Metal Alkoxides as Precursors for Thin-Film Growth [and Discussion]

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Metal alkoxides as precursors for thin-film growth

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The metal alkoxides $[M(OR)_x]_n$ are excellent precursor compounds for synthesizing pure metal oxides, glasses and ceramics by either the MOCVD or the sol–gel technique depending on the volatility and solubility of the metal alkoxide. Factors controlling the volatility of metal alkoxides are discussed together with possible mechanisms for the oxide deposition processes.

Introduction

Metal alkoxides $[M(OR)_x]_n$, where M is the metal of valency x, R is an alkyl group and n is the degree of polymerization, have a wide range of physical properties. At one extreme are the highly polymeric insoluble non-volatile solids (e.g. the methoxides of the alkali metals, alkaline earths and several trivalent metals) and at the other extreme are the relatively volatile monomeric liquids such as $Ti(OPr^i)_4$, $Zr(OBu^t)_4$ and $Hf(OBu^t)_4$ that are soluble in a wide range of organic solvents. Most metal alkoxides are extremely readily hydrolysed to the metal oxide and this imposes a severe discipline on the preparative chemist who must ensure that all stages of a synthesis are done under rigorously dry conditions. However, metal alkoxides are not particularly flammable and do not present any special hazards. This ease of hydrolysis or thermolysis of metal alkoxides to give pure metal oxides makes these compounds very attractive as precursors for depositing metal oxide films. Moreover, the volatile metal alkoxides can be obtained in a very high state of purity by distillation.

The chemistry of the metal alkoxides is well documented (see Bradley *et al.* 1978) and accordingly the synthesis and general chemical reactions of metal alkoxides will not be dealt with in this article. More recent reviews have been published by Mehrotra (1983) and Chisholm (1983). This paper deals primarily with the deposition of metal oxides by metallo-organic chemical vapour deposition (MOCVD) from the volatile metal alkoxides and to a lesser extent with the sol–gel process.

Volatility

Metal alkoxides with the lower alkyl groups (e.g. methyl or ethyl) are usually coordination polymers in which the metal achieves a higher coordination number by utilizing the propensity of the alkoxide ligand to bridge two (μ_2-OR) or three (μ_3-OR) metals. For the trivalent, tetravalent and pentavalent metals the degree of polymerization is often low as in $Al_4(OPr^i)_{12}$, $Ti_4(OEt)_{16}$, $Nb_2(OMe)_{10}$, but for monovalent and divalent metals infinite-sheet structures are probably formed. Branching of the alkyl chain has a dramatic effect on the degree of polymerization due to steric hindrance preventing the bridging by the bulky alkoxide groups. Tertiary alkyl groups are particularly effective often leading to the formation of monomeric metal alkoxides having relatively high volatility. Thus the tetrakis-tertiary butoxides of titanium, zirconium and hafnium are all monomeric with significant vapour pressures at room

Table 1. Volatile tertiary butoxides of titanium, zirconium and hafnium
(Bradley & Swanwick 1958, 1959)

temperature/K	vapour pressure/(mm Hg)		
	$Ti(OBu^t)_4$	$Zr(OBu^t)_4$	$Hf(OBu^t)_4$
300	0.049	0.066	0.069
320	0.25	0.34	0.36
340	1.00	1.35	1.48
360	3.26	4.42	4.80
380	9.04	12.30	13.05
400	21.41	29.77	30.49

temperature as shown in table 1. It is noteworthy that with increasing molecular mass $Ti(OBu^t)_4 < Zr(OBu^t)_4 < Hf(OBu^t)_4$ there is an *increase* in volatility as a result of the effect of molecular mass on the entropy of vaporization because these compounds have practically identical enthalpies of vaporization. The larger atom of thorium requires a bulkier tertiary alkoxide to achieve the monomeric state, thus $Th(OBu^t)_4$ ($n = 3.4$) b.p. 160 °C/0.1 mm, $Th(OCEt_3)_4$ ($n = 1.0$) b.p. 148 °C/0.05 mm, and $Th(OCMeEtPr^i)_4$ ($n = 1.0$) b.p. 139 °C/ 0.05 mm. However, the monomeric tertiary heptyloxides of thorium are considerably less volatile than the monomeric tertiary butoxides of titanium, zirconium and hafnium because of the greater number of carbon and hydrogen atoms in the C_7 ligands.

