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Oxide ferroelectric thin films: synthesis from organometallic compounds and properties

V N Vertoprakhov, L D Nikulina, I K Igumenov

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Abstract. Chemical methods for the preparation of oxide ferroelectric thin films from organometallic compounds published over the last 10 – 15 years are considered systematically and generalised. Layers of these films are promising for the creation of non-volatile memory elements and for use in nano- and microelectronic devices. The bibliography includes 318 references.

I. Introduction

Progress in microelectronics requires novel materials for information storage and retrieval. Switches based on chalcogenide semiconductors containing transition metal oxides embedded into glassy matrices of phosphorus, barium, germanium and lead oxides are known. Memory elements based on them stand 10^3 recirculation cycles. However, these materials did not find further development.[1] Non-volatile memory elements that exist in two states corresponding to storage of either the logical zero or unity have been designed based on transistors with the structure metal – dielectric – floating gate semiconductor. Superlarge integrated circuits (SLIC) with high information capacities have been developed on their base.

In the course of intense investigations into the design of novel devices for information storage and processing it has been demonstrated that the effect of spontaneous polarisation in ferroelectrics (Fig. 1) can be exploited in the manufacture of non-volatile memory elements. In this case, the maximum number of recirculation cycles (Y) reaches $10^{10} – 10^{12}$. A drawback of such materials consists of their fatigue, which is reflected in a decrease in the residual polarisation with an increase in the number of recirculation cycles. This fact impedes wide application of ferroelectrics in SLIC technology. With this regard, the search for novel materials with enhanced ferroelectric properties is urgently needed. In our opinion, the use of ferroelectrics in the form of thin films or layers with parameters approaching those of the bulk materials is highly promising. The energy consumption, levels of control, electrical and mechanical loads, and optical and acoustic losses are relatively low for such films. Methods for the preparation of the films should be compatible with modern technology for the production of semiconducting microdevices. This issue has been the focus of several dedicated international symposia.[2 – 6] The relation between the structure of the films and their physical properties has been considered in monographs[7,8] and reviews.[9 – 14]

The methods for the preparation of ferroelectric thin films (FETF) can arbitrarily be classified into physical and chemical methods. For instance, thermal evaporation, high-vacuum sputtering induced by electron or ion beams, magnetron sputtering and laser ablation belong to the physical methods. Meanwhile, the sol – gel process, gas-phase deposition of layers from organometallic compounds [Metal-Organic Chemical Vapour Deposition (MOCVD)] or solid precursors (with or without the use of plasma), the hydrothermal method and the Langmuir – Blodgett method are classified as chemical methods. It is of note that the MOCVD method for the preparation of thin films is superior to other techniques for the following reasons:[15]

— it is compatible with the technology of SLIC production;

— it is applicable to the preparation of films in a wide range of thicknesses and areas;

— it yields films with high-quality surface morphologies suitable for further lithographic processing with the required spatial resolution.

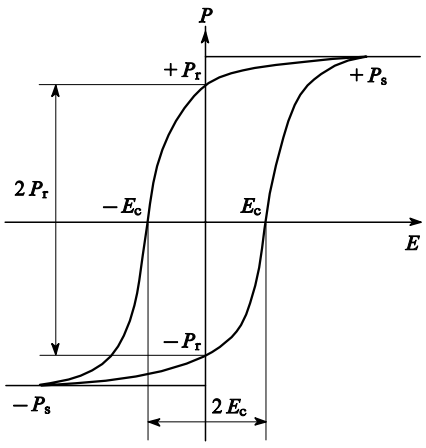


Figure 1. Polarisation curve of a ferroelectric film.
$\pm P_r$ is the residual polarisation at $E = 0$, $\pm P_s$ is the spontaneous polarisation, $\pm E_c$ is the coercive force.

V N Vertoprakhov, L D Nikulina, I K Igumenov A V Nikolaev Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, prosp. Acad. Lavrent'eva 3, 630090 Novosibirsk, Russian Federation. Fax (7-383) 334 44 89, tel. (7-383) 330 66 46, e-mail: verto@che.nsk.su (V N Vertoprakhov), Lnik@che.nsk.su (L D Nikulina), tel. (7-383) 330 94 87, e-mail: igumen@che.nsk.su (I K Igumenov)

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The typical required thickness of ferroelectric thin films lies in the range from nanometers to a few hundred nanometers. Since nearly all ferroelectrics are complex oxides or solid solutions thereof, it is the partial pressure and chemical state of oxygen in the gas phase that play a crucial role in the vacuum deposition of films. The application of MOCVD to the synthesis of films can be stipulated, for instance, by the technology of capacitor manufacturing, where the multistage process of formation of ferroelectric layers and electrical electrodes above them is replaced by a single operation. Other chemical methods have their own advantages.

The authors of the present review aspired to survey the state-of-the-art advances in the field of preparation of FETF by chemical methods from various classes of organometallic precursors. Only selected types of films are concerned. Compounds manifesting piezoelectric properties, the potential of which has not been explored in sufficient detail so far, are left beyond the scope of this paper. These include complex oxides, such as $(Pb,Ba)_2Nb_5O_{15}$, $Bi_7Ti_4Nb_4O_{21}$, $ACu_3Ti_4O_{12}$ [$A = Bi^{3+}$ or Ln^{3+}(Y, La, Sm, Dy)], $MBi_4Ti_4O_{15}$ (M = Pb, Ca, Sr), $(Ba,Sr)Nb_2O_6$ and $Sr_2(Nb,Ta)_2O_7$.

II. Methods for thin film preparation

1. A MOCVD technology of film preparation

The technology of FETF preparation by chemical vapour deposition (CVD) has been reviewed in detail.[16] Film deposition from the vapour of organometallic compounds represents a particular case of this process based on the use of volatile organometallic compounds as the starting material. Presently, the major regularities relating the volatility of a compound to its composition and structure are realiably established, which facilitates the selection of a proper compound among the wide assortment of alkoxides, β-diketonates and mixed ligand–metal complexes. A precursor to be used in the synthesis of a complex oxide film by the chemical vapour deposition process should comply with several requirements: first, the metal should be in the form of its oxide that is deposited on a support; second, it is desirable that all the volatile starting compounds belong to the same class. This will exclude transesterification reactions in the gas phase and violations of the stoichiometry of the resultant films.

Considerable reduction of temperatures for film preparation can be achieved by either modifyng the entire technological process (which is not always possible) or substituting one class of volatile starting compounds for other classes. Metal alkoxides possess the lowest evaporation temperatures among all suitable starting compounds. Alkoxide ligands efficiently screen the central metal atom, which favours a significant increase in the volatility. Meanwhile, alkoxides of alkaline-earth metals are characterised by a rather low thermal stability, they are prone to polymerisation and are moisture-sensitive. In contrast, metal β-diketonates are evaporated and condensed from the gas phase at temperatures up to 300 °C. This temperature can be substantially lowered (to 100–150 °C) if mixed ligand–metal compexes or their adducts are employed. Among metal β-diketonates, compounds based on dipivaloylmethane (DPM) are used most often, these afford high-purity films. Only in two studies,[17,18] strontium hexafluoroacetylacetonate in combination with tetraglyme was used to yield films with fairly good ferroelectric properties.

The nature of the metal atom is of particular importance in the synthesis of ferroelectrics. As a rule, it is heavy metals, such as barium, lead or bismuth, that are used. As the chemistry of volatile compounds of alkaline-earth metals, zirconium and titanium is being developed, an increasing number of publications appear that describe new compounds with a broad set of interesting properties. The prevailing part of these studies is devoted to adducts of metal (primarily, zirconium or titanium) β-diketonate complexes with oxygen-containing organic ligands. The probability of the preparation of FETF with desirable properties is enhanced if the starting compound contains oxygen in an amount

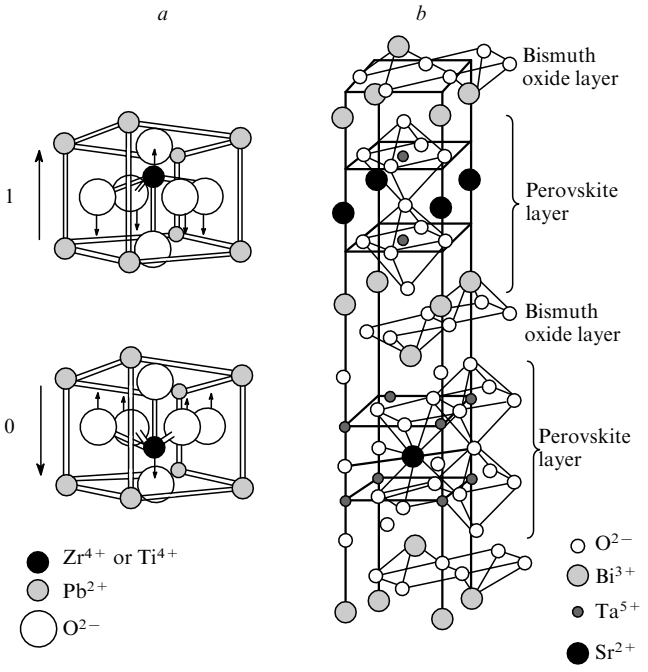


Figure 2. Unit cells of typical ferroelectric crystals.[12] (*a*) Cubic perovskite $Pb(Zr,Ti)O_3$; shifts of the Zr^{4+} or Ti^{4+} atoms upon polarisation are shown; vertical arrows to the left denote two states of the memory cell: the positive direction of polarisation is denoted as '1', the negative direction is denoted as '0'; (*b*) perovskite-like $SrBi_2Ta_2O_9$ composed of alternating layers of perovskite and bismuth oxide.

sufficient for the formation of the target film with the perovskite stoichiometry (Fig. 2).[12] For this purpose, additional oxygen-containing ligands are often introduced into the adducts.

