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REVIEW

Metal alkoxides and β-diketonates as precursors for oxide and non-oxide thin films

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Single-components or multicomponent oxide thin films are of interest for electronic and optoelectronic devices, optical applications, catalysis, corrosion protection etc. Their preparation by chemical routes is based on the hydrolytic (sol-gel process) or pyrolytic (MOCVD) conversion of precursors. Derivatives having M-O bonds, namely metal alkoxides, carboxylates or β-diketonates, are the most common sources of metal oxides. The properties of alkoxides are appropriate for sol-gel as well as MOCVD applications, whilst the limited hydrolytic susceptibility but good volatility of β-diketonates is most convenient for MOCVD purposes. The low temperature and flexibility of sol-gel routes, and the presence of residual OH groups in the final films, are favorable for the encapsulation of organic or organometallic derivatives, the anchoring of enzymes and in general for the development of functional and composite coatings. The facile formation of heterometallic alkoxides is also attractive for the development of coatings based on multimetallic formulations. MOCVD is favorable for the build-up of heterostructures and epitaxial layers. Although metal alkoxides and β-diketonates are usually oxide precursors, nitride or sulfide films can be obtained by reacting with the appropriate reagents. Fluorinated ligands enhance volatility but often result in the formation of metal fluorides.

Keywords: Alkoxides, β-diketonates, MOCVD, sol-gel, thin films, oxides, metals, fluorides, sulfides, heterometallic complexes

INTRODUCTION

Thin films of various inorganic materials today play an important role in practical applications as well as in fundamental science: microelectronics, optics, optoelectronics, sensors, solar cells, corrosion protection are well-known examples.[1] At first, physical methods (sputtering, laser ablation, etc.) were predominant techniques for obtaining films. Chemical methods attract increasing attention, but they often require more elaborate precursors. Thin films can be prepared by spraying, dip-coating or spinning of an appropriate metal precursor solution onto a solid substrate, and are developed mainly for oxide-based materials; solubility of the precursors is a prerequisite. Metal Organic Chemical Vapor-Phase Deposition (MOCVD) techniques concern a larger variety of ceramics, oxides as well as non-oxides, and are better adapted to obtaining epitaxial coatings than are sol-gel techniques, but they need volatile and pyrolyzable precursors.

The versatility of chemical routes derives largely from the variety of molecular precursors available as sources. This review sets out to illustrate the potential of precursors having M-O bonds such as metal alkoxides $M(OR)_n$, and β-diketonates, $M(OCRCHCR'O)_n$ (R, R' = alkyl, aryl, perfluoroalkyl)—which can be easily purified by distillation or sublimation—for the formation of oxide thin films, but also fluoride, metal, carbide or oxycarbide, nitride and sulfide coatings, depending on experimental conditions (temperature, substrate, inert or reactive carrier gas, etc.), and to outline the underlying problems. Metal carboxylates display attractive features for sol-gel applications, especially for the formation of fibers; however, their volatility is generally not relevant for MOCVD and they will therefore not be considered here.[2]

CHOICE OF PRECURSORS

General considerations

The formation of thin films by chemical routes is based mainly on the hydrolytic or pyrolytic conversion of precursors. The most common pre-

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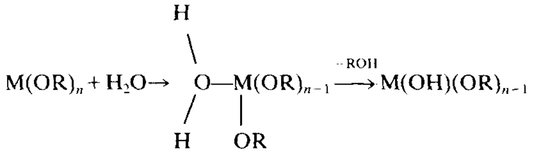
cursors of metal oxides are compounds which already contain an M–O linkage, namely alkoxides $[M(OR)_n]_m$ (or oxoalkoxides), carboxylates $[M(O_2CR)_n]_m$ or β-diketonates $[M\{OCRCHCR'O\}_n]_m$ ($OCRCHCR'O = \beta$-dik = β-diketonate; n = oxidation state; m = molecular complexity or degree of association), but their properties are quite different.

Metal alkoxides

Homoleptic metal alkoxides $[M(OR)_n]_m$ (R = a *saturated* or unsaturated organic group; $n = 1$–6) can be obtained for most elements (with the exception of some noble metals) by various synthetic routes.[3,4] They are generally thermodynamically stable, but handling requires more care (inert, dry atmosphere; anhydrous solvents) than for β-diketonates.

The most relevant properties of metal alkoxides for their use in materials science are solubility and volatility. Both of these properties are dependent on the degree of association m and can be tailored by an appropriate choice of R and especially its steric demand. Solubility and volatility usually vary in the order OtBu > OiPr > OEt > OMe for classical alkoxo groups. A reasonable solubility can be achieved in most cases (Main-Group and d^0 transition-metal alkoxides) with isopropoxide derivatives, while volatility might require tert-butoxide or larger alkoxo groups such as tert-heptyl oxide (R = CMeEtiPr). Classical (unfunctionalized) alkoxide groups are however no longer able to achieve solubilization of d^n transition-metal alkoxides such as those of copper(II), cobalt(II), nickel(II) and zinc(II).[3,4] Functional OR groups such as aminoalkoxides, e.g. $OC_2H_4NMe_2$,[5,6] 2-methoxyethoxide[7] and/or bulky ligands such as trialkylsiloxo groups R_3SiO[8] and aryl oxides such as 2,4,6-tri(tert-butyl)phenoxide[9] are generally able to overcome insolubility and in some cases to provide an appropriate volatility (Table 1). The bulky siloxide ligand $OSi(Bu)_3$ is for instance able to stabilize a dinuclear barium species $Ba_2[OSi(tBu)_3]_4$ (THF) displaying an interesting volatility (sublimes 80 °C/1 torr).[10] Flexible aminoalkoxides (e.g. $OC_2H_4NMe_2$) appear more favorable than alkoxyalcohols for ensuring volatility.[5,6] Fluorinated OR groups, the most commonly used being $OCH(CF_3)_2$ and $OC(CF_3)_3$, can also be a means to increase volatility.[11]

Besides solubility and volatility, a most attractive property of metal alkoxides is their easy chemical modification by exchange reactions, giving heteroleptic $M(OR)_{n-x}Z_x$ (Z = β-dik, OR′, NR_2, OAc, etc.) alkoxides, with a large variety of reactants, especially those bearing hydroxyl functionalities. Such reactions are a means of tailoring precursors for specific applications, and allow molecular engineering.[13,14] The main uses of such modifications in materials science are the stabilization of metal alkoxides for greater convenience in solutions (storage), better control of hydrolysis rates, and to obtain a more appropriate rheology via the addition of various additives, often functional or polyfunctional alcohols or carboxylic acids. With the exception of silicon derivatives, metal alkoxide hydrolysis is extremely facile, leading to solvated hydroxides or oxides with liberation of alcohol as a volatile by-product.[4] After the initial hydrolysis, due to the nucleophilic attack of the metallic center by water, the reaction proceeds by a chain of polycondensation steps (Eqns [1]–[3]) leading to systems whose rheology can be tuned by a variety of experimental parameters and especially the hydrolysis ratio $h\{h = [H_2O]/[M(OR)_n]\}$. Table 2 summarizes the parameters which govern the hydrolysis rates of homo- and hetero-leptic alkoxides.[4] Mastering these parameters, whose behavior can be rationalized on the basis of the Partial Charge Model,[15] should allow a control of the rheology of the solutions, of the morphology of the particles and thus of the microstructure of the final material.



$$M(OR)_n + H_2O \rightarrow \underset{H\quad OR}{\overset{H}{O{-}M(OR)_{n-1}}} \xrightarrow{-ROH} M(OH)(OR)_{n-1} \quad [1]$$

$$2M(OH)(OR)_{n-1} \rightarrow (OR)_{n-1}M{-}O{-}M(OR)_{n-1} + H_2O \quad [2]$$

$$M(OH)(OR)_{n-1} + M(OR)_n \rightarrow (OR)_{n-1}M{-}O{-}M(OR)_{n-1} + ROH \quad [3]$$