With the trivalent metals it is difficult to prevent alkoxide bridging and aluminium tertiary butoxide (b.p. 134 °C/0.25 mm) is dimeric whereas lanthanum tertiary butoxide (sublimes 280 °C/10^{-4} mm) is probably tetrameric. Work in progress at Queen Mary College (D. C. Bradley and H. Chudzynska, unpublished work) has shown that in yttrium tri-alkoxides volatility can be enhanced by using bulkier tertiary alkoxide ligands containing CF_3 groups in place of CH_3, which also takes advantage of the lower intermolecular forces between perfluororganic groups. Monovalent and divalent metal alkoxides present a major problem because of the difficulty in screening the metal effectively with only one or two alkoxide groups however bulky. For example, lithium tertiary butoxide (sublimes at 110 °C/0.1 mm) is probably hexameric and beryllium bis-tertiary butoxide (sublimes at *ca.* 100 °C/10^{-3} mm) is trimeric. The enhancement of volatility due to perfluoroalkyl groups is also apparent in the alkali metal perfluoro-tertiary butoxides which are tetrameric and can be sublimed (e.g. $K_4(OC_4F_9)_4$ sublimes at 142 °C/0.2 mm).

Another challenging problem concerns the availability of volatile heterometal alkoxides $M_aM'_bM''_c(OR)_x$ containing two or more different metals in one polynuclear species. These compounds are potentially precursors for the deposition of heterometal ferroelectric and pyroelectric oxides such as $BaTiO_3$, $SrTiO_3$, $PbTiO_3$, $LiNbO_3$, $KTa_xNb_{1-x}O_3$, $KSr_2Nb_5O_{15}$ and the high T_c superconductor $YBa_2Cu_3O_{7-\delta}$. A wide range of heterometal alkoxides have been obtained, namely: $LiNb(OR)_6$, $NaTa(OR)_6$, $MgNb_2(OR)_{12}$, $BaTa_2(OR)_{12}$, $NbAl(OR)_8$, $LiZr_2(OR)_9$, $KZr_2(OR)_9$, $MgZr_4(OR)_{18}$, $AlZr(OR)_7$, $ScAl_3(OR)_{12}$, $YAl_3(OR)_{12}$ and $LnAl_3(OR)_{12}$. Although some of these compounds can be distilled *in vacuo* unchanged others undergo some disproportionation with the more volatile metal alkoxide being enriched in the vapour. This behaviour is unsuitable for the MOCVD process but these heterometal alkoxides are still very useful precursors for the sol–gel process providing they are soluble in a suitable solvent.

Metallo-organic chemical vapour deposition

In the MOCVD process a carrier gas (N_2 or Ar) is equilibrated with the vapour of the liquid metal alkoxide in a bubbler kept at a convenient constant temperature and then passed into a horizontal reactor containing the heated substrate onto which the metal oxide is deposited. The substrate may be heated by radio frequency coupled to a carbon susceptor or by resistance heating. In a modification of this process developed by the late Professor Faktor a solution of the metal alkoxide in a volatile organic solvent is injected directly into a heated wall vertical reactor by using a stepping-motor metered syringe. The organic solvent is 'flash evaporated' and the metal alkoxide vapour carried over the heated substrate by an inert gas. This technique offers considerable scope for depositing heterometal oxides containing two or more different metals because the appropriate metal alkoxides may be dissolved in the organic solvent at predetermined concentrations thus avoiding the individual sources required by the conventional MOCVD technique. I am exploring the use of the 'flash evaporation' method with the non-volatile metal alkoxides that can be made soluble in a suitable organic solvent by judicious choice of alkyl groups.

The MOCVD technique has been used to deposit Al_2O_3, TiO_2, ZrO_2, Ta_2O_5, $LiNbO_3$, $PbTiO_3$, $BaTiO_3$ and $PbSc_{0.5}Ta_{0.5}O_3$ and a bibliography of this work has recently been published elsewhere (Bradley 1989).

An advantage of the MOCVD technique for depositing metal oxide films is the comparatively low temperature (ca. 150 °C) at which most metal alkoxides can be decomposed. Earlier work by Bradley & Faktor (1959) on the thermal stability of zirconium tetra-alkoxides $Zr(OR)_4$ showed that stability decreased in the order $Zr(OEt)_4 > Zr(OPr^i)_4 > Zr(OBu^t)_4$. Detailed studies on the decomposition of the tertiary alkoxide vapour in an all-glass apparatus at around 200–500 °C showed that the facile decomposition resulted in fact from the hydrolysis of the metal tertiary alkoxide by water produced by the dehydration of the tertiary alcohol. A rapid heterogeneous dehydration of the tertiary alcohol occurs on a glass surface producing water vapour and alkene:

$$R^tOH \rightarrow alkene + H_2O,$$
$$Zr(OR^t)_4 + 2H_2O \rightarrow ZrO_2 + 4\ alkene + 2H_2O.$$
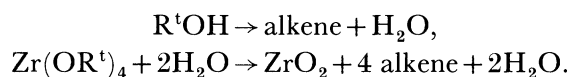
It seems probable that in the MOCVD of metal oxides from metal tertiary alkoxides the process is initiated by the metal tertiary alkoxide molecules reacting with water adsorbed on the surface of the heated substrate. Because one water molecule generates two tertiary alcohol molecules in the hydrolysis a chain reaction can occur. The alkene elimination (dehydration) is less facile for secondary alcohols and very much slower for primary alcohols and this explains the higher thermal stability of the metal primary alkoxides which presumably thermolyse by a different mechanism. In some cases, e.g. $Pb(OBu^t)_2$ or $Cu(OBu^t)$, the metal alkoxide deposits the metal instead of the metal oxide and subsequent treatment with oxygen is required.