MOCVD has proven to be the method of choice for the synthesis of FETF from precursors belonging to these classes.

2. The sol–gel method for the preparation of films from solutions

The technology of the synthesis of films from solutions by the sol–gel method includes preparation of a sol followed by its conversion into a gel. In the first step, a highly disperse colloidal solution, *i.e.*, a sol, with a composition corresponding to that of the target film is formed. An increase in the concentration of the dispersed phase results in the formation of additional bonds between molecules in the solution, which favours gelation. Further increase in the volume concentration and surface area of the dispersed phase gradually changes the plastic properties of the gel. In order to deposit the compound in the form of a thin film, the gel is placed onto a rapidly spinning support for a few seconds. If a compound does not form a gel, its solution is just deposited on the support, which is further subject to annealing: first, to remove the solvent, then to decompose the organometallic starting compound, and finally to crystallise the target phase. Therefore, the method of decompostion of an organometallic precursor deposited from a solution (Metal-Organic Deposition, or MOD) represents a particular case of the sol–gel method as applied to thin film preparation.

In this method, metal hydroxides, salts of organic and inorganic acids and alkoxides are used as the starting compounds. Among salts of inorganic acids, chlorides are used most often. In the cases of metal alkoxides and carboxylates, the originally formed sol that is further annealed is highly homogeneous. It is advisable that hydrolysis of metal alkoxides and carboxylates be performed in aqueous and ethanolic solutions, respectively.

In a recently proposed method for the preparation of ferroelectric nanostructures with a crystallite size of 10 nm (see

Ref. 19), porous silicon produced by anodic etching in a 15% solution of HF in aqueous ethanol is used as a support. The porosity of the near-surface layer as high as 66% is reached at an etching rate of 23 nm s^{-1}. Wafers of porous silicon are immersed into a solution of starting compounds which enters the pores of the matrix. The material acquires ferroelectric properties after annealing.

3. Hydrothermal process

In the hydrothermal method, a support, starting compounds and a solvent are placed into an autoclave. The solubility of the starting compounds increases on heating under high pressures and a thin film of a metal oxide is deposited onto the support upon cooling of the mixture. It was shown that the resultant films possess poor ferroelectric properties, which limits the usage of this method.

Like in the sol–gel method, metal hydroxides, alkoxides and salts of inorganic and organic acids are used as the starting compounds in the hydrothermal method.

4. The Langmuir–Blodgett process

The Langmuir–Blodgett process includes three steps:

— creation of a monolayer of film-forming molecules on a water surface and formation of a compact floating film. The molecules within the film have a polar (or hydrophilic) group bound to a long hydrocarbon chain that is long enough to provide insolubility of the whole molecule in water (as in the case of, *e.g.*, stearic acid or octadecylaminomethyldehydrocarbotine, n-$C_{18}H_{37}NHCH_2C_{26}S_2H_{11}$);[20]

— formation of a layer of starting compounds (most often, salts of inorganic acids are used) on top of the monolayer film;

— transfer of the layer onto a support upon withdrawal of the latter from the solution.

The required thickness of the target film can be achieved by drying the film and repeating the procedure several times.

A distinctive feature of this method is the possibility to produce continuous films at extremely small thicknesses (tens of Å).

III. Ferroelectric thin films for non-volatile memory elements

1. Tantalum pentaoxide films

Films of tantalum pentaoxide in the pure form are not used in non-volatile memory elements. A serious drawback of such films as compared to standard SiO_2 films is larger leakage current. To correct for this, silicon supports are covered with a layer of silicon dioxide or silicon oxynitride prior to the deposition of a Ta_2O_5 layer. The films can be produced using both sol–gel technology and the MOCVD method.[21,22] Metal alkoxides are used as the starting compounds in both cases (Table 1). The sol–gel technology is based on hydrolysis that is sometimes performed in the presence of an acidic catalyst, *e.g.*, HCl.[30] The sol is prepared at room temperature from a mixture of $Ta(OEt)_5$ and aqueous-ethanolic HCl. Titanium ethoxide $Ti(OEt)_4$ can be used as a dopant precursor in order to dope ferroelectric films of tantalum pentaoxide with titanium. The doping level is varied over the range from 8 mol.% to 46 mol.% with respect to TiO_2.[30] Following deposition, the film is annealed at 600–900 °C in an atmosphere of N_2O, which acts as an oxidant.

Typical conditions for the CVD deposition of Ta_2O_5 films from organometallic precursors have been reported by Murawala *et al.*[23] by the example of tantalum pentaethoxide: the support temperature was 475 °C, the temperature of $Ta(OEt)_5$ deposition was 160–190 °C, N_2 and O_2 were used as a gas carrier and an oxidant, respectively, the rate of deposition was 6.4 nm min^{-1}. Rapid annealing at 700–900 °C afforded films with a specific electrical resistivity of 10^{14}–10^{15} Ω cm, a leakage current $< 10^{-8}$ A cm^{-2} at a voltage of 1.2 V and a break-down voltage not exceeding 5 MV cm^{-1}. These conditions allow preparation of films suitable for the manufacture of memory elements with a capacity of 256 MB.[16,23,24]

2. Films of yttrium–manganese double oxide ($YMnO_3$)

Films of $YMnO_3$ can be synthesised both by the sol–gel and the CVD methods. In the former method, yttrium and manganese acetates were suggested as the most useful precursors.[37–44] Yttrium isopropoxide is also sometimes utilised. Ethanolic sol-

Table 1. Conditions of synthesis of ferroelectric thin films of Ta_2O_5 and their properties.

Starting compounds	Preparation method	Support	Process conditions			Properties of FETF [a]			Ref.
			T_v /°C	T_p /°C	P /Torr	ε	I /A cm^{-2}	n	
$Ta(OEt)_5$, O_2	CVD	Si, Ta_xSi_yO	–	260, 700	–	38	–	–	22
$Ta(OEt)_5$, O_2	CVD	n,p-Si	160–190	475, 700, 900	–	25–38	–	–	23
$Ta(OEt)_5$, O_2	CVD	p-Si(100)	–	500, 700	–	–	10^{-10}	–	24
$Ta(OEt)_5$, N_2, O_2, O_3	CVD	Si, TiN	–	400, 800	–	22–24	–	–	25
$Ta(OEt)_5$, O_2	CVD	Pt/Ti/Si	140–170	400	0.4	22–25	2×10^{-8}	–	26
$Ta(OEt)_5$, AcOH, EtOH	sol–gel	quartz, glass	–	150–450	–	–	–	1.78–1.97	27
$Ta(OEt)_5$, O_2	CVD	Si	–	–	–	25 [b] 56–59 [c]	–	–	28
$Ta(OEt)_5$, O_2	CVD	Ru/Si	–	400–700	–	–	10^{-8}	–	29
$Ta(OEt)_5$, HCl + H_2O, $Ti(OEt)_4$ (see [d]), EtOH	sol–gel	n-Si	–	600–900	–	25, 90	–	–	30
$Ta(OEt)(OPr^i)_4$, ÇHF, $Ti(OPr^i)_2(DPM)_2$ (see [d])	CVD	Si	130–240, 130–168	390, 800	1	30.2	10^{-8}	–	31
$Ta(OBu^n)_5$, $Ti(OBu^n)_4$, CCl_4, 2-Pr^iOH	sol–gel	Si/SiO_2, Au	–	400	–	–	–	–	32
$Ta(OEt)_5$, O_2, O_3	CVD	Si_3N_4/Si	–	300, 900	–	–	–	–	33
$Ta(OEt)_5$, Ar, O_2	CVD	Si_3N_4/Si	–	350, 600–800	$(2-5) \times 10^{-3}$	–	–	–	34
$Ta(OEt)_5$, O_2, N_2O	CVD	Si	–	400, 800	–	–	–	–	35
$Ta(OEt)_5$, N_2, O_2	CVD	Pt/Si	140	400, 550	3	38	8×10^{-9}–10^{-6}	–	36

[a] ε is permittivity, I is the leakage current density, n is the refraction index. [b] Amorphous state. [c] Crystal. [d] Dopants.

utions of diethanolamine and 2-ethoxyethanol are typically used as solvents. The increase in the coordination number of yttrium upon introduction of an additional ligand (*i.e.*, diethanolamine) into the coordination sphere of the metal atom increases the solubility of the starting compounds in organic solvents. The preparation of the films from polymerised salts of organic acids is accompanied by intense gas evolution during thermolysis. With this regard, the temperature is typically raised stepwise, first to 300 – 400 °C, and then higher.[40,42] Platinum is normally used as the material of the top layer of the supports.