Although β-diketones, carboxylic acids and functional alcohols are polydentate ligands and lead generally to an increase in the metal's coordination number (Table 3) and thus to a decrease of its hydrolytic susceptibility, their behavior as modifiers is quite different. β-Diketones act mostly as chelating ligands, thus often resulting in a decrease of the degree of oligomerization m and a more favorable volatility. The hydrolysis behavior of β-diketonatoalkoxides $M(OR)_{n-x}(\beta\text{-dik})_x$ depends on the degree of substitution x; however,

Table 1 Tailoring the properties of metal alkoxides via the R group

Compound	Solubility[b]	Volatility (°C/torr)	Structural data	Ref.
$[Cu(OR)_2]_\infty$; R = Me, tBu, iPr	Insoluble	Non-volatile	Polymeric	12
$Cu_3(OtBu)_4[OC(CF_3)_3]_2$	Soluble	Sublimes 110/?		11
$Cu_4(OtBu)_6[OC(CF_3)_3]_2$	Soluble	Sublimes 90–120/? With decomposition	X-ray: two Cu three-coordinate, two Cu four-coordinate	11
$[Cu(OC_2H_4OR')]_m$; R′ = Me, Bu	Insoluble (R′ = Me); soluble (R′ = Bu)	Non-volatile	R′ = Me: polymeric	7
$[Cu(OC_2H_4OC_2H_4OMe)_2]_m$	Soluble (0.1–0.6 M)	Non-volatile	$m \geq 5$ in solution, dangling ether oxygens (^1H NMR)	7
$Cu(OC_2H_4NMe_2)_2$	Soluble	Sublimes $80/10^{-4}$	Monomeric in solution	6
$Cu(OCHMeCH_2NMe_2)_2$	Soluble in hexane	Volatile ($60/10^{-4}$)	X-ray: Cu four-coordinate	6
$Cu(OC_2H_4NMeC_2H_4NMe_2)_2$	Soluble in hexane	Volatile ($110/10^{-4}$)	X-ray: Cu five-coordinate	6
$Cu[OSi(OtBu)_3]_2py_2$[a]	Soluble in pentane	?	X-ray: Cu four-coordinate	8
$[Zn(OR)_2]_\infty$ R = Me, Pr, tBu	Insoluble	Non-volatile	Polymeric	5
$[ZnOCEt_3)]_m$	Soluble in hexane	Bp $220/10^{-4}$	$m = 4$, age-dependent	5
$[Zn(OCMeEt_2)_2]_m$	Insoluble	Sublimes $180/10^{-4}$ (34%)[b]		5
$[Zn(OC_2H_4OMe)_2]_m$	py, $MeOC_2H_4OH$[a]	Non-volatile		5
$[Zn(OC_2H_4OC_2H_4OMe)_2]_m$	py, $Me(OC_2H_4)_2OH$[a]	Non-volatile		5
$[Zn(OC_2H_4NMe_2)_2]_m$	$Me_2NC_2H_4OH$	Sublimes $170/10^{-4}$		5
$[Zn(OCHMeCH_2NMe_2)_2]_m$	Soluble in hexane	Bp $170/10^{-4}$ (80%)	$m = 3$ in solution	5
$[Zn(OC_2H_4NMeC_2H_4NMe_2)_2]_m$	Soluble in hexane	Sublimes with reaction ($-H_2$) $170/10^{-4}$	$m = 3$ before heating X-ray: $Zn(OCH{=}CHNMeC_2H_4NMe_2)_2$, Zn six-coordinate	5
$Zn(OC_6H_2\text{-}2,4,6\text{-}tBu_3)_2(THF)_2$	Soluble	?	X-ray: Zn four-coordinate	9

[a] py, pyridine. [b] Solubility in hydrocarbons; if polar solvents are required, they are listed here. [c] Percentage recovery after sublimation or distillation.

the formation of colloids is generally favored over that of gels since the β-diketonate ligands act as polymerization lockers.[25] 2-Methoxyethoxide is the functional alkoxide for which the most X-ray structural data on derivatives are available at present. It has been observed to display a variety of coordination modes[26] (Scheme 1). Although chelation has been observed for barium[27] and molybdenum[28] derivatives, its main tendency is to act as a bridging or a bridging–chelating ligand. This favors the formation of large (but generally highly soluble) oligomers such as $[M(OC_2H_4OMe)_n]_m$ ($m = 9$, M = Ca,[29] Cd;[30] m = 10, M = Y[17]) or even infinite polymers [M = Cu(II),[7] Pb(II),[31] Bi(III)[32, 33]] and precludes volatility. Solubility of the infinite polymers can be imparted by more lengthy hydrocarbon chains ($OC_2H_4OC_2H_4OMe$, OC_2H_4OBu) as illustrated in the case of copper(II) derivatives.[7] The coordination behavior of 2-methoxyethoxide shows that it behaves as a 'network former' favorable to the stabilization of homogeneous gels and this observation explains its frequent use for obtaining coatings. Flexible polyhydroxylated ligands such as ethylene glycol can also behave as crosslinking reagents. More constrained functional polyalcohols such as triethanolamine favor the formation of alkoxides of lower nuclearity, but they might act as network formers through intermolecular hydrogen bonding involving OH functionalities.[34]

Table 2 Hydrolysis parameters of homoleptic and heteroleptic alkoxides

1. Electronegativity of the metal and polarity of the M—O—C bonds
2. Nature of alkoxo group R
   —modifies the molecular complexity
   —rate increass with chain lengthening
   —sensitivity to hydrolysis
      tertiary R > secondary R > primary R
      $OR > OSiR_3$
3. pH (acid or basic catalysis)
4. Solvent and dilution
5. Temperature
6. Degree of hydrolysis h ($h = [H_2O]/[M(OR)_n]$)
   —$h < n$: fibers, chains, coatings
   —$h < 1$: molecular clusters
   —$h > n$: gels, three-dimensional polymers
7. Modified precursors $M(OR)_{n-x}Z_x$ (Z = OH, OAc, β-dik, etc.)
   —rate decreases with
      the functionality of the precursor (number of OR groups)
      an increase of the metal coordination number
   —hydrolytic susceptibility
      OR > OAc > β-dik

The lability of the metal–alkoxo bond is also illustrated by the easy formation of mixed-metal species $MM'(OR)_{n+n'}$, which often occurs by simple mixing of metal alkoxides ('double' alkoxides) or between metal alkoxides and carboxylates, β-diketonates, etc.[35] Such derivatives provide homogeneity at a molecular level, and thus might improve the homogeneity of the final multicomponent material obtained via the sol–gel route, and could be a way to overcome mismatched hydrolysis rates. However, relatively few mixed-metal alkoxides corresponding to formulation of materials are known. The formation of heterometallic alkoxides, as a result of Lewis acid–base reactions, can often be a means to achieve depolymerization and thus solubilization of polymeric alkoxides. However, such reactions might be less facile than expected and sometimes be inoperant in strictly anhydrous conditions (Hubert-Pfalzgraf, unpublished results). Although heterometallic β-diketonatoalkoxides have been obtained by reactions between $[M(OR)_n]_m$ and $[M'(\beta\text{-dik})_{n'}]_{m'}$,[23, 36, 37] such reactions might also offer only homometallic $M(OR)_{n-x}(\beta\text{-dik})_x$ derivatives owing to redistribution phenomena.[18] Reactions between alkoxides and β-diketonatoalkoxides have thus been exploited as a route to heterometallic species; the formation of $Ba_2Cu_2(OR)_4(acac)_4(ROH)_2$ and of $YCu_3(thd)_4(OR)_5$ ($R = C_2H_4OMe$; acacH = acetylacetone = pentane-2,4-dione; thdH = 2,2,6,6-tetramethylheptane-3,5-dione) illustrates this strategy.[38] Data on the reactivity of mixed-metal species are scarce. Their reactivity remains dominated by the lability of the M–OR bond, but a problem which needs to be addressed is that of whether the heterometallic unit is maintained or not, and finally of the homogeneity at a molecular level when the various reactions (addition of modifiers, hydrolysis–polycondensation etc.) proceed. Homoleptic or heteroleptic mixed-metal alkoxides can be used in MOCVD if they meet the requirements of volatility and stability. Volatile heterometallic alkoxides such as $[Ln(Al(OiPr)_4]_3$ [Ln = Y, La, Ce etc.) have been reported.[39, 40]

