Metal Alkoxides as Precursors for Electronic and Ceramic Materials

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Contents

I. Introduction

The metal alkoxides $M(OR)_x$ (M = a metal of valency x; R = alkyl or aryl group) are excellent precursors for the deposition of metal oxides, and current interest in using metal oxides in optoelectronics, high-T_c superconductors, and ceramics has led to a resurgence of interest in the chemistry of these compounds.

My interest in metal alkoxides dates back to 1947 when I began graduate research on the synthesis of zirconium tetraalkoxides, $Zr(OR)_4$, under the supervision of the late Professor William Wardlaw. Our most exciting discovery was the dramatic effect of chain branching in the alkyl group R on the volatility of the zirconium alkoxide due to steric control of the molecular complexity (degree of oligomerization) of the molecule $[Zr(OR)_4]_n$ (n = molecular complexity). Monomeric zirconium tetra-*tert*-butoxide, $Zr(OCMe_3)_4$, was sufficiently volatile (bp 89 °C/5.0 mmHg) for us to envisage the possibility of its use for the separation of zirconium and hafnium by fractional distillation of the *tert*-butoxides. However, we were thwarted by two factors: one that the zirconium and hafnium compounds differed in boiling points by only about 2 °C and the other that the *tert*-butoxides were very prone to thermal decomposition to the metal oxide at the temperatures (150–200 °C) required to produce high vapor pressures. The subsequent studies of the mechanism of thermolysis of zirconium alkoxides by the late Marc Faktor when he was my graduate student laid the foundations for our present understanding of the MOCVD process for the deposition of metal oxides using metal alkoxides as volatile precursors. Interestingly, there was no commercial interest in exploiting this process in the 1950s. Back in 1950 we were joined by a dynamic research student from India, Ram Charan Mehrotra, with whom it was a pleasure and an inspiration to work. Professor Mehrotra continued working in this field after his return to India, and his group has in recent years made extremely important advances in the synthesis of heterometal alkoxides, i.e., compounds containing two, three, or four different metals in a cluster molecule. In 1978 we published our book entitled *Metal Alkoxides*,[1] which is a basic reference source to which I refer readers who are not familiar with the field. The more recent reviews by Mehrotra (*Transition Metal Alkoxides*[2]) and Chisholm (*Metal Alkoxides: Models for Metal Oxides*[3]) are highly recommended.

In this article I shall restrict my coverage to those aspects of the chemistry of metal alkoxides that are particularly relevant to the use of these compounds as precursors for metal oxides in the electronics and ceramics industries. This will entail a short section on the preparation and purification of metal alkoxides followed by sections on structure and volatility, oxide alkoxide intermediates, the MOCVD technique, and the sol–gel technique.

Professor Bradley was born on November 7th, 1924. He received his university education at Birkbeck College (University of London), where he obtained the B.Sc. (1st Class Honours in Chemistry, 1946), Ph.D. (Physical Inorganic Chemistry, 1950), and D.Sc. (1959) degrees. His first university appointment was at Birkbeck College, where he was Lecturer in Inorganic Chemistry (1949–1959), and his first professorial appointment was at the University of Western Ontario, Canada (1959–1965). In 1965 he was appointed to the Chair of Inorganic Chemistry at Queen Mary College, London, and served as Head of Department from 1979 to 1983. Since 1965 he has served on many committees of Queen Mary College and the University of London. He has been Chairman of the University Board of Studies in Chemistry and has served as a member of the University Academic Council and the Senate. He has also played an active role in the Royal Society of Chemistry, being a member of Council and serving successively as Hon. Secretary/Treasurer, Vice-President, and President of the Dalton Division. At present he is a member of Council of the Royal Institution and became Secretary in 1988. During the past 40 years his research work has involved pioneering work in the synthesis and characterization of novel metalloorganic compounds such as metal alkoxides, metal dialkylamides, metal dithiocarbamates, metal organoimido complexes, and metal bis(trimethylsilyl)amides of the transition metals and lanthanides. Recently, his research has involved the synthesis of volatile organometallic compounds of aluminum, gallium, and indium as precursors for the deposition of group III–V semiconductors by chemical vapor deposition. Over 200 original papers have been published, and his work has been recognized by his election to the Fellowship of the Royal Society (1980) and the award of the Ludwig Mond Medal and Lectureship of the Royal Society of Chemistry (1987). In addition to giving plenary lectures at International Conferences, he has also given invited courses of lectures in Australia, Brazil, the People's Republic of China, Hungary, and India.