In the case of the CVD synthesis of $YMnO_3$, DPM-based organometallic compounds are used as the starting compounds. The temperature modes of the process are nearly the same.

Parameters of the methods for the preparation of thin films of $YMnO_3$ and the physical properties of the resultant films are summarised in Table 2.

3. Films of barium and strontium titanates ($BaTiO_3$, $SrTiO_3$) and of their solid solutions

Different starting compounds are used for the synthesis of ferroelectric films of $BaTiO_3$, $SrTiO_3$ and of their solid solutions, depending on the method selected. Metal hydroxides and salts of various inorganic acids, *e.g.*, chlorides,[57] are employed in solution methods (Table 3). This approach excludes side chemical reactions yielding products with uncontrolled compositions during the synthesis of FETF. However, combination of different technologies for the preparation of oxide films with desired properties implies simultaneous use of several classes of compounds in a single process. Zeng *et al.*[64] proposed a new method based on titanium alkoxides and barium carboxylates which combines the sol – gel and hydrothermal methods. The gel employed for the preparation of a $BaTiO_3$ film was then subjected to hydrothermal treatment. A solution was applied onto a support followed by

Table 2. Conditions of synthesis and properties of ferroelectric thin films of $YMnO_3$.

Starting compounds	Method	Solvent, oxidant	Support	T /°C	P /Torr	Properties of FETF					Ref.
						ε	$\tan\delta$	P_r	E_c	I	
$Y(OAc)_3 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$	sol – gel	diethanolamine, 2-ethoxyethanol	$Pt/Ti/SiO_2/Si$	125, 400, 700, 900	–	–	–	–	–	–	37
$Y(OAc)_3 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$	"	diethanolamine, 2-ethoxyethanol, EtOH	$Pt/Ti/SiO_2/Si$	125, 400, 700, 900	–	20	0.05	–	–	–	38
$Y(OAc)_3 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$	"	MeOH	Pt/Si	400, 450 – 800	–	23(am), 30(cr)	–	0.5, 6(cr)	50, 20(cr)	–	39
$Y(OAc)_3 \cdot 3H_2O$, $Mn(OAc)_2 \cdot 3H_2O$	"	diethanolamine, 2-ethoxyethanol	Pt/sapphire, Y_2O_3/Si	125, 150, 300, 800	–	–	–	–	–	–	40
$Y(C_{10}H_{19}CO_2)_3$, $Mn(MeCp)(CO)_3$	CVD	–	p-Si(111)	165, 450, 600	–	30	–	–	–	–	41
$Y(OAc)_3 \cdot 3H_2O$, $Mn(OAc)_2 \cdot 3H_2O$	sol – gel	diethanolamine, 2-ethoxyethanol	Si	125, 150, 300, 700	–	–	–	–	–	10^{-7} – 10^{-6}	42
$Y(OAc)_3 \cdot 4H_2O$, $Mn(OAc)_2 \cdot 4H_2O$	"	the same	Pt/sapphire	125, 400, 800 – 900	–	–	–	–	–	10^{-6} – 10^{-2}	43
$Y(C_{10}H_{19}CO_2)_3$, $Mn(MeCp)(CO)_3$	CVD	EtOH, O_2	$Y_2O_3/Si(100)$	162, 500, 750, 850	3	–	–	–	–	10^{-7} – 10^{-3}	44

Note. Hereinafter, $\tan\delta$ is the dielectric loss tangent, P_r is the residual polarisation (μC cm^{-2}), E_c is the coercive force (kV cm^{-1}), I is the leakage current density (A cm^{-2}); the following notations are adopted: am is an amorphous layer, cr is a crystalline layer.

Table 3. Conditions of synthesis of ferroelectric thin films of $BaTiO_3$, $SrTiO_3$ and $(Ba,Sr)TiO_3$ from metal hydroxides or salts of inorganic acids and their properties.

Starting compounds	Method	Solvent	Support	T /°C	Properties of FETF					Ref.
					ε	$\tan\delta$	P_r	E_c	I	
$Ba(OH)_2 \cdot 8H_2O$, $Ti(OPr^i)_4$	sol – gel	methanol	–	600	–	–	–	–	–	45
$Ba(OH)_2$, Ti	hydrothermal	water	Ti/TiC/Si	100 – 200	450 – 500	0.04 – 0.1	–	–	–	46
$SrCO_3$, $Ti(OPr^i)_4$	MOD	water, citric acid, ethylene glycol [a]	Si(111)	150, 250 – 455, 550 – 1000	–	–	–	–	–	47
$Ba_2Ti_2O_5CO_3$, $Sr_2Ti_2O_5CO_3$	MOD	acetylacetone	–	–	–	–	–	–	–	48
$Ba(OH)_2 \cdot 8H_2O$, $Ba(AcO)_2$, $Ti(OEt)_4$	hydrothermal	water, ethanol, NH_4OH	–	150	–	–	–	–	–	49

Table 3 (continued).

Starting compounds	Method	Solvent	Support	T /°C	Properties of FETF					Ref.
					ε	$\tan\delta$	P_r	E_c	I	
$BaCl_2 \cdot 2H_2O$, NaOH, Ti	hydrothermal	water	Ti	240	400 – 500	–	–	–	–	50
$Ba(OH)_2 \cdot 8H_2O$, Ti	"	"	–	110 – 200	200	–	–	–	–	51
$SrCO_3$, $Ti(OPr^i)_4$	sol – gel	water, citric acid, ethylene glycol [a]	Pt/Ti/SiO_2/Si	600	250	0.01	–	100	10^{-7}	52, 53
$Ba(OH)_2 \cdot 8H_2O$, $Sr(OH)_2 \cdot 8H_2O$, $Ti(OBu^n)_4$	–	water, acetic acid, butanol, ethylene glycol [a]	Pt/Si(100), 60/40	350, 600 – 800	492	–	7.2	102.7	–	54
$Ba(OH)_2$, $Sr(OH)_2$, $TiCl_4$	–	water, NaOH	Pt/Si(100) 90/10	950	–	–	–	–	–	55
$Ba(OH)_2 \cdot 8H_2O$, $Sr(OH)_2 \cdot 8H_2O$, $Ti(OPr^i)_4$	–	methanol	Pt/Ti/SiO_2/Si, 70/30	150, 650, 1275	600 – 800	0.04 – 0.07	–	–	–	56
$BaCl_2 \cdot 2H_2O$, $SrCl_2 \cdot 2H_2O$, $TiCl_4$	–	oxalic acid [b]	–	40 – 45	–	–	–	–	–	57
$BaCO_3$, $SrCO_3$, $Ti(OPr^i)_4$	sol – gel	citric acid [b]	Pt/Ti/SiO_2/Si	700	–	–	–	–	–	58
$Ba(OH)_2$, $Sr(OH)_2$, TiO_2	hydrothermal	water	Ti, Si/Ti, Si/Pt/Ti, TiO_2	100, 150, 200	–	–	–	–	–	59
$Ba(OH)_2$	"	"	titanium foil	100, 150, 215	–	–	–	–	–	60
$Ba(OH)_2$	"	"	TiO_2	150, 200	–	–	–	–	–	61
$Ba(OH)_2 \cdot 8H_2O$	"	"	TiO_2, $SrTiO_3$, $LaAlO_3$	90, 150	–	–	–	–	–	62
$BaCO_3$, $SrCO_3$, $Ti(OPr^i)_4$	sol – gel	water, citric acid, ethylene glycol [b]	Pt/Ti/SiO_2/Si	150, 600, 800	–	–	–	–	–	63

[a] It is used to initiate polycondensation. [b] Here and in other tables, saturated aqueous solution of acids.

annealing for 30 min at 150 °C, then the support with a film was placed in a teflon container, an aqueous solution of barium hydroxide was added and the container was loaded into an autoclave. Hydrothermal treatment lasted for 1 – 6 h at 100 – 200 °C. Crystalline films with a good surface morphology have been prepared by this procedure at such low temperatures.[64]

McKinley and Sandler [25] prepared thin films of nanocrystalline barium titanate on silicon supports from solutions of barium and titanium alkoxides using the sol – gel method. Hydrolysis was effected by water, whereas the polymerisation was carried out in a monoglyme solution. The process of gel formation proceeded very slowly at 20 – 22 °C. After deposition of the film onto the support, its polarisation curve was obtained and the stability of its dielectric properties over a temperature range from −85 to +200 °C was established.

McCormick and Slamovich [65] used titanium ethoxide for the preparation of barium titanate films. A mixture of titanium ethoxide, barium acetate and tetramethylammonium hydroxide in an alkaline medium (pH > 13) was heated in an autoclave to 150 °C at a rate of 3 °C min^{-1}, at which temperature the hydrothermal synthesis lasted for 2 h. However, in addition to the films, an appreciable amount of powder was formed, which negatively affected the properties of the films.

Films with good dielectric properties were obtained [47, 52, 53, 58] by dissolving $SrCO_3$ and $Ti(OPr^i)_4$ in a mixture of citric acid and ethylene glycol (see Table 3) and annealing at 550 – 1000 °C following the solution deposition onto a support.