Metal β-diketonates

Homoleptic metal β-diketonates $[M(OCRCHCOR')_n]_m$ ($n = 1–4$), although generally less soluble than metal alkoxides, especially

Table 3 Influence of the modification of alkoxides on properties and structure

Compound[a]	Solubility[b]	Volatility (°C/torr)	Structural data	Ref.
$Y_5(\mu\text{—}O)(OiPr)_{13}$	Soluble	Sublimes $180/10^{-3}$ (30%)[c]	X-ray: Y six coordinate	16
$[Y(\mu, \eta^2\text{—}OR)_2(OR)]_{10}$, $R = C_2H_4OMe$	Very soluble	Non-volatile	X-ray: Y seven-coordinate	17
$Y_3(OC_2H_4OMe)_5(\eta^2\text{-acac})_4$	Soluble	Volatile (MS)[d]	X-ray: Y eight-coordinate	18
$Ti(OR)_4$, R = iPr, tBu	Liquids	R = iPr, bp, 91.5/5	Monomeric, Ti four-coordinate	3
$[Ti(teaH\text{-}3)(OtBu)]_2$	Soluble	Volatile	X-ray: Ti six-coordinate	19
$[Ti(teaH\text{-}3)(\mu, \eta^2\text{-}OAc)]_2$	Soluble	Volatile (MS)	X-ray: Ti seven-coordinate	19
$Ti(OiPr)_3(acac)$	Soluble	Volatile	EXAFS, XANES: Ti five-coordinate	20
$Ti(OtBu)_2(bzac)_2$	Soluble	?	X-ray: Ti six-coordinate	20
$Ti_6O_4(OiPr)_8(OAc)_8$	Soluble	Non-volatile	X-ray: Ti six-coordinate	21, 22
$[Cu(OC_2H_4OiPr)_2]_m$	Insoluble	Non-volatile	Polymeric	23
$[Cu(OC_2H_4OiPr)(\eta^2\text{-acac})]_4$	Soluble	Sublimes $70/10^{-3}$	X-ray: Cu five-coordinate	23
$[Cu(OtBu)_2]_\infty$	Insoluble	Non-volatile	Polymeric	12
$Cu_6(\mu\text{-}OtBu)_6(\mu_4\text{-}OAc)_4(\mu_4\text{-}OAc)_2$[e]	Soluble in THF; mol. wt increases over time giving a higher, still soluble oligomer	?	X-ray: four Cu five-coordinate, two Cu four-coordinate	24

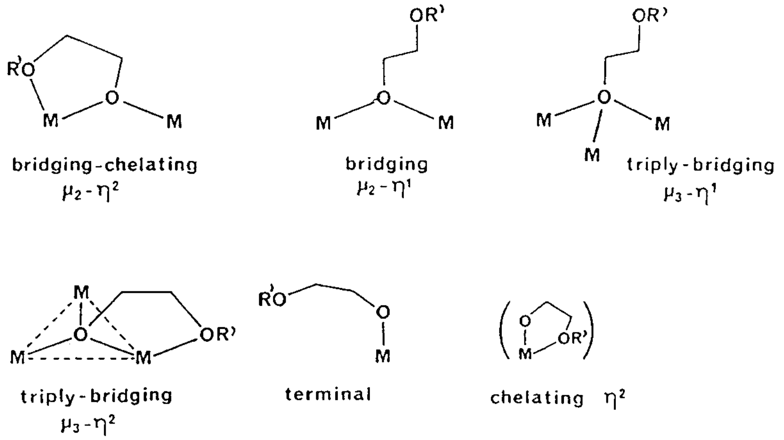
[a] tea, triethanolamine; teaH-3 indicates the number of hydroxyl hydrogens abstracted; bzac = benzoylacetone. [b] solubility in hydrocarbons. [c] Percentage recovery. [d] MS, volatility under mass spectrometry conditions. [e] Obtained by causing $Bi(OtBu)_3$ and $Cu(OAc)_2$ to react; not readily formed by the reaction $Cu(OAc)_2 + NaOtBu$.

in non-polar solvents, can be made soluble by an appropriate choice of the alkyl groups.[41,42] However, such compounds are poorly hydrolyzable at room temperature, and thus are generally only used in conjunction with metal alkoxides for sol–gel applications, especially for d^n transition metals. The main interest of metal β-diketonates resides in their volatility, and thus in their use as precursors for obtaining thin films by MOCVD.[43]

The criteria to be met by precursors for MOCVD applications are more drastic than for their conversion in solution.[44] Besides being available as a well-defined, pure, non-toxic compound, they should display volatility and sufficient vapor pressure and mass transport at a reasonable temperature (<200 °C) and pressure, and the vapor should have a stable composition during the evaporation process in order to obtain a deposit homogeneous in composition, microstructure and properties. They should also display thermal stability during prolonged heating in vacuum, be pyrolyzable at low temperature, and form no stable intermediates during the pyrolysis. The position of an eventual absorption band and its extinction coefficient are additional criteria to consider for UV or laser photo-assisted techniques. Tailoring the ligands in order to control the degradation process and thus to prevent retention of impurities (mostly carbon) in the films would also be of value. Finally, for mixed-metal deposition, it is also preferable to select precursors displaying similar volatilities.

Metal β-diketonates have been described for almost all elements, including bismuth,[45] and they can be synthesized in aqueous or non-aqueous media.[41–43] The delocalization of the electronic density through the ring generally leads to a good thermal stability, as well as strong absorptions in the near-UV spectra (250–350 nm), and this latter property is attractive for photochemical deposition.[44,46] Metal β-diketonates are often more volatile than alkoxides, since their molecular complexity m is usually lower owing to the bidentate character of the β-diketonate ligand and its tendency to act more as a chelating than as a bridging (assembling) agent. Sievers has provided volatility data for many metal β-diketonates[47–49] and has shown that thermogravimetric analysis is a powerful tool for comparison of their thermal behavior.[50] As for metal alkoxides, their volatility is mainly governed by the steric bulk of the ligand and by the nature of the metal. For a given class of metals and β-diketonate ligands, the volatility increases with a decrease in the radius of the metal. Regarding the alkaline-earth metals, barium is therefore the most difficult element to volatilize as a β-diketonate, whilst calcium is the easiest among the three metals barium, calcium and strontium. On the other hand, the heaviest rare-earth β-diketonates are the most volatile, the volatility of the yttrium derivatives being, for instance, similar to that of the erbium ones.[43,51,52]

By contrast with the M–OR bond, that of M–β-dik is poorly labile; tailoring is thus mostly achieved via the R and R′ groups. Bulky substituents (R, R′ = tBu) and fluorinated alkyls have a beneficial effect of volatility, while aryl groups (R = R′ = Pr) lower it, and the general order is in favor of the fluorinated derivatives according to the variation M(F-dik)$_n$ > M(thd)$_n$ > M(acac)$_n$ [F-dikH: R = R′ = CF$_3$ hexafluoroacetylacetone