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TABLE I. Volatilities of $M(OR)_4$ Compounds

R	$Ti(OR)_4$	$Zr(OR)_4$	$Th(OR)_4$
C_2H_5	103 °C/0.1 mmHg	180 °C/0.1 mmHg	>200 °C/10^{-4} mmHg
$(CH_3)_2CH$	49 °C/0.1 mmHg	160 °C/0.1 mmHg	200 °C/0.05 mmHg
$(CH_3)_3C$	64.5 °C/0.4 mmHg	55 °C/0.2 mmHg	160 °C/0.1 mmHg
$(CH_3)_2(C_2H_5)C$	98 °C/0.1 mmHg	95 °C/0.1 mmHg	208 °C/0.3 mmHg
$(CH_3)(C_2H_5)_2C$	139 °C/0.8 mmHg	150 °C/1.2 mmHg	148 °C/0.1 mmHg

II. Preparation and Purification of Metal Alkoxides

The methods for synthesizing metal alkoxides are well established[1] and require only a brief review here.

The simplest method involves the direct reaction between the metal M and the alcohol ROH (eq 1).

$$M + xROH \rightarrow M(OR)_x + (x/2)H_2 \qquad (1)$$

This reaction is limited to the more electropositive metals and occurs spontaneously with the alkali metals. The influence of the alkyl group in the alcohol on reactivity with the metal is exemplified by the rapid reaction of sodium and ethanol in contrast to the very slow reaction of sodium with *tert*-butyl alcohol.

With the divalent and trivalent metals it is necessary to add a catalytic amount of iodine (Mg) or mercury(II) chloride (Al, lanthanides) to initiate the reaction by cleaning the metal surface.

The easiest laboratory method for the synthesis of the alkoxides of higher valent metals utilizes the reaction between an alkali metal alkoxide and the halide (usually chloride) of the higher valency metal (eq 2). However,

$$TiCl_4 + 4NaOEt \rightarrow Ti(OEt)_4 + 4NaCl \qquad (2)$$

this method is unsuitable for metals (e.g., Zr, Hf, Nb, and Ta) whose alkoxides form stable heterometal alkoxides incorporating the alkali metal: viz., $NaZr_2(OR)_9$ and $NaTa(OR)_6$. In such cases it is necessary to use anhydrous ammonia as the reagent for dechlorination of the metal (eq 3).

$$ZrCl_4 + 4NH_3 + 4ROH \rightarrow Zr(OR)_4 + 4NH_4Cl \qquad (3)$$

If a particular metal chloride is too unstable, e.g. Ce(IV) or Pu(IV), but a stable hexachlorometalate is accessible, then the latter may be used instead[4] (eq 4).

$$(pyH)_2{}^+[MCl_6]^{2-} + 6ROH + 6NH_3 \rightarrow M(OR)_4 + 2py + 6NH_4Cl \qquad (4)$$

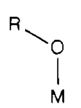
Even this method has its limitations because the hexachlorometalate(IV) is sometimes (e.g., Sn or Pb) too inert to react with alcohol and ammonia.

Miscellaneous other methods of synthesis are documented in ref 1, but it is noteworthy that more work has subsequently been carried out on the direct electrochemical synthesis of the alkoxides of Sc, Ti, Y, Zr, Nb, Ta, Ga, and Ge.[5]

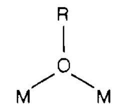
III. Structure and Volatility of Metal Alkoxides

Volatility is of prime consideration in assessing the feasibility of a metalloorganic compound as a precursor in chemical vapor deposition.