Thin films of $BaTiO_3$, $SrTiO_3$ and (Ba,Sr)TiO_3 were also prepared from the respective metal carboxylates (Tables 4 and 5). They were grown on titanium supports using barium acetate solutions. Films with grain sizes of ~50 – 340 nm were obtained in the temperature range 120 – 200 °C and a solution flow rate of 1 – 50 cm^3 min^{-1}. The design of the reactor made it possible to supply the solution in a cyclic manner, which facilitated control over the process.[45] Films of $BaTiO_3$ with high permittivities were prepared from organometallic precursors by spin-coating with subsequent annealing. Xu *et al.*[66] employed titanium alkoxide-carboxylate $(MeO)_2Ti(n\text{-}C_9H_{19}CO_2)_2$ and barium carboxylate $Ba(n\text{-}C_9H_{19}CO_2)_2$ and xylene as a solvent. First, a layer with a thickness of 350 nm was deposited onto a silicon support that was spinning with a velocity of 1500 rpm and the coated support was then annealed at 500 – 800 °C for 1 h. The thickness of the film was increased to 4 – 8 μm by repeating the procedure. The resultant films with grain sizes of 0.034, 0.1 and 0.2 μm manifested permittivities of 200, 500 and 1200, respectively. The spontaneous polarisation of the films with grain size of 0.2 μm was 3 μC cm^{-2} and $\tan\delta = 0.1$ (at 1 MHz).

An interesting new modification of the sol – gel – hydrothermal technique for the preparation of thin films of $BaTiO_3$ on silicon supports developed by Zeng *et al.*[64] has already been mentioned above. The gel used for the preparation of the film served as a precursor that was subjected to hydrothermal treatment, $Ba(AcO)_2$ and $Ti(OBu^n)_4$ being the starting compounds (see Table 4).

Table 4. Conditions of synthesis of ferroelectric thin films of $BaTiO_3$, $SrTiO_3$ and $(Ba,Sr)TiO_3$ from salts of carboxylic acids and their properties.

Starting compounds	Method	Solvent	Support	T /°C	Properties of FETF					Ref.
					ε	$\tan\delta$	P_r	E_c	I	
$Ba(n\text{-}C_9H_{19}CO_2)_2$, $Ti(n\text{-}C_9H_{19}CO_2)_2(MeO)_2$	sol–gel	xylene	–	500–800	200–1200	–	–	–	–	66
$Sr(AåO)_2$, $Ti(OBu^n)_4$	MOD	acetic acid, propanol, acetylacetone	$Pt/Ti/SiO_2/Si$	750–800	–	–	–	–	–	67
$Ba(AcO)_2$, $Ti(AcO)_4$	MOD	–	t/Si, SiO_2	550–700	255	0.025	2.2	25	–	68
$Ba(AcO)_2$, $Ti(OPr^i)_4$	sol–gel	acetic acid, 2-methoxyethanol	$Pt/Ti/SiO_2/Si$	350, 700	370	–	3.2	30	–	69
$Ba(AcO)_2$, $Ti(AcO)_4$	hydro-thermal	water	Ti	120–200	–	–	–	–	–	70
$Ba(OH)_2\cdot 8H_2O$, $Ba(AcO)_2$, $Ti(OEt)_4$	"	water, ethanol, NH_4OH	–	150	–	–	–	–	–	49
$Ba(AcO)_2$, $Ti(OBu^n)_4$	"	water	–	100–200	–	–	–	–	–	64
Ba, Ti naphthenates	MOD	toluene	$SrTiO_3$	470, 850	230	–	–	–	–	71
$Ba(n\text{-}C_7H_{15}CO_2)_2$, $Ti(OPr^i)_4$		ethanol, acetylacetone	Si	400	16–17	0.015	–	–	–	72
$Sr(AcO)_2$, $Ti(OBu^n)_4$	MOD	acetylacetone, acetic acid, 2-methoxyethanol	$LaNiO_3$/ $(La,Sr)CoO_3$, $(La,Sr)MnO_3$/ Pt/Si	350, 750	–	–	–	–	–	73
$Sr(AcO)_2$, $Ti(OEt)_4$	sol–gel	acetic acid, 2-methoxyethanol	$Au/BaTiO_3$/ InP	–	–	–	–	–	–	74
Ba, Ti naphthenates	MOD	toluene	$LaAlO_3$	470, 950	–	–	–	–	–	75
$Ba(n\text{-}C_7H_{15}CO_2)_2$, $Ti(DPM)_2(OMe)_2$	CVD	–	–	–	–	–	–	–	–	76
$Ba(n\text{-}C_7H_{15}CO_2)_2$, $Ti(OPr^i)_4$	CVD	–	p-Si(100)	500, 550	250	0.1	–	–	10^{-5}	77
$Ba(AcO)_2$, $Sr(AcO)_2\cdot 0.5H_2O$, $Ti(OBu^n)_4$	sol–gel	acetic acid, methanol	$Pt/Ti/SiO_2/Si$	250, 390–450, 600, 730	–	–	–	–	–	78
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OBu^n)_4$	"	acetic acid, 2-methoxyethanol	$LaAlO_3$	750, 1100	–	–	–	–	–	79
$Ba(n\text{-}C_7H_{15}CO_2)_2$, $Sr(n\text{-}C_7H_{15}CO_2)_2$, $Ti(OPr^i)_4$	"	ethanol, acetylacetone	$Pt/SiO_2/Si$	150, 350, 450–700	592	0.028	–	–	–	80
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OBu^n)_4$	"	acetylacetone	$Pt/Ti/SiO_2/Si$	750	–	–	–	–	–	81
$Ba(AcO)_2$, $Ti(OAlk)_4$	"	acetic acid, propan-2-ol, ethanol	Pt	600, 800, 1000	167–500	0.015–0.06	3.2	14	–	82

Cole *et al.*[87] reported the following physical characteristics of the films prepared in this way: $\varepsilon = 205–450$, $\tan\delta = 0.09–0.013$, $I = 2\times10^{-11}–10^{-10}$ A cm^{-2} (see Table 5).

Thin films of $BaTiO_3$ and $SrTiO_3$ can also be prepared from the gas phase.[93,94] In this case, volatile metal β-diketonates or adducts based on them are used as starting compounds. This approach is also applicable for solid solutions $(Ba,Sr)TiO_3$. The starting compounds are evaporated and condensed onto a support at temperatures up to 300 °C. For the $(Ba,Sr)TiO_3$ films, the deposition temperature was significantly (by almost 100–150 °C) reduced, which did not deteriorate the properties of the resultant films (Table 6). The best results were achieved by Fitsilis *et al.*[114]

4. Films of lead titanate ($PbTiO_3$)

Films of $PbTiO_3$ with good ferroelectric properties were synthesised by solution methods from lead and titanium naphthenates (Table 7). The films grown on a $TiSi_2$ support possessed high electroconductivity, which made possible their use as bottom plate electrodes in capacitors.[121]

Preparation of $PbTiO_3$ from lead carboxylates using diols $HOC_nH_{2n}OH$ ($n = 3–5$), *i.e.*, propane-1,3-diol, butane-1,4-diol and pentane-1,5-diol, as solvents was reported by Pardo *et al.*[123] Exothermic effects at temperature ranges of 255–261 °C, 311–326 °C, 449–467 °C and 500–525 °C were detected by complex thermal analysis. These effects are due to oxidative

Table 5. Parameters of the solution synthesis and properties of ferroelectric thin films of (Ba,Sr)TiO_3.

Starting compounds	Solvent	Support	T /°C	Properties of FETF					Ref.
				ε	$\tan\delta$	P_r	E_c	I	
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OPr^i)_4$	ethanol, water, acetic acid, pentane-2,4-dione	Ba/Sr	–	198 – 224	0.04	–	–	–	83
$Ba(n\text{-}C_7H_{15}CO_2)_2$, $Sr(n\text{-}C_7H_{15}CO_2)_2$, $Ti(OPr^i)_4$ $Zr(OPr^i)_4$	xylene	Pt/Ti/SiO_2/Si	750	1000			300	3.47×10^{-7}	84
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OBu^n)_4$	acetic acid, 2-methoxyethanol	Pt/Si, 70/30	300, 750	100 – 280, 563	0.02 – 0.04	–	–	–	85
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OBu^n)_4$	acetic acid, acetylacetone	Pt/Ti/SiO_2/Si	350, 750	–	–	3.5	86	–	86
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OPr^i)_4$	–	Pt	350, 750	205 – 450	0.09 – 0.013	–	–	2×10^{-11} – 10^{-10}	87
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OBu^n)_4$	2-methoxyethanol, acetylacetone	Pt/Ti/SiO_2/Si	400, 750	–	–	–	–	–	88
$BaCl_2\cdot2H_2O$, $SrCl_2\cdot2H_2O$, $TiCl_4$	water	–	40 – 45	–	–	–	–	–	57
$Ba(AcO)_2$, $Sr(AcO)_2$, $Ti(OPr^i)_4$	ethylene glycol	Pt/TiO_2/SiO_2/Si	400, 550 – 750	–	–	–	–	–	89
$Ba(n\text{-}C_7H_{15}CO_2)_2$, $Sr(n\text{-}C_7H_{15}CO_2)_2$, $Ti(n\text{-}C_7H_{15}CO_2)_2$	2-ethylhexanoic acid, 2-methoxy-ethanol, xylene	Pt/TiO_2/SiO_2/Si	700	–	–	–	–	–	90
$Ba(n\text{-}C_7H_{15}CO_2)_2$, $Sr(n\text{-}C_7H_{15}CO_2)_2$, $Ti(OBu^n)_2(acac)_2$	2-ethylhexanoic acid	Pt/Si	250 – 800	–	–	–	–	–	91
$Ba(AcO)_2$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	acetic acid, ethylene glycol	$LaAlO_3$	600, 1000	–	–	–	–	–	92

Table 6. Conditions of MOCVD synthesis of ferroelectric thin films of (Ba,Sr)TiO_3 solid solutions from metal β-diketonates with various ligands and their properties.