Scheme 1

(hfacH) or $R = C_3F_7$, $R' = tBu$ 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyloctane-4,6-dione (fodH)]. Tetramethylheptanedione derivatives are the most widely used in practice, especially for heavy elements such as lanthanides, transition or alkaline-earth metals, whilst the use of acetylacetonate derivatives, which are cheaper and more favorable in terms of ceramic yield but also less volatile, is limited to the most volatile elements such as copper or aluminum.[53] β-Diketonatoalkoxides are often more volatile than the parent alkoxides; their properties, especially position and intensity of the UV-Vis spectra for photo-assisted MOCVD techniques, can be tuned by an appropriate choice of the alkoxide ligand and the substituents of the diketone. Thermal stability over a long period can be a crucial issue for an MOCVD precursor: decomposition reactions are often induced by impurities,[31] but can be an intrinsic problem when high temperatures are required to ensure appropriate mass transport; for instance barium derivatives are generally poorly volatile, even as β-diketonates.[54,55]

Since β-diketones are poorly assembling ligands, in contrast to OR ones, depolymerization of metal β-diketonates can be quite easily achieved by a variety of Lewis bases L, mostly oxygen or nitrogen donors for hard metals such as alkaline rare earths or lanthanides, while softer ligands such as alkynes or phosphines are more appropriate for copper(I).[41,42] This means that the formulation and therefore the structure and the properties can be highly dependent on the synthetic procedure. In fact, metal β-diketonates, especially of large oxophilic elements, are often obtained as adducts with alcohols or water molecules, as observed for instance for $Ba(thd)_2(MeOH)_3,MeOH$,[56] $[Ca(hfac)_2(H_2O)_2]_2$, $[Ba(hfac)_2(H_2O)]_\infty$[57] and $[Y(thd)_3(H_2O)]_2$.[58] For compounds having water molecules in the metal coordination sphere, the behavior of this ligand, innocent or non-innocent, in MOCVD applications remains to be clarified. It might favor the formation of oxo or hydroxo aggregates especially for oxophilic, large elements and/or for acetylacetonate derivatives; $Ba(OH)(thd)_9(H_2O)_3$,[59] $Er_8(\mu_4\text{-}O)(thd)_{10}(OH)_2$[41,42] and $M_4(\mu_3\text{—}OH)_2(acac)_{10}$ (M = Y, Nd)[43] (see also Caulton, K G, unpublished results) illustrate this behavior. Saturation of the metal coordination sphere requires tuning of both spatial and electronic requirements of the ligand. The large size of barium, and thus its tendency to form aggregates as a means to reach high coordination numbers, leads to a poor volatility of barium β-diketonates. The ability to form adducts has been considered for $[Ba(thd)_2]_m$ or $[Ba(hfac)_2]_m$, and various potential ligands such as thdH, THF, amines (NH_3, Et_3N, etc.) have been added to the carrier gas in order to improve transport and stability.[61,62] The ligands can indeed control the nuclearity of the precursor in the solid state. Cyclic or open polyether $Ba(hfac)_2$ adducts were observed to enhance drastically the volatility of $Ba(hfac)_2$ by encapsulation of the metal: $[Ba(hfac)_2]_m$ is not volatile below 205 °C (10^{-5} mm Hg), whilst $Ba(hfac)_2$(tetraglyme) and $Ba(hfac)_2$(18-CRW-6) (18-CRW-6 = 1,4,7,10,13,16-hexaoxacyclo-octadecane) sublime at 120 °C (10^{-2} mm Hg) and 150–200 °C (10^{-3} mm Hg) respectively; barium fluoride (BaF_2) deposits are obtained.[54,55,63,64] Stable amine adducts have also been isolated: $[Ba(thd)_2]_{3,4}$ can be converted into a monomeric species $Ba(thd)_2(TMEDA)_2$ (melting at lower temperature, i.e. 130 °C) by a bidentate ligand such as *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) in the solid state (as shown by X-ray diffraction) and in solution (Labrize, F and Hubert-Pfalzgraf, L G, unpublished results). However, stability towards dismutation reactions in the vapor phase of these adducts needs to be considered for MOCVD applications. Dismutation reactions occur in the vapor phase for $Ba(thd)_2(TMEDA)_2$ and similar results have been observed for $[Ba(thd)_2(NH_3)_2]_2$.[66] These dissociation reactions can be partially overcome by adding L in the carrier gas.[63,64] Intramolecular stabilization should be more advantageous than intermolecular stabilization for achieving optimal CVD source criteria.[43,67] Functionalized β-diketonates based on alkoxyalkyl-substituted β-diketones have been reported recently for copper(II) and barium.[67]

By contrast with alkoxides, β-diketonate ligands are not favorable for the formation of stable and isolable homoleptic mixed-metal species, although heteronuclear $CaBa(thd)_3^+$ fragments have been detected by mass spectrometry on mixtures of calcium and barium derivatives.[43,68] Volatile fluorinated derivatives $(CsLn(hfac)_4$ (Ln = Y, Eu) are known; their stability might be due to Cs–F interactions.[35,41,42] Volatile mixed-metal β-diketonatoalkoxides such as $Cu(acac)_2(OSiMe_3)_2Al(\mu\text{-}OSiMe_3)_2$[23] and $Cu_2Ba[OCH(CF_3)_2]_4(thd)_4$ (Labrize, F and Hubert-Pfalzgraf, L G, unpublished results) have been isolated, and investigation of their thermal behavior is currently in progress. The large choice in OR and β-diketone ligands should allow a fine tuning of volatility, stability and absorption spectra of mixed-metal β-diketonatoalkoxides.

THIN FILMS FROM SOLUTION

General considerations

The preparation of thin films from solutions is mainly based on sol–gel processing, and films represent the earliest commercial application of this technology.[1,69,70] This method is based on the formulation of non-aqueous (often alcoholic) solutions of oxide precursors with the metal cations in the desired stoichiometry. Two methods are commonly used to prepare films by the sol–gel process. In both cases, initial deposition is achieved at room temperature, with simple and inexpensive equipment, and is easy to scale up.[71] The first method, namely dip-coating, involves the immersion of the substrate into the solution of precursors (sometimes prehydrolyzed and thus with a limited useful time, or stabilized with alkanolamines (triethanolamine, diethanolamine), which precludes precipitation, as observed for the $Ti(OiPr)_4$–H_2O–iPrOH system)[72] and its pulling out at a controlled uniform speed. This leaves a film of solution on both sides of the substrate, and further hydrolysis occurs in the air. From a practical point of view, the reaction rates for hydrolysis and condensation for the gel formation should be higher than for crystallization. The second method, namely 'spin-coating', involves the application either of a chemically polymerized form of the precursor or of a colloidal suspension of a chemically converted oxide, to a substrate, generally circular, by spinning, with subsequent evaporation of the solvent or of the suspending medium.[73] The properties of the films, and thus their applications, are largely dependent on the thermal treatment. Deposition by the 'dip-coating' technique is usually followed by annealing of the dried 'gel' film at relatively low temperatures to pyrolyze the organic residues (OH, OR groups), to densify and crystallize the film into the desired crystal structure. This also achieves better adhesion, and thus mechanical resistivity to the substrate—especially glass—by formation of chemical bonds via the Si–OH and M–OH or M–OR groups, and controls densification and porosity. A single-layer sol–gel film can be deposited with a thickness of up to 5000 Å (500 nm) [but mostly less than 1000 Å (100 nm)] after annealing. Thicker films are obtained by multiple deposition/annealing cycles. The difficulty of producing high-quality films (without cracks) with thicknesses greater than 1 μm is one of the major disadvantages of the dip-coating method.[69,70] Dipping–pyrolysis is an alternate dipping technique generally applied to carboxylate or β-diketonate solutions for which the conversion of the precursors requires pyrolysis as a result of their poor hydrolytic susceptibility.[74,75]

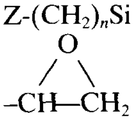
One alternative of the 'spin-coating' method is to use colloidal suspensions of an oxide (adequate suspensions are based on monodisperse particles all of about the same size, in the range 10–30 nm, in order to avoid consistent scattering and relatively high concentration of oxides, ca 3 %). By the choice of a wettable, volatile solvent, the coating operation can be achieved at room temperature without further thermal treatment. This leads to highly porous films (up to 60 %) and poor mechanical resistivity, but is generally more suitable for building up multilayered stacks, especially for optical applications such as antireflective coatings.[73,76,77] Residual porosity may also find applications in membranes and in catalysis.