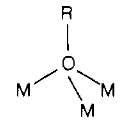
Our systematic studies on the alkoxides in the 1950s established that the steric effect of the alkyl group had a controlling influence on the volatility of the metal alkoxide.[1] Thus the alkoxides containing less bulky alkyl groups (e.g., methyl and ethyl) proved to be oligomers (e.g., dimers, trimers, and tetramers) due to the bridging propensity of the alkoxide group, which may be bonded through its oxygen to two (μ_2) or three (μ_3) metals by means of conventional two-electron covalent bonds (I–III). The driving force is of course the tendency of the metal to expand its coordination number from its covalency number to a higher value such as 6 in an octahedral complex. For most of the metal alkoxides the strength of the alkoxide bridges is sufficiently great to preclude the alternative mechanism for coordination expansion, namely the addition of another ligand L containing a donor atom.[1]



I
terminal



II
bridging (μ_2)



III
bridging (μ_3)

Mass spectral evidence has shown that some oligomeric metal alkoxides retain their structural integrity in the vapor state,[1] and clearly much more energy is required to vaporize a trimer or dimer than a monomer. Thus alkoxyboranes, which are monomeric $B(OR)_3$, are very much more volatile than aluminum alkoxides, which are oligomers [e.g., tetrameric $Al_4(OR)_{12}$], and alkoxysilanes, $Si(OR)_4$, are more volatile than the oligomeric titanium tetraalkoxides, $[Ti(OR)_4]_n$. Even when the alkoxide bridges are not very strong and monomers are formed on heating, extra energy is required to depolymerize the oligomers with consequent lowering of volatility.

The monomeric metal alkoxides can be prevented by steric hindrance from intermolecular bond formation (bridging) by utilizing very bulky alkyl groups, and a relatively volatile metal alkoxide can be obtained. The *tert*-alkyl groups are the ones par excellence for preventing bridging and promoting higher volatility. Besides coordination expansion of the metal, another significant factor is the metal's atomic radius since the larger the metal, the bulkier will be the alkoxide group necessary to prevent alkoxide bridging. Thus zirconium and hafnium form monomeric tetra-*tert*-butoxides but the larger thorium atom forms a less volatile oligomeric *tert*-butoxide and requires the larger *tert*-heptyl oxide ($R = CMeEtPr^i$) to produce a monomer.[6] Unfortunately, the use of the very bulky *tert*-heptyl oxide groups to screen the thorium atom invokes a penalty in terms of volatility because the monomeric $Th(OCMeEtPn^i)_4$ is a very large polyatomic molecule with a much higher boiling point (139 °C/0.05 mmHg) than the monomeric *tert*-butoxides of zirconium and hafnium (bp ca. 54 °C/0.1 mmHg). In Table I are listed some volatility data on the tetraalkoxides of titanium, zirconium, and thorium. Examples of some representative transition-metal alkoxides exhibiting moderate volatility (i.e., readily distilled or sublimed in vacuo) are given in Table II.

Other limitations to the volatility of metal alkoxides are apparent in the alkoxides of monovalent and divalent metals.[1] With only one alkoxide group per metal atom in the alkali metal alkoxides it is impossible even with *tert*-alkoxide groups to prevent alkoxide bridging,

TABLE II. Some Volatile Transition-Metal Alkoxides

$Ti(OBu^t)_4$	$V(OBu^t)_4$	$Cr(OBu^t)_4$
$Zr(OBu^t)_4$	$Nb(OPr^i)_5$	$Mo(OPr^i)_4$
$Hf(OBu^t)_4$	$Ta(OPr^i)_5$	$W(OPr^i)_6$
$Th(OHx^t)_4$	—	$U(OBu^t)_6$

and lithium *tert*-butoxide for example is hexameric with a higher boiling point (110 °C/0.1 mmHg)[7,8] than zirconium *tert*-butoxide. A similar case exists for the divalent metals where for example beryllium di-*tert*-butoxide is trimeric and relatively nonvolatile (sublimes at 100 °C/10^{-3} mmHg). The only appreciably volatile alkoxide of copper obtained to date is copper(I) *tert*-butoxide, which, although tetrameric, can be sublimed (ca. 100 °C/1 mmHg).[10]

It is noteworthy that the volatility of the alkoxides of monovalent or divalent metals may be considerably enhanced by combination as a heterometal alkoxide with a higher valency metal alkoxide. Thus the nonvolatile $NaOPr^i$ will combine with $Zr(OPr^i)_4$ to give $NaZr_2(OPr^i)_9$, which can be distilled in vacuo. Some examples of volatile heterometal alkoxides are given in Table III.

