growth kinetics are limited by surface reaction rates, variation of the ligand can lead to different microstructures for compositionally identical films.

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