Metal oxide films of a large variety of metals have been deposited by sol–gel methods.[15,69,70] Electrochromic vanadium pentoxide and tungsten oxide (WO_3) films have been obtained from V_2O_5,nH_2O gels[78] and tungsten oxo- and oxochloro-alkoxides respectively.[79,80] Access to binary lanthanide oxide coatings by sol–gel techniques remains limited, probably as a result of the poor development until recently, of their alkoxide chemistry. Graded Refractive Index Films (GRIN) have been developed mainly for silica.[69,70]

The hydroxyl groups OH can act as a 'handle' for anchoring enzymes and catalysts. The surface hydroxyl sites of amorphous titania (TiO_2) coatings have been used for the dispersion of palladium, a metal active in olefin hydrogenation, via an allyl derivative.[81] The lability of the metal–alkoxide linkage has been exploited for anchoring $Nb(OEt)_5$ via Si–OH bonds. The removal of the organic groups by subsequent treatment with water and oxygen affords a single molecular layer of Nb_2O_5 displaying high selectivity in ethanol dehydration reactions.[82] The selective reaction of vanadium alkoxides with surface OH groups of silica (SiO_2) or alumina (Al_2O_3) supports offers a way to form single or double layers of V_2O_5 at the surface of oxide particles and thus leads to catalysts which display an increase in oxidizing character, whereas the dehydration activity decreases.[78] Vanadium alkoxides have also been grafted on titania, the resulting catalyst being active in reduction of nitric oxide (NO).[83] The control of the catalyst dispersion and particle size, giving access to monolayers, might reveal systems having unique catalytic properties.

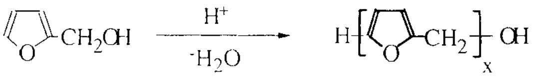
Thin films can also be obtained by pyrolysis of an aerosol (pyrosol process), generally produced by the ultrasonic spraying of an organometallic solution.[84] The conditions to be satisfied by the source compounds (mostly β-diketonates) are solubility in an appropriate solvent (often an alcohol) and a low decomposition temperature (but higher than the boiling point of the solvent). This process has only recently been exploited for the generation of films of materials other than SiO_2 such as high-T_c superconductors and magnetic materials. Deposition rates can be higher than those achieved by conventional chemical vapor deposition processes. Since the precursors are transported as droplets—with a solvent, preferably a coordinating one—stability problems of the source compounds may be more easily overcome than for MOCVD.

Organic–inorganic and composite coatings

Sol–gel chemistry is based mainly on inorganic polymerization reactions which can be controlled by the design of molecular precursors.[4, 12–14] The synthesis of gels, sols and films is achieved in organic solutions at temperatures much lower than for conventional methods or even MOCVD. A unique feature of sol–gel processing is therefore the obtainment of organic–inorganic coatings via differential hydrolysis of heteroleptic alkoxides or by incorporation of organic molecules or dyes into the metal gel matrix (for instance for non-linear optics),[86, 87] and thus of coatings with specific properties (scratch resistance, ionic conductivity,[13, 14] etc.) or displaying functionalities (sensors). Organically modified silicon derivatives (ORMOSILS) $Z\text{-}(CH_2)_nSi(OR')_3$ ($Z = NH_2$, OH, $CH{=}CH_2$,  $\overset{O}{\overset{/\ \ \backslash}{-CH{-}CH_2}}$, etc.) have been the most widely used so far for achieving these goals.[88] The Z groups can be designed to be used as anchoring groups to the substrate or for specific reactants such as enzymes or antibodies. Transparent films of thickness 10–50 μm could be obtained by cohydrolysis of $Me_2Si(OEt)_2$ and homoleptic metal alkoxides $M(OR)_n$ ($M = Si$, Al, Ti, Zr).[89] Investigation by multinuclear MAS NMR (^1H,^{13}C,^{29}Si) and X-ray absorption techniques at the Ti K_α-edge (XANES and EXAFS) has shown that the system can be described as a composite with poly(dimethylsiloxane) chains and TiO_2-based nanoparticles. These siloxane chains are responsible for the formation of thick films without cracks. Organic dyes such as rhodamine 6G and coumarin 4 have been embedded in these $SiMe_2O.MO_x$ films. Transparent water-repellent fluorine-doped zirconia (ZrO_2) coatings have been deposited on steel by dipping of solutions containing zirconium tetraoctylate or zirconium acetylacetonate and fluoroalkylsilanes such as $(RO)_3Si(CH_2)_2(CF_2)_nCF_3$ ($n = 5$–7), aged for 24 h in order to ensure reaction between the alkoxide and the silane. Similar experiments, but using zirconium isopropoxide or n-butoxide led to white and discontinuous films as a result of the very fast hydrolysis of these metal alkoxides.[90] Titania and zirconia films incorporating a cationic rhodium(I) complex $[Rh(TMPP)_2(CO)]BF_4$ (TMPP = 2,4,6-trimethoxyphenylphosphine) reversibly bind carbon monoxide under ambient conditions and show promise for the development of CO sensors.[91]

Shrinkage and thus cracks represent one of the greatest difficulties for the elaboration of high-quality coatings. Silicon alkoxides based on polymerizable OR groups ($OCH_2CH{=}CH_2$, $O(CH_2)_2OCOCH{=}CH_2$) are good candidates for the formation of non-shrinkable sol–gel composites.[92] The potential of thermolabile or photolabile OR groups such as *o*-nitrobenzyl oxide are currently being investigated.[93]

The possibility of transforming applied films by subsequent chemical reactions, in either the gel-like or the solid state, in the presence of reacting gases (ammonia, hydrogen sulfide, etc.), opens up the possibility of modifying composition and properties and has been exploited so far to obtain oxynitride, nitride[94, 95] and sulfide[96] materials. The polymerization and pyrolysis of metal furfuryl oxides represents another strategy for preparing non-oxide ceramics from oxygen-containing metallorganic precursors and has been used for SiC, AlN and more recently TiN.[97] Dehydration of furfuryl alcohol (Fu) promoted by acid catalysis gives a polymeric resin (Eqn [4]). Hydrolysis of $Ti(OBu)_3(OFu)$ in acidic medium offers a polymer which is converted by pyrolysis into TiC (under argon at 1150 °C) and into TiN (under ammonia at 1000 °C).