IV. Metal Oxide Alkoxide Intermediates

The metal alkoxides are renowned for their facility to undergo hydrolysis to form the metal oxide.

$$M(OR)_4 + 2H_2O \rightarrow MO_2 + 4ROH \quad (5)$$

It was clearly of interest to explore the nature of the metal oxide alkoxides, which should form a bridge between the oligomeric metal alkoxides $[M(OR)_x]_n$ and the macromolecular metal oxides, and Bradley and co-workers have studied the controlled hydrolysis of various metal alkoxides in boiling alcoholic solutions using an ebulliometric technique to determine the number-average degree of polymerization of the hydrolysis products in solution.[1] A striking feature of these results was the fact that although the degree of polymerization n increased with the degree of hydrolysis, the value of n was relatively small for quite high degrees of hydrolysis, and attempts were made to fit the results to a structural model for the metal oxide alkoxides. Only a few of these compounds have been isolated as crystals, and thus there is a dearth of X-ray crystal structures. In the initial hydrolysis of titanium tetraethoxide, a crystalline product deposited having an analysis close to $Ti_6O_4(OEt)_{16}$[11] but a preliminary X-ray study revealed the presence of a Ti_7O_{24} oxometal framework of distorted titanium–oxygen edge-shared octahedral units.[12] The organic groups were not properly located in the structure but it seems reasonable to suppose that the species $Ti_7O_4(OEt)_{20}$ was formed although Turova and Turevskaya prefer the variable composition $[Ti_7O_4(OH)_n(OEt)_{20-n}]$ (n = 1–2).[13] In the controlled hydrolysis of niobium pentaethoxide the crystalline oxide ethoxide $Nb_8O_{10}(OEt)_{20}$ was isolated and its structure determined by X-ray crystallography.[14] This structure is also based on edge-sharing metal–oxygen distorted octahedra.

The only zirconium oxide alkoxide structure determined to date is the fascinating tridecazirconium species $Zr_{13}O_8(OMe)_{36}$ whose X-ray crystal structure was determined by Morosin.[15] The structure consists of a central eight-coordinated (distorted cubic) zirconium bridged to 12 seven-coordinated zirconiums each bonded to two oxygens, four bridging methoxides, and one terminal methoxide. Chisholm and co-workers have recently isolated and structurally characterized by X-ray crystallography the interesting Mo(IV) oxide alkoxides $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}OR)(\mu_2\text{-}OR)_3(OR)_6]$ (R = neopentyl or isopropyl)[16] and $[Mo_4O_4(\mu\text{-}O)_2(\mu_3\text{-}O)_2(\mu_2\text{-}OPr^i)_2(OPr^i)_2(py)_4]$.[17] These remarkable molecules, which are based on octahedrally coordinated Mo(IV), contain metal–metal bonds and exhibit all possible bonding types for the oxo and alkoxo ligands. The hexanuclear species $Mo_6O_{10}(OPr^i)_{12}$ contains molybdenum with an "average valency" of 5.33 in an S-chain of molybdenum atoms in a centrosymmetric structure containing five-coordinated and six-coordinated molybdenum atoms.[18]

Turning now to the nontransition metals, Turova et al.[19] have obtained the crystal structure of the first hydrolysis product of lead(II) diisopropoxide. The hexanuclear cluster $Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OPr^i)_4$ has a regular octahedron of lead atoms, each bonded to two μ_3-oxo and two μ_3-isopropoxo ligands with T_d symmetry for the Pb_6O_8 framework.

Recent research in our laboratory has led to the isolation and X-ray structure determination of the pentanuclear indium(III) oxide isopropoxide $[In_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_5]$.[20] The five indium atoms are bonded to the μ_5-oxo atom in a tetragonal-pyramidal configuration, and each indium has a distorted octahedral coordination. Analogous compounds have been obtained for scandium, yttrium, and ytterbium.[20]

Some metal oxide alkoxides have been obtained by partial thermolysis of the metal alkoxide. Thus the crystalline initial hydrolysis product formulated as $Ti_6O_4(OEt)_{16}$ disproportionated on heating in vacuo, giving the volatile $Ti(OEt)_4$ and leaving $Ti_3O_4(OEt)_4$ as a nonvolatile residue[11] (eq 6). Bradley and Faktor[21]

$$Ti_6O_4(OEt)_{16} \rightarrow Ti_3O_4(OEt)_4 + 3Ti(OEt)_4 \quad (6)$$

studied the thermolysis of zirconium tetraalkoxides under a dry nitrogen atmosphere at temperatures in the range 220–340 °C and noted that the *tert*-alkoxides (*tert*-butyl and *tert*-amyl) decomposed much more readily than the isopropoxide, generating alkene and alcohol as the volatile products and leaving a solid residue whose analysis was in the range $Zr_2O_3(OR)_2$ to ZrO_2 (eq 7).