Sol–gel process

The sol–gel process utilizes the most characteristic property of the metal alkoxides, namely their ease of hydrolysis even at room temperature. The metal alkoxide is dissolved in a suitable organic solvent, usually the parent alcohol, and the solution allowed to hydrolyse with a controlled amount of water to produce a sol. The sol is then applied to the surface of the

substrate by dip-coating or spraying and on exposure to water vapour in the air is further hydrolysed to a gel. The gel coating is then heated to remove the solvent and the metal oxide coating is compacted by baking at a higher temperature (*ca.* 400–500 °C). The sol–gel method is particularly attractive for depositing oxides from non-volatile metal alkoxides and for producing heterometal oxides. In the latter case the mixture of metal oxides is formed at the molecular level in the sol and the ceramic material or glass can be produced at a much lower temperature than in the 'grind and bake' method involving a mixture of oxides. Studies have been done on the controlled hydrolysis of some metal alkoxides in their parent alcohols by Bradley and co-workers (referenced in Bradley *et al.* 1978) and a few metal oxide alkoxides $[MO_x(OR)_y]_n$ have been characterized by single-crystal X-ray diffraction, e.g. $[Ti_7O_4(OEt)_{20}]$, $[Nb_8O_{10}(OEt)_{20}]$. These results showed that the degree of polymerization of the metal oxide alkoxides may be quite low even for highly hydrolysed species. Recently, some other structures have been determined, e.g. $[Zr_{13}O_8(OMe)_{36}]$ (Morosin 1977), $[Mo_3O(OR)_{10}]$, $[Mo_4O_8(OR)_4(py)_4]$, $[Mo_6O_{10}(OR)_{12}]$ (Chisholm 1983), $[Pb_6O_4(OR)_4]$ (Yanovskii *et al.* 1982) and $[In_5O(OR)_{13}]$ (Bradley *et al.* 1988). These species give some ideas concerning the type of intermediate compounds formed in the early stages of the sol–gel process. Although the sol–gel method has been used primarily in bulk preparation of ceramic oxides and glasses there are many examples of film deposition, e.g. Ta_2O_5, $BaTiO_3$, $SrTiO_3$, $MgAl_2O_4$, $PbTiO_3$, $MgTiO_3$, $PbFe_{0.5}Nb_{0.5}O_3$, lead lanthanum zirconate titanate (PLZT), potassium tantalate niobate (KTN) and lead zirconate titanate (PZT) of electronic materials (see Bradley (1989) for references).

Conclusions

A wide range of metal alkoxide precursors for the deposition of metal oxide films is available and work is in progress in several laboratories to synthesize and characterize new compounds. Considerable progress has already been achieved in the deposition of metal oxides by either the MOCVD or the sol–gel techniques. Further research is clearly required to elucidate the mechanisms of these processes although some progress has been made.

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Discussion

J. M. THOMAS, F.R.S. (*Royal Institution of Great Britain, London, U.K.*). It seems that progress in the study of the various metal alkoxides described by Professor Bradley is held up by the

difficulty in obtaining single crystals for X-ray structural analysis. This is a familiar problem, which often plagues our own work on microporous, molecular sieve-type catalysts. One way forward is to use the Rietveld powder profile method of refinement, based on neutron diffraction or X-ray diffraction data. My colleague, A. K. Cheetham, and I were able to obtain details of Si–Al ordering (Cheetham *et al.* 1982), and of the nature of the catalytic site (Cheetham *et al.* 1984) in zeolitic solids, from, for example, neutron diffraction data. Cheetham *et al.* (1984) have also used the Rietveld method for *ab initio* structure determination by using high-resolution data acquired from central facilities at the Rutherford Appleton Laboratory (ISIS) and Brookhaven. There may well be scope for Professor Bradley's solids to be elucidated in this manner.

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D. C. BRADLEY, F.R.S. I have encountered two types of problem with the X-ray crystallography of metal alkoxides in addition to the particular problem of their sensitivity to water vapour. One problem arises from disorder due to the alkyl groups whereby apparently good-looking single crystals do not diffract well and I doubt whether the Rietveld powder profile method would offer any advantage. The other problem arises with the insoluble metal alkoxides which are probably microcrystalline and might well be suitable for the Rietveld powder profile technique. I shall follow Professor Thomas's advice and consult Professor Cheetham about this aspect.