[4]

Multicomponent (mixed-metal) films

Mixed-metal oxides represent a large proportion of electroceramics (superconductors, ferroelectrics, etc.), but film deposition of such materials through the sol–gel process is quite recent.[1] High-T_c superconductors and electro-optical ceramics such as $Bi_4Ti_3O_{12}$, $Pb(LaZrTi)O_3$ (PLZT) and $PbNb_{2/3}Mg_{1/3}O_3$ (PNM) are, with $LiNbO_3$ and $LiTaO_3$, the systems which have been the most studied.[98] Chemical low-temperature routes are particularly attractive for lead-containing materials, since lead oxide is quite volatile by comparison with other metal oxides and therefore control of the stoichiometry of lead-based materials is tedious. All alkoxide routes appear limited; the few examples include preparation of PNM,[99, 100] of the polycrystalline spinel $MgAl_2O_4$,[101] and of lithium or potassium niobate or tantalate,[102] for which the formulation of the mixed-metal alkoxide, $MgAl_2(OiPr)_8$ and $MM'(OR)_6$ (M = Nb, Ta respectively), is in agreement with that of the material. It has been possible to obtain epitaxial thin films of $LiNbO_3$ on sapphire.[103, 104] The use of a mixed-metal $MgNb_2(OC_2H_4OMe)_{12}$ species[105] has been shown to promote the formation of the perovskite phase for PNM. To overcome difficulty in handling alkoxides and in their availability, commonly accessible compounds such as β-diketonates, but more often carboxylates, have been used. Prehydrolyzed solutions of $Ba_2Cu_2(OR)_4(acac)_4(ROH)_2$ ($R = C_2H_4OMe$), associated with $Y_5O(OiPr)_{13}$, have been used for $YBa_2Cu_3O_{7-x}$ superconducting coatings of 5 μm thickness.[38] Acetates (generally hydrated) or the more soluble 2-ethylhexanoates have been used as the source of lead or lanthanum in conjunction with metal alkoxides (mostly n-propoxides or n-butoxides for titanium and zirconium, ethoxides for niobium or tantalum), for materials such as PZT, PLZT, PNM etc., the solvent being an alcohol, often 2-methoxyethanol.[99, 100, 106–108] This solvent appears to provide a way of achieving dehydration by refluxing (b.p. 124 °C), as well as condensation (elimination of organic esters, as can be shown by IR ($\nu(CO_2) = 1730\ cm^{-1}$).[109] Additives for hydrolysis are either acids (0.1–0.2M-HNO_3 or acetic acid) or ammonia solutions.[110] Studies on the influence of the precursor remain limited. The choice of the titanium precursor $Ti(OR)_4$ (R = nPr or iPr) was reported to have an effect on the development of microstructure, particularly for $PbTiO_3$ films.[106] Clusters and grains were observed in the case of the n-propoxide and were attributed to a less continuously crosslinked network as compared with the films derived from the isopropoxide. Using the modified alkoxide $Ti(OiPr)_2(acac)_2$ instead of $Ti(OiPr)_4$ allowed an increase in the thickness of crack-free $PbTiO_3$ films up to 1 μm in base-catalyzed conditions.[107, 108] Using the same titanium precursor associated with lead acetate and pentane-1,5-diol instead of 2-methoxyethanol permitted the production of films up to *ca* 5μm in thickness by repeated coatings prior to firing.[11] Significant substrate effects on the crystallization have been reported. For instance, epitaxial or highly aligned films of $Pb(ZrTi)O_3$ and PNM form on lattice-matched substrates ($SrTiO_3$, MgO, platinum) whereas crystallization is more difficult and requires higher annealing temperatures when deposition is effected on non-lattice-matched or amorphous substrates (SiO_2).[98] Preferential orientation has also been observed to depend on the sol–gel chemistry; $Li_2B_4O_7$ films (on SiO_2) were randomly oriented when prepared from metal alkoxide solutions, but acid additives (acetic or hydrochloric) induced orientation.[112]

THIN FILMS BY MOCVD

Oxide films grown by MOCVD are less numerous than those obtained by sol–gel processing, especially for binary systems, although MOCVD allows a close control of growth parameters and thus of stoichiometry and microstructure, and can achieve high-quality, epitaxial films. As a low-temperature route, the technique might limit interdiffusion phenomena, and MOCVD has thus a great potential for the formation of 'buffer' layers and for the construction of the heterostructures required by electronic devices.[113, 114] Laser-asisted MOCVD is attractive for lowering of deposition temperatures as well as for selective doping during growth by using different wavelengths, but its use has been relatively limited so far.[115]

As already mentioned, the selection of an appropriate precursor for MOCVD applications is a more difficult task than for precursors to be transformed in solution. Sublimation conditions, thermal gravimetric analysis (TGA) and differential calorimetry (DSC) allow a first screening. Vapour pressure measurements are nearly nonexistent on metal alkoxides, whilst the reports on metal β-diketonates are numerous, often with quite different values, probably as the result of variable purities.[41,42,45,116,117] In order to maintain a constant flux of chemical delivery by the carrier gas to the substrate, the condition of saturation equilibrium must be uniformly maintained through growth run-time. This is best achieved in the distillation of a liquid source by bubbling the carrier gas through the heated compound. Solids are generally sublimed by percolating the carrier gas through the heated precursor. Such a process of vaporization is no longer equilibrium-controlled, and therefore is largely dependent on surface area (particle size) and long-term solid-state stability. Although these problems can be overcome by an appropriate design of the solid-source container,[118,119] the use of liquid sources (or low-melting solids) appears preferable.

Metal β-diketonates are generally solids; alkoxides, whilst mostly solids, also exist as viscous liquids for most early transition-metal [$Ti(OR)_4$, R = Et, iPr; $VO(OR)_3$, R = Bu; $M_2(OEt)_{10}$, M = Nb, Ta; $Cr(OtBu)_4$, etc.] and Main-Group elements (boron, aluminum, silicon, tin, antimony),[3] including a recent barium derivative, $Ba[(OC_2H_4O)_2Me]_2$.[120] However, this compound, although monomeric, is non-volatile like most barium alkoxides reported so far.[54,55] Despite their solid character, metal β-diketonates have been more widely used as MOCVD precursors than metal alkoxides, as a result of their better hydrolytic stability and higher volatility. They have been used to deposit films of metals, metal oxides, fluorides and more recently sulfides[121] if the decomposition is achieved in a hydrogen sulfide atmosphere. β-Diketonate derivatives are thermally converted to metal oxides in the case of oxophilic metals (Groups 1–6, lanthanides), whilst metallic films are generally obtained for late transition metals (platinum, copper, gold, palladium, iridium, etc.). However, these metallic films are often highly laden with carbon (up to 50%) or oxygen.[122] Thermolysis in the presence of hydrogen or laser pyrolytic deposition appear to be a means of improving the purity of the deposit as well as of decreasing temperatures for deposition.[115,122] Fluorinated ligands enhance volatility, but favor the formation of metal fluorides, as observed for instance for hexafluoroacetylacetone derivatives $M(hfac)_n$ (M = Al, Be, Ba, etc.).[122] Barium fluoride (BaF_2) can be converted wholly or partially to the oxide by use of water vapor or high-temperature annealing. The formation of metal fluorides is probably favored by their high thermal stability as well as by the existence of metal–fluorine interactions in most of the fluorinated precursors structurally characterized so far, such as for instance $[Ca(hfac)_2(H_2O)_2]_2$ [Ca–F interactions 2.52 Å (0.252 nm).[43] Similar behavior is observed for fluorinated alkoxides.[124] Plasma-enhanced MOCVD (PE MOCVD) could be a means of avoiding undesired fluoride materials.[125]

Besides volatility, lowering of deposition temperatures is another issue to be addressed for the optimization of a CVD precursor, and has been mostly considered on copper β-diketonates since copper films attract much interst as interconnections in integrated circuits. Although copper(II) β-diketonates are a source of metal films, they do not thermally decompose below 300 °C. Copper(I) β-diketonate complexes $Cu(\beta\text{-dik})L_n$ (L = PME_3, PEt_3; $n = 1, 2$) are also appropriate for a a CVD approach to copper films.[126,127] Using $(hfac)Cu(PMe_3)$, copper films were deposed at temperatures as low as 150 °C. Studies of the reaction chemistry have indicated that they are obtained by thermal decomposition, but above 150 °C deposition can take place by disproportionation according to Eqn [5].