Starting compounds	Support	Process conditions			Properties of FETF			Ref.
		T_v /°C	T_p /°C	P /Torr	ε	$\tan\delta$	I	
$Ba(DPM)_2$, $Sr(DPM)_2$, $TiO(DPM)_2$, THF	Pt/SiO_2/Si	250	480	10	230	0.013	6.7×10^{-6}	95
$Ba(DPM)_2$, $Sr(DPM)_2$, $TiO(DPM)_2$, THF	RuO_2/Si, Pt/SiO_2/Si	250	420	1.5	190	0.018	4.6×10^{-8}	96
$Ba(DPM)_2$, $Sr(DPM)_2$, $Ti(OPr^i)_4$	Pt/Ti/SiO_2/Si	186 – 204, 174 – 188, 36	450, 500	7	–	–	4.6×10^{-7}	97
$Ba(DPM)_2$, $Sr(DPM)_2$, $TiO(DPM)_2$, THF	Ru/Si, Ru/TiN/Ti/Si	250	420	1.5	–	–	–	98
$Ba(DPM)_2\cdot(C_8H_{12}N_5)_2$, $Sr(DPM)_2\cdot(C_6H_{18}N_4)_2$, $Ti(OPr^i)_4$	$SrTiO_3$, MgO	–	750 – 800	–	–	–	–	99
$Ba(DPM)_2\cdot TG$, $Sr(DPM)_2\cdot TG$, $Ti(DPM)_2(OPr^i)_2$, Bu^nOAc	Pt/SiO_2/Si	–	420 – 570	–	–	–	–	100
$Ba(DPM)_2\cdot(phen)_2$, $Sr(DPM)_2\cdot(phen)_2$, $Ti(OPr^i)_4$	Pt/MgO	215 – 220, 200 – 205, 35	650	–	400 – 590	–	10^{-8} – 10^{-7}	101
$Ba(DPM)_2$, $Sr(DPM)_2$, $TiO(DPM)_2$	–	–	420	1.5	200	–	2×10^{-7}	102

Table 6 (continued).

Starting compounds	Support	Process conditions			Properties of FETF			Ref.
		T_v /°C	T_p /°C	P /Torr	ε	tan δ	I	
$Ba(DPM)_2$, $Sr(DPM)_2$, $Ti(DPM)_2(OPr^i)_2$	Pt/Si	215–250, 215–230, 130–200	400–500	200	–	–	–	103
$Ba(HFA)_2 \cdot TG$, $Sr(HFA)_2 \cdot TG$, $Ti(OPr^i)_4$	–	–	650–800	–	–	–	–	104
$Ba(DPM)_2$, $Sr(DPM)_2$, $Ti(DPM)_2(OPr^i)_2$	–	–	480–580	–	260–290	–	–	105, 106
$Ba(DPM)_2 \cdot TG$, $Sr(DPM)_2 \cdot TG$, $Ti(OPr^i)_4$	$Pt/RuO_2/Ta/Si/SiO_2/Si$	190, 190, 20	550	2	240	0.01	4.0×10^{-7}	107
$Ba(DPM)_2 \cdot (phen)_2$, $Sr(DPM)_2 \cdot (phen)_2$, $Ti(OPr^i)_4$	Pt/MgO	210–220, 195–205, 35	650	130–670	1000	–	2.3×10^{-9}	108
$Ba(DPM)_2 \cdot COT$, $Sr(DPM)_2 \cdot COT$, $Ti(OPr^i)_4$	$SrTiO_3$	115, 138, 20	620	1.3–1.4	400	0.02	–	109
$Ba(DPM)_2$, $Sr(DPM)_2$, $Ti(OPr^i)_4$	RuO_2/Ru	175–205 175–205, 20–36	550	–	80–170	–	–	110
$Ba(DPM)_2 \cdot (TEP)_2$, $Sr(DPM)_2 \cdot (TEP)_2$, $Ti(OPr^i)_4$	Pt/MgO	135, 105–110, 40	650	1.33	600–1200	–	–	111
$Ba(DPM)_2$, $Sr(DPM)_2$, $Ti(DPM)_2(OBu^t)_2$, THF	–	–	250–650	–	–	–	–	112
$Ba(DPM)_2 \cdot TG$, $Sr(HFA)_2 \cdot TG$, $Ti(DPM)_2(OPr^i)_2$	–	–	440	1.3	–	–	–	113
$Ba(DPM)_2$, $Sr(DPM)_2$, $Ti(DPM)_2(OPr^i)_2$	Pt/Si	–	565–655	–	185–208	0.002	10^{-10}	114
$Ba(DPM)_2$, $Sr(DPM)_2$, $Ti(DPM)_2(OBu^t)_2$, THF	–	–	250–640	10	–	–	–	115
$Ba(DPM)_2 \cdot PA$, $Sr(DPM)_2 \cdot PA$, $Ti(DPM)_2(OPr^i)_2$	–	250 250	600	1.4	260	0.003	–	116
$Ba[(R^1R^2)C(OX)COHCOR^3]_2$ (see [a]), $Ti(DPM)_2(OPr^i)_2$, $Sr(DPM)_2$, $TiO(DPM)_2$, $Sr(DPM)_2$	SiO_2	100, 250, 160, 250	127, 550, 650	–	–	–	–	117
$Ba(DPM)_2 \cdot (PMDT)$, $Sr(DPM)_2 \cdot (PMDT)$, $Ti(DPM)_2(OPr^i)_2$	$Ru/SiO_2/Si$	–	700	2	–	0.006	2×10^{-8}	118

Note. The following notations are adopted: COT is cyclooctatetraene, TEP is tetraethylenepentamine, HFA is hexafluoroacetylacetone, TG is tetraglyme, PA is a polyamine, PMDT is pentamethyldiethylenetriamine.
[a] X = OMe, R^1 = Me, R^2 = Me, Bu^i, Bu^t, n-C_6H_{13}, R^3 = Pr^i, Bu^t, hexan-2-yl; $R^1 = R^2 = -(CH_2)_5-$, R^3 = Ph; X = H, R^1 = Pr^i, R^2 = H, R^3 = Bu^t; $R^1 = R^2$ = Me, R^3 = Ph; $R^1 = R^2$ = H, R^3 = Ph; R^1 = Bu^t, R^2 = H, R^3 = Bu^t.

Table 7. Conditions of synthesis of ferroelectric thin films of $PbTiO_3$ from metal carboxylates and their properties.

Starting compounds	Method	Solvent	Support	T /°C	Properties of FETF				Ref.
					ε	tan δ	P_r	E_c	
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_4$	sol–gel	2-methoxyethanol	$Pt/SiO_2/Si$, Al_2O_3, MgO	750–800	250–300	–	–	–	119
$Pb(AcO)_2 \cdot 3H_2O$ $Ti(OPr^i)_4$	the same	2-methoxyethanol	SiO_2, $SrTiO_3$	125, 330, 550	–	–	3.5	50	120
Pb,Ti naphthenates	"	naphthenic acid	$TiSi_2/Si$	–	–	–	16.0	52.9	121

Table 7 (continued).

Starting compounds	Method	Solvent	Support	T /°C	Properties of FETF				Ref.
					ε	$\tan\delta$	P_r	E_c	
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_4$	sol–gel	propan-2-ol, diethanolamine	$In_2O_3/Sn/SiO_2$	110, 600–700	–	–	–	–	122
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_2(acac)_2$	the same	propane-1,3-diol	Si(100)	350–600	–	–	–	–	123
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_4$, $Al(OPr^n)_3$	"	2-methoxyethanol	Si	520, 550–700	356	–	9	84	124
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_4$	"	2-methoxyethanol, acetylacetone	Pt/MgO, Si(100)	360, 575	–	–	–	–	125
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_2(acac)_2$	"	propane-1,3-diol	$TiO_2/SiO_2/Si$, Pt/Si	350, 650	–	–	–	–	126, 127
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OBu)_4$	"	2-methoxyethanol	Pt/Ti/Si	70, 120, 300, 600	–	–	–	–	128
$PbCl_2$, n-$C_{17}H_{35}CO_2H$, $Ti(OH)_2(AmL)_2$	Langmuir–Blodgett	stearic acid, chloroform	–	–	–	–	–	–	129
$PbCl_2$, n-$C_{17}H_{35}CO_2H$, $K_2TiO(C_2O_4)_2$	the same	stearic acid, chloroform, NH_4OH	–	500, 700	–	–	–	–	130
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OBu)_4$	MOD	2-methoxyethanol	$Pt/TiO_2/Si$	350, 600	–	–	–	–	131
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_4$	sol–gel	acetic acid	$Pt/TiO_x/SiO_2/Si$	110, 450, 650	109	–	–	–	132
$Pb(AcO)_2\cdot 3H_2O$, PbO	the same	2-methoxyethanol	–	550, 600	–	–	–	–	133
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_4$	"	2-methoxyethanol, ethylene glycol	–	600	90–120	–	–	–	134
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_4$	"	citric acid, ethylene glycol	$Pt/Ti/SiO_2/Si$	60–70, 150, 350, 500	570	–	13.62	121.43	135
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OPr^i)_4$	"	the same	$Pt/Ti/SiO_2/Si$	80–90, 150, 400, 700	457	0.03	17	75	136
$Pb(AcO)_2\cdot 3H_2O$, $Ti(OBu)_4$, $Ba(AcO)_2$	"	acetic acid, 2-methoxyethanol	Pt/Si, quartz	300, 650	118	–	12	65	137