$$4Zr(OR)_4 \rightarrow ZrO_2 + 2Zr_2O_3(OR)_2 + 5(\text{alkene}) + 5ROH \quad (7)$$

More recently, Morgan and co-workers[22] have obtained tractable glassy or resinous polymers of the type

TABLE III. Some Volatile Heterometal Alkoxides

$LiZr_2(OPr^i)_9$	$LiNb(OBu^t)_6$	$NaZr(OBu^t)_5$	$NaTa(OPr^i)_6$	$KZr(OBu^t)_5$	$KTa(OPr^i)_6$
$MgZr_4(OPr^i)_{18}$	—	$CaZr_4(OPr^i)_{18}$	$CaNb_2(OPr^i)_{12}$	$BaZr_3(OPr^i)_{14}$	$BaNb_2(OPr^i)_{12}$
$Al_2Zr(OPr^i)_{10}$	$AlTa(OPr^i)_8$	$Ga_2Zr(OPr^i)_{10}$	$GaNb(OPr^i)_8$	—	—
$ScAl_3(OPr^i)_{12}$	$YAl_3(OPr^i)_{12}$	$LaAl_3(OPr^i)_{12}$	$LaGa_3(OPr^i)_{12}$	$PrAl_3(OPr^i)_{12}$	$GdGa_3(OPr^i)_{12}$
$CrAl_3(OPr^i)_{12}$	$FeAl_3(OPr^i)_{12}$	$MnAl_2(OPr^i)_6$	$CoAl_2(OPr^i)_8$	$NiAl_2(OPr^i)_8$	$CuAl_2(OPr^i)_8$

$[AlO(OR)]_n$, $[Ti_3O_4(OR)_4]_n$, and $[Zr_3O_4(OR)_4]_n$ by thermolysis of the metal alkoxide at 300 °C under nitrogen or argon. These compounds were soluble in common organic solvents.

Although silicon is not a metal, the hydrolysis of tetraalkoxysilanes, $Si(OR)_4$, is of considerable importance in the sol–gel process for the formation of silicate materials, and it is noteworthy that Klemperer et al.[23] have recently published some very significant results on the acid hydrolysis of tetramethoxysilane. They studied the products of the hydrolysis of $Si(OMe)_4$ (3 M) in methanol (14 M) by water (1.8 M) containing hydrochloric acid (0.05 M) after a period of 5 h. The mixture of polysilicate species of general formula $Si_xO_y(OMe)_a(OH)_b$ was then esterified with diazomethane to convert hydroxyl groups to methoxo groups, i.e., $Si_xO_y(OMe)_a(OH)_b \rightarrow Si_xO_y(OMe)_{a+b}$. The mixture was then analyzed by capillary gas chromatography, mass spectroscopy, and ^{29}Si NMR spectroscopy. The power of this technique is shown by the number of individual polymers identified in the system ($[Si_2O(OMe)_6]$, $[Si_3O_2(OMe)_8]$, $[Si_4O_4(OMe)_8]$, $[Si_4O_3(OMe)_{10}]$, $[Si_5O_5(OMe)_{10}]$, $[Si_5O_4(OMe)_{12}]$, $[Si_6O_6(OMe)_{12}]$, $[Si_6O_5(OMe)_{14}]$, $[Si_7O_7(OMe)_{14}]$, $[Si_7O_6(OMe)_{16}]$, $[Si_8O_8(OMe)_{16}]$, $[Si_8O_7(OMe)_{18}]$) and the identification of various isomeric species for the acyclic molecules containing four or more silicon atoms.