$$2(\beta\text{-dik})CuL_n \rightarrow Cu^0 + Cu(\beta\text{-dik})_2 + 2nL \quad [5]$$

This provides the possibility of deposition without ligand decomposition, the latter often being responsible for incorporation of carbon and other impurities. Similar results have been observed for (hfac)Cu(COD) (COD = 1,5-cyclo-octadiene) and various alkyne adducts.[128] However, in the presence of hydrogen, the deposition of high-purity copper films from cyclo-octadiene precursor appears to proceed by direct reduction of the copper(I) species and thus without disproportionation.[129]

Metal alkoxides generally display lower vapor pressure than β-diketonates. The copper(I) tert-butoxide $[Cu(OtBu)]_4$, for instance, sublimes slowly at 10^{-5} torr, and its chemical vapor deposition at 400 °C yields thin films of metallic copper on a variety of substrates: glass, silicon, quartz, aluminum and graphite.[130] Its more volatile adduct, $Cu(OtBu)(PMe_3)$, (sublimation 80 °C/10^{-3} torr) is a source of copper as well.[131]

These results establish that metal films can be deposited from an alkoxide as precursor. If the walls of the reactor are dosed with small amounts of water, the deposit resulting from $[\mathrm{CuOtBu}]_4$ corresponds to copper(I) oxide ($\mathrm{Cu_2O}$) instead of the metallic film.[130] Thermolysis of the low-valent Group 6 metal alkoxides $\mathrm{M_2(OR)_6}$ (M = Mo, W; R = tBu, cyclo-$\mathrm{C_6H_{11}}$) was investigated. The butoxides are cleanly converted to $\mathrm{MO_2}$ at 200 °C. $\mathrm{Mo_2(O\text{-}cyclo\text{-}C_6H_{11})_6}$ undergoes thermolysis in two distinct stages at 210 °C: elimination of cyclohexane, cyclohexene, cyclohexanone and cyclohexanol results in the formation of a material of composition $\mathrm{Mo_2C_4O_4}$, stable up to 550 °C, which is finally converted to a carbide, γ-$\mathrm{Mo_2C}$, by elimination of carbon monoxide and carbon dioxide. The tungsten cyclohexyl oxide derivatives display comparable behavior, but yield tungsten metal. The partitioning of products between $\mathrm{MO_2}$ and $\mathrm{M_2C}$ (M = Mo or W) as a function of R = tBu versus cyclohexyl indicates the potential versatility of metal alkoxides as precursors.[132] Aluminum silicate and zirconium silicate have been deposited using $[\mathrm{Al(OSiEt_3)_3}]_2$[133] or $\mathrm{AlMe_2[OSi(OtBu)_3]}$ and $\mathrm{Zr[OSi(OtBu)_3]_4}$[134] respectively. The $\mathrm{OSi(OtBu)_3}$ ligand appears favorable for the elimination of isobutene at low temperature (150–200 °C) and thus for a low carbon content of films. $\mathrm{VO_2}$ films were prepared by heating $\mathrm{VO(OiBu)_3}$ at 550–650 °C under $\mathrm{O_2}$; $\mathrm{V_2O_5}$ films were obtained above 650 °C. The $\mathrm{VO_2}$ films are useful as temperature-sensing material since $\mathrm{VO_2}$ has a metal-to-semiconductor transition at 60–70 °C.[135]

The careful selection of MOCVD variable process parameters has allowed the preparation of graded-index thin films with specific index profiles of $\mathrm{Al_2O_3}$ using $[\mathrm{Al(OiPr)_3}]_4$.[136]

Comparisons of the potential of various precursors with respect to deposition behavior, crystal structure and orientation of the films are scarce. $\mathrm{Ta_2O_5}$ films with an orthorhombic structure were grown using $\mathrm{Ta(OEt)_5}$ or $\mathrm{Ta(thd)_4Cl}$. The diketonate precursor promoted the formation of oriented films on quartz or silicon substrates.[137] Whilst sodium alkoxides are generally poorly volatile, their fluorinated counterparts display convenient volatility for CVD experiments. Thin films of sodium fluoride (NaF) have recently been obtained for the first time using $\mathrm{NaOCH(CF_3)_2}$, $\mathrm{NaOC(CF_3)_3}$, Nahfac or Nahfod. The best-quality films were obtained using sodium hexafluoroisopropoxide *in vacuo* at a substrate temperature of 250–300 °C.[138]

The influence of the carrier on the nature of the final material can be illustrated by the formation of PbS coatings by ALE (Atomic Layer Epitaxy) using lead alkoxides $[\mathrm{Pb(OtBu)_2}]_m$ and $\mathrm{Pb_4O(OtBu)_6}$, $\mathrm{H_2S}$ being the source of sulfur. The tetranuclear nature of the oxoalkoxide promotes growth rates but the alkoxides display a more narrow processing window (temperature/pressure) than a precursor having a Pb–S linkage such as lead diethylthiocarbamate.[139]

MOCVD routes to mixed-metal oxide materials have been investigated mostly for high-T_c superconductors (whose applications in microelectronics require high critical currents and therefore epitaxial coatings) and ferroelectrics for electro-optical devices. The coatings are generally obtained by using several 'source' precursors, although volatile mixed-metal species have been reported in the literature.[3,39,40] The heterometallic alkoxide $\mathrm{LiNb(OR)_6}$ is among the few which have a stoichiometry appropriate for depositing a material, namely $\mathrm{LiNbO_3}$, and can be representative of the problems encountered for the optimization of mixed-metal MOCVD precursors.[140] Although $\mathrm{LiNb(OR)_6}$ is volatile, the control of the deposition parameters is sometimes hampered by dissociation reactions. The problem has been overcome by using a lithium β-diketonate (Lithd) and $\mathrm{Nb(OMe)_5}$.[39,40] $\mathrm{LiNbO_3}$ has been deposited on a variety of substrates (*ca* 450 °C), but epitaxial layers require annealing in oxygen at higher temperatures. For $\mathrm{PbTiO_3}$ films, titanium isopropoxide was associated with an alkyl derivative, $\mathrm{PbEt_4}$, using argon as the carrier gas. No additional oxygen was necessary. The film deposited on a quartz substrate heated at 500 °C was shown to be conducting, dense, with good surface morphology and strong texture direction.[141] $\mathrm{Pb(OtBu)_2}$ was used by Brierley as the volatile lead source with $\mathrm{Ti(OiPr)_4}$ giving 5 μm-thick $\mathrm{PbTiO_3}$ deposited at 450 °C and annealed in air at 800–900 °C.[62] Although these authors could not deposit $\mathrm{PbSc_{0.5}Ta_{0.5}O_3}$ (PST) directly from the metal precursors, the PST perovskite phase was obtained in a two-stage process: deposition of cubic $\mathrm{ScTaO_4}$ by MOCVD using $\mathrm{Ta(OEt)_5}$ and a scandium fluorinated β-diketonate $\mathrm{Sc(fod)_3}$, followed by diffusion of PbO from a surface layer.[39,40]