Note. The following notations are adopted: AmL is $MeCH(O)CO_2NH_4$, EDTA is ethylenediaminetetraacetate.

processes and thermodestruction of the starting compounds. The films prepared from solutions in the diol with $n = 3$ revealed a homogeneous microstructure, whereas those prepared from solutions in higher diols ($n = 4$ and 5) were heterogeneous. With a decrease in the thickness of the $PbTiO_3$ films, their ferroelectric properties degraded. This was related to the oxygen vacancies that diffuse from the film surface along the grain boundaries into the bulk. In order to compensate for this process, Iijma and Sanada [124] replaced part of titanium ions in $PbTiO_3$ by aluminium. Films with the composition $Pb(Ti_{0.85}Al_{0.15})O_{3-x}$ and a thickness of 0.14 μm were prepared in air by the sol–gel method (the annealing temperature was ~700 °C) from solutions of lead acetate trihydrate, titanium tetraisopropoxide and aluminium triisopropoxide in 2-methoxyethanol. The ferroelectric properties of the resultant films as a function of the annealing temperature were investigated.

Low temperature of the hydrothermal method for the synthesis of $PbTiO_3$ films makes it attractive.[138–140] However, no high-quality films suitable for use in devices with non-volatile memory elements have been produced so far by this method. Sugai *et al.*[129, 130] have attempted to prepare ferroelectric ultrathin layers of $PbTiO_3$ by the Langmuir–Blodgett method (see Table 7) using lead dichloride and titanium bis(ammonium lactate) or potassium titanium oxalate as starting compounds and a solution of stearic acid in chloroform as a solvent. Monolayer films were prepared, which were irradiated with UV light and then annealed. As a result, a dense film with a thickness of 0.2 nm was obtained. Ferroelectric films with thicknesses of 30–50 nm possessing a perovskite-like structure dominantly exposing (111), (101) or (110) crystal faces were produced by repeating this procedure 250–300 times.

5. Films of solid solutions $Pb(Zr,Ti)O_3$ and $Pb(Sr,Ti)O_3$

Lead carboxylates are most commonly used as starting compounds in the preparation of FETF based on solid solutions $Pb(Zr,Ti)O_3$ and $Pb(Sr,Ti)O_3$ (also referred to as PZT and PST, respectively) by solution methods (Table 8). Lead carboxylates are well soluble in organic solvents, such as propan-2-ol or 2-methoxyethanol. Zirconium, titanium and strontium alkoxides are also soluble in these solvents, which favours the formation of high-quality films with uniform thicknesses. It should be taken into account that it is preferable to use starting compounds belonging to the same class, but this is not always possible (see Table 8).

More complex processes (as regards both the synthetic method and the starting compounds used) are also applied to prepare FETF of PZT solid solutions (Table 9). This may be exemplified by syntheses from metal alkoxides and chelate complexes as well as the hydrothermal synthesis envisaging two consecutive steps, *viz*., generation of growth nuclei and film

Table 8 Conditions of synthesis of ferroelectric thin films of $Pb(Zr,Ti)O_3$ and $Pb(Sr,Ti)O_3$ and their properties.

Starting compounds	Method	Solvents	Composition Zr/Ti	Support	T /°C	Properties of FETF				Ref.
						ε	$\tan\delta$	P_r	E_c	
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	sol – gel	acetic acid, ethylene glycol, water	40/60 60/40	Al	600	260	–	6.6	26.7	141
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OBu)_4$, $Ti(OPr^i)_4$	"	2-methoxyethanol, diethanolamine	50/50	$Pt/Ti/SiO_2/Si$, Ir	480, 650	730	–	20.7	–	142, 143, 144
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OBu)_4$, $Ti(OPr^i)_4$	"	2-methoxyethanol	52/48	$Pt/Ti/SiO_2/Si$	600	–	–	–	–	145
$Pb(AcO)_2$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	"	"	40/60, 52/48, 70/30	$Pt/Ti/SiO_2/Si$,	150, 400, 550, 600, 700	66 – 75 1010 – 1300	–	41 – 45 38 – 66	–	146, 147
$Pb(AcO)_2$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	"	"	52/48	$SrTiO_3$, MgO	650 – 700	448	–	15	–	148
$Pb(AcO)_2$, Zr,Ti methylcellosolvates	"	2-methoxyethanol, acetic anhydride	52/48	$Pt/Ti/SiO_2/Si$	600, 650	–	–	–	–	149
Pb,Zr,Ti naphthenates	"	naphthenic acid	52/48	$SrTiO_2/Nb$	600 – 750	–	–	–	–	150
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	"	ethanol, acetone, propanol, propane-1,2-diol	52/48	Al_2O_3	–	–	–	–	–	151
$Pb(AcO)_2$, $ZrO(AcO)_2$, $Ti(OBu)_4$	"	2-methoxyethanol	52/48	Pt/Ti	300 – 600, 700	1000 – 1100, 500 – 700	–	–	–	152
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	"	2-methoxyethanol, acetylacetone	50/50	$Pt/Ti/SiO_2/Si$	150	1000	–	–	–	153
$Pb(AcO) \cdot 3H_2O$, $Zr(OPr)_4$, $Ti(OPr^i)_4$	"	2-methoxyethanol	53/47	–	350 – 420	–	–	–	–	154
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_2(acac)_2$	"	propane-1,3-diol, pentane-2,4-dione, 1,1,1-tris(hydroxymethyl)ethane	53/47	Pt/GaAs	600, 650	950	–	24	32	155
$Pb(AcO) \cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	"	propane-2-ol	–	ITO/glass	300, 350, 450, 500	532	–	49.58	–	156
$Pb(OR)_2$, $Zr(OR)_4$, $Ti(OEt)_2(OR)_2$ (R is neodecanoate)	MOD	xylene	52/48	Si_3N_4/Si, Pt/Si	400 – 600, 600 – 700, 800	–	–	11.8	76.0	157
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OBu)_4$, $Ti(OPr^i)_4$	sol – gel	2-methoxyethanol, propan-2-ol	20/80	$Pt/Ti/SiO_2/Si$	95, 350, 600	–	–	31.9	120.8	158
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OBu)_4$, $Ti(OPr^i)_4$	"	2-methoxyethanol	40/60	$Pt/Ti/SiO_2/Si$	200, 400, 650	–	–	30	–	159
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	"	–	53/47	Pt/Si	600 – 700	930 – 990	–	20 – 25	38	160
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(NO_3)_4 \cdot 5H_2O$, $Ti(OBu)_4$	"	2-methoxyethanol	50/50	$Pt/Ti/SiO_2/S$	–	–	–	–	–	161
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(acac)_4$, $Ti(OPr^i)_4$	MOD	acetic acid, water	53/47	$Pt/Ti/SiO_2$	100	1040	–	26	39	162
$Pb(AcO)_2$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	sol – gel, MOD	propan-2-ol	53/47	$Pt/Ti/SiO_2/Si$	350 – 550	1600	–	34.8	41.7	163
$Pb(AcO)_2$, $ZrO(NO_3)_2$, $Ti(OBu)_4$	sol – gel	–	52/48	Pt/diamond	300, 500 – 700	–	–	5.1	300	164

Table 8 (continued).

Starting compounds	Method	Solvents	Composition Zr/Ti	Support	T /°C	Properties of FETF				Ref.
						ε	$\tan\delta$	P_r	E_c	
$Pb(AcO)_2\cdot 3H_2O$, $Zr(NO_3)_4\cdot 5H_2O$, $Ti(OBu)_4$	sol – gel	2-methoxyethanol, acetylacetone	50/50	$Pt/Ti/SiO_2/Si$	550	520	–	11	45	165, 166
$Pb(AcO)_2\cdot 3H_2O$, $Zr(acac)_4$, $Ti(OPr^i)_4$, $Ti(OPr^i)_2(acac)_2$	"	2-methoxyethanol	30/70	$Pt/Ti/SiO_2/Si$	124, 500	–	–	–	–	167
$Pb(AcO)_2\cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	"	2-methoxyethanol	10/90, 90/10	$Pt/Ti/SiO_2/Si$	300, 600	–	–	–	–	168
$Pb(AcO)_2\cdot 3H_2O$, $Zr(NO_3)_4\cdot 5H_2O$, $Ti(OBu)_4$	"	2-methoxyethanol, acetylacetone	50/50	$Pt/Ti/SiO_2/Si$	125, 450, 500, 550, 600	730 – 1020	–	11.2	–	169
$Pb(AcO)_2\cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	MOD	propan-2-ol	–	$Pt/Ti/SiO_2/Si$	350 – 550	–	–	–	–	170
$Pb(AcO)_2\cdot 3H_2O$, $Zr(OPr^i)_4$, $Ti(OPr^i)_4$	sol – gel	ethanol	–	$Pt/SiO_2/Si$	110, 350, 400 – 600	–	–	–	–	171

Table 9. Conditions of MOCVD synthesis of ferroelectric thin films of $Pb(Zr,Ti)O_3$ from the gas phase and their properties.