V. MOCVD Technique for Depositing Metal Oxides

Volatile metal alkoxides offer several attractions as precursors for the deposition of metal oxides. They can be purified to a high degree by distillation or sublimation in vacuo, and being intrinsically noncorrosive, the pure compounds may be stored indefinitely out of contact with water vapor. Since the metal is normally strongly bonded to oxygen by the alkoxide group, the metal alkoxide contains more than enough oxygen to satisfy the metal's requirement in forming the oxide. The key to the success of the metal alkoxide as a precursors is the ease of removal of the organic groups in the form of volatile nonreactive products of reaction. As mentioned in the Introduction, the ease of decomposition of zirconium tetra-*tert*-butoxide to zirconia was impressed upon us many years ago when we attempted to separate zirconium and hafnium by fractional distillation of the *tert*-butoxides. Kinetic studies in a closed all-glass system on gaseous $Zr(OBu^t)_4$ at 200–250 °C showed that the decomposition occurred by a chain reaction mechanism due to hydrolysis of the zirconium alkoxide by water produced by the dehydration of the tertiary alcohol[24] (eq 8 and 9). The dehydration of the

$$Zr(OBu^t)_4 + H_2O \rightarrow ZrO(OBu^t)_2 + 2Bu^tOH \quad (8)$$

$$2Bu^tOH \rightarrow 2CH_2{=}CMe_2 + 2H_2O \quad (9)$$

tertiary alcohol is catalyzed by the glass surface, and the overall decomposition to ZrO_2 is given in eq 10. In

$$Zr(OBu^t)_4 \rightarrow ZrO_2 + 4CH_2{=}CMe_2 + 2H_2O \quad (10)$$

a carefully baked out glass apparatus the zirconium *tert*-butoxide vapor remained unchanged for many hours due to the induction period before the concentration of water vapor had built up sufficiently to produce a rapid reaction. The hydrolytic thermal decomposition depicted above clearly affords a facile mechanism for the deposition of metal oxides from metal *tert*-alkoxides. Since it is difficult to remove residual adsorbed water vapor from most surfaces, it is easy to visualize the rapid deposition of films of metal oxides on a range of material substrates.

Mazdiyasni and Lynch[25] first developed the metal alkoxide precursor route for the deposition of ZrO_2, HfO_2, and yttria-stabilized zirconia as high-purity ceramic materials. The oxides of yttrium, dysprosium, and ytterbium were also deposited from their isopropoxides at 200–300 °C under nitrogen.[26]

More recently, it was reported that Al_2O_3 could be deposited on InP by thermolysis of aluminum isopropoxide vapor in nitrogen at low pressure,[27] and Wang et al.[28] deposited TiO_2 and Ta_2O_5 from the metal ethoxides. We have deposited films of TiO_2, ZrO_2, and Ta_2O_5 on various substrates at temperatures below 200 °C using the volatile metal alkoxides as precursors.[29]

While the deposition of a binary metal oxide like ZrO_2 is comparatively easy, difficulties arise when ternary or quaternary heterometal oxides are required. Thus there is considerable interest in growing films of ferroelectric oxides for their electrooptic effects and nonlinear optical properties. The ilmenite ternary oxide structures $LiNbO_3$ and $LiTaO_3$ are very attractive together with tungsten bronzes $KSr_2Nb_5O_{15}$ and $Sr_xBa_{1-x}Nb_2O_6$ and the perovskite materials $KTa_xNb_{1-x}O_3$ and $PbMg_{0.33}Nb_{0.67}O_3$ to name but a few. More recently, high-T_c superconducting oxides such as $YBa_2Cu_3O_{7-\delta}$ have claimed attention and offer a challenge to the practitioner of MOCVD. Let us take lithium niobate as an example to illustrate the problem. In principle, it would seem obvious to use lithium alkoxides and niobium pentaalkoxides as precursors but there is the problem that the niobium alkoxides are much more volatile than the lithium alkoxides. In fact, lithium and niobium alkoxides combine to form the heterometal alkoxide $LiNb(OR)_6$ (see Table III), which has the correct stoichiometry for depositing $LiNbO_3$. Unfortunately, the volatilization of $LiNb(OR)_6$ sometimes leads to some disproportionation due to the disparity in volatilities of the parent alkoxides[29] (eq 11). Curtis and Brunner[30]

$$LiNb(OR)_6 \rightarrow LiOR + Nb(OR)_5 \quad (11)$$

appear to have solved this problem by using the lithium derivative of the β-diketone 2,2,6,6-tetramethylheptane-3,5-dione, which is more volatile than a lithium alkoxide. The lithium β-diketonate was heated at 250 °C and $Nb(OMe)_5$ at 200 °C in a stream of argon containing oxygen and passed over the substrate at 450 °C in a hot-wall reactor. $LiNbO_3$ was thus deposited on a variety of substrates but epitaxial deposition occurred only on $LiNbO_3$ or $LiTaO_3$ substrates after annealing in oxygen at higher temperatures.