$\mathrm{YBa_2Cu_3O_{7-x}}$ films have been obtained on a variety of substrates (MgO, $\mathrm{ZrO_2}$, $\mathrm{SrTiO_3}$, $\mathrm{LaAlO_3}$, $\mathrm{Al_2O_3}$, Ag, etc.) using tetramethylheptanedionates as precursors and various active reactant gases ($\mathrm{O_2}$, $\mathrm{O_3}$, $\mathrm{N_2O}$).[62] Volatilization of the barium derivative is achieved *ca* 100 °C higher than for $Cu(thd)_2$ or $Y(thd)_3$. $Bi_2Sr_2Ca_2Cu_3O_x$ (BSCCO) films were obtained using $M(thd)_2$ (M = Sr, Ca, Cu) as sources for the divalent metals whilst $Bi(C_6H_5)_3$ or $Bi(OEt)_3$ was used for bismuth.[142] UV irradiation (low-pressure mercury lamp or KrF excimer laser) of the metal β-diketonates was effective in promoting crystallization of $Bi_2Sr_2CuO_x$ films at 500 °C (*ca* 700 °C is usually required). Nd_2O_3, CeO_2 and Nd_2CuO_4 thin films have been grown on quartz and MgO using $Ce(thd)_4$ and $Nd(thd)_3$.[143, 144]

Mechanistic considerations

MOCVD is a complex process and involves both gas-phase and surface reactions, which can be controlled by controlling deposition conditions. It consists of several steps: evaporation of the precursors, pyrolysis of precursors and reaction of decomposition fragments to give the coating material, and elimination of side reactions and undesirable impurities (often carbon). The chemistry of the MOCVD process has only recently attracted some attention, and data are mostly limited to semiconductors;[145, 146] some information is available on alkoxides, but data are still nearly non-existent for β-diketonates. Knowledge of the decomposition pathways should provide useful information for the design of precursors since attention has to be paid not only to volatility, but also to the necessity for substituents which are prone to facile hydrocarbon elimination.

Systematic studies have shown that, as a general feature, tertiary alkoxides are more thermolabile than secondary ones, which in turn are more thermolabile than primary ones.[39, 40] Decomposition can be enhanced by hydrolysis due either to residual water on surfaces or to dehydration reactions of tertiary alcohols. Such reactions are favored by hot-wall, glass reactors and closed systems. The presence of residual water may even change the nature of the film, as observed for $[Cu(OtBu)]_4$ (and shown by labeling experiments).[130]

Kinetic studies on the decomposition of $Zr(OtBu)_4$ at 200–250 °C in a closed glass-wall system have established that the decomposition proceeds through a chain mechanism due to the hydrolysis of the alkoxide by water, resulting from the dehydration of the tertiary alcohol. The reaction is induced by the free butanol due to partial hydrolysis of $Zr(OtBu)_4$ by water adsorbed on the glass walls and leads to the overall reaction:[39, 40]

$$Zr(OtBu)_4 \rightarrow ZrO_2 + 4CH_2{=}CMe_2 + 2H_2O \quad [6]$$

Comparison of the decomposition of $[Zr(OiPr)_4(iPrOH)]_2$, $Zr(OiPr)_4$, and $Zr(OtBu)_4$ at 400–450 °C in vacuum has shown that the isopropoxide derivatives deposit at lower temperatures, the volatile by-products being isopropanol and propene. Freshly deposited ZrO_2 thin films have been found to dehydrate isopropanol catalytically to propene. This catalytic activity, however, is lost after exposure to air.[147] Similar observations account for the high amount of propene observed in the pyrolysis of $Nb(OiPr)_5$ at 400 °C giving amorphous Nb_2O_5 films.[148]

The flash vacuum pyrolysis of titanium alkoxides $Ti(OR)_4$ (R = Et, Pr, tBu, CH_2CMe_3, $CH_2\overline{CHCH_2C}H_2$) under dynamic vacuum at 550–700 °C and subsequent analysis of the volatiles (^1H and ^{13}C NMR, GC and GCMS techniques) provide another systematic study of decomposition pathways.[149] With the exception of the neopentyl derivatives, no significant dehydration is observed. Depending on the nature of R, alcohols, ethers, alkenes and carbonyl derivatives are obtained. The absence of products arising from C_α–C_β bonds cleavage—a fragmentation mode known to be especially facile for tertiary and secondary alkoxy radicals—excludes such a process. On the other hand, the ratio of alcohol to ether increases markedly on going from primary to secondary to tertiary alkoxide, and thus with increasing steric hindrance at the α-carbon. The neopentyl derivatives appear to undergo decomposition mainly by attack on the γ-hydrogen. The carbonyl compounds—mostly observed for $Ti(OR)_4$ (R = Et, iPr)—probably result from a β-hydrogen abstraction step. Pyrolysis of $Ce(OCtBu_3)_3$ and of $[LiOCtBu_3]_4$ provides a mechanistic description of the pathways involved for decomposition of metal alkoxides lacking accessible β-hydrogens. The formation of isobutene and of $[Ce(OCHtBu_2)_3]_2$ is the predominant process.[150]

The decompositions of $[Cu(OtBu)]_4$[130] and of $Cu(OtBu)(PMe_3)$[131] are, to our knowledge, the only examples of metal alkoxides giving a metallic deposit and for which mechanistic data are available. Mass spectrometric analysis of the gaseous by-products reveals tBuOH as the only species in the case of $[Cu(OtBu)]_4$. This suggests a decomposition mechanism involving cleavage of the Cu–O bonds, giving butoxy radicals, which subsequently abstract H atoms from surface-bound hydroxyls of the glass reactor.[130] For Cu(OtBu)(PMe_3), it appears that the Cu–O bond may not be cleanly cleaved since PMe_3 can scavenge oxygen impurities giving $OPMe_3$ and the overall decomposition reaction becomes:[131]

$$\text{(tBuO)Cu(PMe}_3) \rightarrow \text{Cu} + \text{PMe}_3 + \text{OPMe}_3 + \text{tBuOH} + \text{acetone} + \text{isobutene} \quad [7]$$

Studies involving mixed-metal compounds are limited to fluorinated derivatives $Na_2Zr[OCH(CF_3)_2]_6$[147] and $BaCu_2(thd)_4[OCH(CF_3)_2]_4$. Preliminary results of the latter show that the composition of the films is strongly dependent on the decomposition temperature.[148]

CONCLUSION AND OUTLOOK

Soluble metal alkoxides and volatile metal β-diketonates are readily available for nearly all elements. The selection of appropriate OR groups—bulky or functional and therefore often polydentates—allows adjustment of their physical properties, solubility and/or volatility, whilst tuning of the substituents can achieve volatility for β-diketonates. Metal alkoxides can meet the criteria for sol–gel as well as for MOCVD applications. However, they are usually less volatile than β-diketonates and their use as MOCVD precursors has been mostly limited to d^0 transition metals (titanium, zirconium, niobium, etc.), and some main group elements (aluminum, bismuth). Since the OR group is a good assembling ligand, it allows the construction of heterometallic units which can act as building blocks. An almost unlimited number of mixed-metal compositions is accessible in mild conditions through the sol–gel process. The molecular composition of these solutions can be quite complex and comprises mixed-metal species with different stoichiometries. The versatility and low temperature of the sol–gel process allow the encapsulation of a large range of organic or inorganic derivatives and thus of functional coatings. To date, 2-methoxyethanol has been used predominantly for the sol–gel processing of thin layers and thus for the chemical modification of the metal alkoxides. However, methoxyethanol is teratogenic, and can cause neurological and hematological damage, even at the ppm level. Alternative sol–gel systems, based for instance on other difunctional and polyfunctional alcohols, on hydroxyacids etc., should be developed in order to promote the sol–gel process as a practical method. Precursors based on thermolabile or photolabile ligands might also be alternatives and should be explored. More systematic studies regarding the relationship between precursors (influence of additives; kinetic data on hydrolysis, especially for multicomponent systems; and so on) and properties of the final material are also required. Comparisons of the potential of various precursors with respect to deposition behavior, crystal structure and orientation of the films are scarce. Mechanistic studies which could allow tailoring of the ligand in order to control volatility, stability and design of low-energy decomposition pathways are a field which is only just emerging for M–O derivatives, and should be developed.

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