Starting compounds	Support	Zr/Ti	Process conditions			Properties of FETF			Ref.
			T_v /°C	T_p /°C	P /Torr	ε	P_r	E_c	
$PbEt_4$, $Zr(DPM)_4$, $Ti(OPr^i)_4$	Pb/MgO	52/48	10, 180, 25	600, 700	660	200 – 350	30 – 40	40 – 65	172
$PbEt_4$, $Zr(DPM)_4$, $Ti(OPr^i)_4$	Al_2O_3 (see [a])	–	182 – 208, 45 – 80	630	10	5000	–	–	173
$Pb(DPM)_2$, $Zr(DPM)_4$, $Ti(OEt)_4$,	Pt/Si, SiO_2/Si, RuO_x/SiO_2	82/18	145 – 165, 210 – 230, 90 – 115	550 – 600	6.0	–	23.3	64.5	174
$Pb(DPM)_2$, $Zr(DPM)_4$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	55/45	140, 155, 35	550	5.0	–	6 – 10	–	175
$PbEt_4$, $Zr(DPM)_4$, $Ti(OPr^i)_4$	Pt/MgO, RuO_2/MgO, $Pt/SiO_2/Si$	15/85, 50/50	–	650	5.0	–	–	–	176
$Pb(DPM)_2$, $Zr(DPM)_4$, $Ti(OPr^i)_2(DPM)_2$	Pt/Si, Pt/MgO	39/61	133, 165, 56.4	600 – 700	–	480	–	–	177
$Pb(DPM)_2$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	Pt/MgO	49/51	–	700	10	425	50	33	178
$Pb(DPM)_2$, $Zr_2(OPr^i)_6(DPM)_2$, $Ti(OPr^i)_2(DPM)_2$	–	–	–	250 – 600	–	–	–	–	179
$Pb(DPM)_2$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	MgO	39/61	141, 31, 41	650	670	–	–	–	180

[a] A solid solution with a variable composition $Pb(Zr_{1-x}Ti_x)O_3$, where $x = 0 – 1$, is formed on Al_2O_3 supports.

growth. Properties of the resultant films strongly depend on the first step. The procedure for the hydrothermal synthesis of PZT films is as follows. A titanium support is immersed into an aqueous solution of lead nitrate, zirconium oxychloride and potassium hydroxide to initiate nucleation; the lead : zirconium ratio should be equal to 2.29 and the concentrations of lead nitrate and potassium hydroxide should be 0.33 and 8.0 mol litre^{-1}, respectively. The solution and the support are slowly heated in an autoclave for 6 – 96 h. Heating at 120 °C for 48 h affords thin polycrystalline films.[181] However, this method is of low potential since it does not yield high-quality films.

A primary requirement of starting compounds to be used in the synthesis of complex oxide films by the CVD method is that the element is deposited as an oxide. Starting from the 1990s, lead, zirconium and titanium alkoxides have been commonly used for the preparation of films of $Pb(Zr,Ti)O_3$ solid solutions. The evaporation temperatures of these compounds are very low (below 35 °C), which constitutes their major advantage over other classes of compounds. Parameters of the CVD method used to grow PZT films on various supports are summarised in Table 10. Among the alkoxides, zirconium derivatives are the least studied. Actually, the choice of suitable starting compounds is limited to two types, *viz*., propoxy- and butoxy-derivatives (see below). Both types of compounds are employed for the preparation of $Pb(Zr,Ti)O_3$ thin films (doped with La^{3+}, Pb^{3+}, Bi^{3+} and Nb^{5+}) from both solutions and the vapour phase. The first application of volatile complexes and adducts of metal β-diketonates dates back to the late 1980s.[172, 194] More recently, zirconium and titanium mixed-ligand complexes, such as metal alkoxy-β-diketonates came in use (see Tables 6, 9 and 11).[95] Thin films of $Pb(Zr,Ti)O_3$ synthesised from mixed-ligand metal β-diketonates (see Tables 9 and 12) acquired the greatest practical importance

Table 10. Conditions of MOCVD synthesis of ferroelectric thin films of $Pb(Zr,Ti)O_3$ from metal alkoxides and their properties.

Starting compounds	Support	Zr/Ti	Process conditions			Properties of FETF			Ref.
			T_v /°C	T_p /°C	P /Torr	ε	P_r	E_c	
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	–	–	0 35 35	605	6.0	–		–	182
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	–	0 35 35	535 – 625	6.0	–	–	–	183
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	50/50	0 30 35	500 – 625	5	1200 220 – 240	1 – 20	–	184, 185
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	–	0 35 30	550 – 600	5.0	–	–	–	186
$Et_3Pb(OCH_2Bu^t)$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	Pt/Si Au/PZT/Pt/Si	–	60 60 60	650	5	–	–	–	187
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OBu^t)_4$	Pt	–	–	550 – 775	–	750 – 1130	30	45 – 80	188
$PbEt_4$, $Zr(OBi^t)_4$, $Ti(OPr^i)_4$	$SrRuO_3/SrTiO_3$	35/65 52/48	32 32 28.5	700	5 – 6	225 – 650	30 – 55	20	189
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	Pt/MgO $Pt/SiO_2/Si$	–	0 35 35	530 – 670	5.0	–	–	–	190
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	–	0 30 30	600	5.0	–	–	–	191
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	$SrRuO_3$ $SrTiO_3$	80/20 65/35	28.5 32 32	700	–	–	–	–	192
$PbEt_4$, $Zr(OBu^t)_4$, $Ti(OPr^i)_4$	RuO_2 SiO_2/Si	50/50	–	–	–	–	20 – 45	35 – 40	193

Table 11. Conditions of MOCVD synthesis of ferroelectric thin films of $PbTiO_3$ from the gas phase and their properties.

Starting compounds	Support	Process conditions			Properties of FETF			Ref.
		T_v /°C	T_p /°C	P /Torr	ε	P_r	E_c	
$PbEt_4$, $Ti(OPr^i)_4$	SiO_2	–	500	0.37	180	–	–	194
$PbEt_4$, $Ti(OPr^i)_4$	MgO	–	500 – 650	6	100 – 130	–	–	195
$PbEt_4$, $Ti(OPr^i)_4$	$SrTiO_3$	16.0 33.0	700	18	–	–	–	196
$Pb(DPM)_2$ $Ti(OPr^i)_4$	p-Si(100)	125 15	400 – 600	1	–	–	–	197
$Pb(DPM)_2$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	–	570	5	50 – 200	–	–	198
$PbEt_4$, $Ti(OPr^i)_4$	MgO	–	510	–	–	–	–	199
$PbEt_4$, $Ti(OPr^i)_4$	Si, MgO	1 30	510	1	–	–	–	200
$PbEt_4$, $Ti(OPr^i)_4$	CeO_2/Si	1 30		900	10^{-6}	26	–	201
$Pb(DPM)_2$, $Ti(OPr^i)_4$	p-Si	125 15	500, 800	1	–	–	–	202
$PbEt_4$, $Ti(OPr^i)_4$	Pt/MgO	–	–	–	–	–	–	203

Table 11 (continued).

Starting compounds	Support	Process conditions			Properties of FETF			Ref.
		T_v /°C	T_p /°C	P /Torr	ε	P_r	E_c	
$PbEt_4$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$, Pt/MgO	0 30	530 – 670	5	–	–	–	190
$PbEt_4$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	–	450, 650	–	–	21	70	204
$Pb(DPM)_2$, $Ti(OPr^i)_4$	$Pt/Ti/SiO_2/Si$	–	–	–	52 – 200	8	–	205
$Pb(DPM)_2$, $Ti(OPr^i)_4$	$LaAlO_3$	120 34	550 – 700	10	–	–	–	206
$PbEt_4$, $Ti(OPr^i)_4$	$Pt/SrTiO_3$, $Pt/LaAlO_3$	35 65	650	13.3	–	–	–	207
$PbEt_4$, $TiCl_4$	Si	−11 −21	170	0.004	–	–	–	208
$Pb(DPM)_2$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	130 45	350 – 400	–	–	–	–	209

Table 12. Conditions of synthesis of ferroelectric thin films of $PbTiO_3$ and $Pb(Zr,Ti)O_3$ doped with La, Mg, Nb, Ca, Al and Bi and their properties.