Nagakawa et al.[31] have deposited lead titanate, $PbTiO_3$, on Pt-coated silicon at low pressure by passing $Ti(OC_4H_9)_4$ vapor in argon under reduced pressure into a reactor containing PbO heated to 1200 °C next to the substrate heated to 400–800 °C. The $PbTiO_3$ film was annealed in a current of oxygen. However, Kwak et al.[32] have reported the deposition of $PbTiO_3$ onto a quartz substrate maintained at 500 °C using tetraethyllead and titanium isopropoxide as precursors with argon as carrier gas. No additional oxygen was required in this process, and the film deposited was shown by SEM to be dense and noncolumnar with good surface morphology. X-ray diffraction at various temperatures showed a reversible tetragonal to cubic phase transition at ca. 540 °C.

Brierley et al.[33] deposited $PbTiO_3$ at 450 °C using $Pb(OBu^t)_2$ and $Ti(OPr^i)_4$ as the volatile precursors, giving films up to 5 μm thick which required annealing at 800–900 °C in air to develop a polycrystalline film having a grain size of 0.5–1.0 μm. Although these authors could not deposit $PbSc_{0.5}Ta_{0.5}O_3$ directly from lead, scandium, and tantalum metalloorganic precursors, they did succeed in developing a two-stage process based on the deposition of cubic $ScTaO_4$ by MOCVD using $Sc(FOD)_3$ and $Ta(OEt)_5$ followed by diffusion of PbO from a surface layer to produce the perovskite phase of PST.

Another approach to the problem of depositing heterometal oxides is the "flash evaporation" technique developed by the late Marc Faktor in these laboratories. In this method the metal alkoxide precursor is dissolved in a volatile organic solvent and is injected into the top of a vertical reactor containing a heated substrate at the bottom. As the droplets of metal alkoxide solution descend, the solvent is very rapidly evaporated and the supersaturated metal alkoxide vapor is decomposed on the hot substrate.

We have recently shown that crystalline barium titanate, $BaTiO_3$, can be deposited on a quartz substrate using the heterometal alkoxide $BaTi(OPr^i)_6$ in 2-propanol solution.[34] This method should lend itself to the deposition of a wide range of heterometal oxides using a suitable solution of the constituent metal alkoxides. It has the advantages of control over stoichiometry and initial deposition of the oxides at comparatively low temperatures (150–200 °C) followed if necessary by annealing at higher temperatures to develop crystallinity.

VI. Sol–Gel Technique for Producing Oxide Glasses and Ceramics

The sol–gel technique has been used for many years, and the metal alkoxides and alkoxysilanes have featured prominently as source materials. The method consists of making a homogeneous solution of the component metal alkoxides in a suitable solvent, usually the parent alcohol, and then causing the hydrolysis under controlled conditions to produce a gel containing the hydrated metal oxide. The gel is then dried, compacted, and fired to produce a ceramic or glassy material at a temperature much lower than that required by the conventional melting process. The advantages of the sol–gel process reside in the high purity of the metal alkoxide precursors, the homogeneity of the components at the molecular level, and the low processing temperature. These features are all of paramount importance in fabricating electronic ceramics. A wide range of electronic materials may be deposited by using the sol–gel process and the literature is voluminous. Rather than attempt to give a comprehensive account of the literature, I have selected a few representative examples of recent papers within which a multitude of other references will be found.

In the field of multicomponent oxide glasses there are the important publications by Dislich[35] and Sakka and Kamiya.[36] In the electronics field the ferroelectric oxides are well represented with $BaTiO_3$,[37] $SrTiO_3$,[38] lead lanthanum zirconium titanate (PLZT),[39] $MgAl_2O_4$,[40] $PbTiO_3$,[41] potassium tantalum niobate (KTN),[42] Ta_2O_5,[43] lead zirconate titanate (PZT),[44] $MgTiO_3$,[45] and $PbFe_{0.5}O_3$.[46]

Interesting overviews of the sol–gel processes recently published by Mackenzie,[47] Ulrich,[48] Brinker,[49] and Livage[50] are recommended references to this field.

VII. References

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