Starting compounds	Method	Dopant	Solvents	Support	T /°C	Properties of FETF			Ref.
						ε	P_r	E_c	
$Pb(AcO)_4 \cdot 3H_2O$, $Ti(OPr^i)_2(acac)_2$, $Sm(AcO)_4 \cdot 3H_2O$	sol – gel	Sm	propane-1,3-diol, acetylacetone	$Pt/TiO_2/SiO_2/Si$	350, 550, 650 – 700	–	–	–	210
$Pb(AcO)_4 \cdot 3H_2O$, $Ti(OBu)_4$, $La(NO_3)_3$	"	La	–	$Pt/Ti/SiO_2/Si$	410 – 600	210	16.5	60	211
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OPr)_4$, $La(acac)_3 \cdot 3H_2O$	"	Pb	2-methoxyethanol	$Pt/Ti/SiO_2/Si$	–	–	–	–	212
$Pb(AcO)_2$, $Ti(OPr^i)_4$, $Nb(OEt)_5$, $Mg(AcO)_2 \cdot 4H_2O$	"	Mg, Nb	2-methoxyethanol	Pt/sapphire	300, 840	2400, 3100	–	–	213
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_4$, $Nb(OEt)_5$, $La(AcO)_3 \cdot nH_2O$	"	La, Nb	2-methoxyethanol, HNO_3, ethylene glycol	$Pt/Ti/SiO_2/Si$	350, 600	611 – 619	–	–	214
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_4$, $CaCl_2$	"	Ca	2-methoxyethanol, HNO_3	Pt/MgO, Si	126, 142, 360, 550	–	–	–	215
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_2(acac)_2$, $Ca(AcO)_2$, $Sm(AcO)_3$	"	Ca, Sm	propane-1,3-diol	$Pt/TiO_2/Si$	85, 350 – 650	–	8.6 – 20.7	11, 9 – 73	216, 217
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_2(acac)_2$, $Sm(AcO)_3$, $Sm(acac)_3$	"	Sm	propane-1,3-diol	$Pt/TiO_2/Si$	350, 650	–	–	–	218
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OBu)_4$, $La(NO_3)_3$	"	La	2-methoxyethanol, xylene	$LaNiO_3$, Si	650 – 700	110	13	50	219
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_4$, $Al(OPr^i)_3$	"	Al	2-methoxyethanol	–	–	365	15	86	220
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_4$, $Ca(AcO)_2 \cdot nH_2O$, $Mn(AcO)_2 \cdot 4H_2O$	"	Ca, Mn	propane-1,2-diol	–	800	–	–	–	221
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_4$, $Zr(OPr^n)_4$, $Bi(NO_3)_3$	"	Bi	2-methoxyethanol, acetic acid, propan-2-ol	$Pt/Ti/SiO_2/Si$	–	–	–	–	222

Table 12 (continued).

Starting compounds	Method	Dopant	Solvents	Support	T /°C	Properties of FETF			Ref.
						ε	P_r	E_c	
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OBu)_4$, $Ca(NO_3)_2 \cdot nH_2O$, $La(NO_3)_2 \cdot nH_2O$	MOD	Ca, La	2-butoxyethanol, HNO_3	Pt/Si	180, 400, 500 – 800	375	–	–	223
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OPr)_4$, $Ti(OPr^i)_4$, $La(AcO)_3$	sol – gel	La	2-methoxyethanol	In_2O_3	130 – 500	–	–	–	224
$Pb(AcO)_2 \cdot 3H_2O$, $Zr(OBu)_4$, $Ti(OPr^i)_4$, $Nb(OEt)_5$, $La(OPr^i)_3$	"	La, Nb	–	$Pt/Ti/SiO_2/Si$	200, 400, 650	–	30	–	111
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OBu)_4$, $Ca(NO_3)_2$, $La(NO_3)_3$	"	Ca, La	2-methoxyethanol	$Pt/Ti/SiO_2/Si$	120, 350, 500, 600	–	–	–	225
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OBu)_4$, $Ca(NO_3)_2$	"	Ca	methanol, ethanolamine	Pt/Ti/Si	400, 550, 600	280	37.7	60.4	226
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OBu)_4$, $Ca(NO_3)_2$, $La(NO_3)_3$	MOD	Ca, La	2-butoxyethanol	$Pt/Ti/SiO_2/Si$	500 – 800	–	–	–	227
$Pb(AcO)_2 \cdot 3H_2O$, $Ti(OPr^i)_4$, $La(AcO)_3 \cdot 1.5H_2O$	sol – gel	La	–	$Pt/TiO_x/SiO_2/Si$	110, 450, 650	428 – 761	–	–	132
$Pb(AcO)_2$, $Zr(OPr^n)_4$, $Ti(OPr^i)_4$, $La(CO_3)_3 \cdot H_2O$	MOD	La	ethylene glycol, acetic acid, citric acid	Si(100)	90, 450 – 700	–	–	–	228, 229

due to their high permittivities. As has been mentioned above, film structures play a crucial role in the preparation of ferroelectric layers. A film can undergo polarisation as a result of mutual shifts of atoms. The introduction of additional oxygen-containing ligands into metal β-diketonate complexes makes it possible to control the structure of the target films and, consequently, obtain films with the desired properties (see Tables 9 and 12).

FETF can be doped with various elements to improve their physical properties, in particular permittivity (see Table 12). As precursors of dopants enhancing the ferroelectric properties, either metal carboxylates (from 0 mol.% to 25 mol.%) [216, 217] or volatile thermally stable β-diketonates of alkaline-earth and rare-earth metals or of such metals as Nb, Al and Bi are used.[212, 214, 218, 220, 222]

6. Films based on strontium/bismuth/tantalum and strontium/bismuth/niobium complex oxides

Films of ternary oxides $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ (also referred to as SBT and SBN, respectively) can be prepared by both the MOCVD and solution methods. It is the hydrothermal technique that is most common among the solution methods. Published data on the preparation of films from bismuth and strontium carboxylates are summarised in Table 13. As for tantalum and niobium, the respective metal alkoxides are used most often. The sol – gel method is less common but it is also in use for the synthesis of SBT- and SBN-based FETF. Acetylacetone is sometimes added to the solution in the preparation of SBT films by the sol – gel method since it promotes growth of films oriented along the crystallographic c axis. The degree of the orientational ordering in

Table 13. Conditions of synthesis of ferroelectric thin films of $SrBi_2Ta_2O_9$ and $SrBi_2Nb_2O_9$ from metal carboxylates and their properties.

Starting compounds	Method	Solvent	Support	T /°C	Properties of FETF				Ref.
					ε	P_r	E_c	Y (see [a])	
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	sol – gel	2-methoxyethanol, isopentylacetate	$Pt/Ta/SiO_2/Si$, $Pt/Ti/SiO_2/Si$	800	–	–	–	–	230
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	"	2-methoxyethanol, acetic acid	–	120, 600	–	–	–	–	231
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	"	–	$Pt/Ti/SiO_2/Si$	450, 700, 800	–	5	–	–	232
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Bi(OEt)_3$, $Ta(OEt)_5$	MOD	2-ethylhexanoic acid, toluene	–	700 – 750	–	3 – 4	1.5	–	233

Table 13 (continued).

Starting compounds	Method	Solvent	Support	T /°C	Properties of FETF				Ref.
					ε	P_r	E_c	Y (see [a])	
$Sr(AcO)_2$, $Bi(NO_3)_3 \cdot 5H_2O$, $Ta(OEt)_5$	MOD	acetic acid, methanol, aminoalcohols	$Pt/ZrO_2/SiO_2/Si$	260, 450, 700, 800	–	8 – 10	–	–	234
$Sr(AcO)_2$, $Bi(NO_3)_3 \cdot 5H_2O$, $Ta(OEt)_5$	MOD	acetic acid, methanol	$Pt/ZrO_2/SiO_2/Si$	260, 450, 700, 800	–	8 – 10	–	10^{10}	235
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	MOD	xylene	$Si_3N_4/SiO_2/Si$, Al_2O_3/Si	400, 600, 750 – 900	–	–	–	–	236
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Nb(OEt)_5$	sol – gel	2-ethylhexanoic acid, ethanol	$SrTiO_3$	120, 550, 600, 700	–	–	–	–	237
$Sr(AcO)_2$, $Bi(C_7H_{15}CO_2)_3$, $Ti(OPr^i)_4$, $Ta(OEt)_5$	MOD	2-methoxyethanol, acetic acid, 2-ethyl-hexanoic acid	$Pt - RhO_x/Si$	650, 750	180 – 225	6.2 – 13.9	80	10^{10}	238
$Sr(AcO)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	MOD	–	$Pt - Rh/Pt - Rh - O_x$	650	150 – 170	–	–	10^{11}	239
$Sr(EDTA)_2$, $Bi(EDTA)_3$, $Bi(NO_3)_3 \cdot 5H_2O$, Nb citrate	MOD	ethylenediamine-tetraacetic acid	–	300, 650	–	–	–	–	240
$Bi(n\text{-}C_7H_{15}CO_2)_3$, $Sr(n\text{-}C_7H_{15}CO_2)_2$, $Ta(OEt)_5$	MOD	2-methoxyethanol, xylene	$Pt/Ti/SiO_2/Si$	250, 340, 800	–	–	–	–	241
$Bi(n\text{-}C_7H_{15}CO_2)_3$, $Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(AcO)_3$	MOD	2-ethylhexanoic acid	$Pt/TiO_x/SiO_2/Si$	400, 750	–	–	–	–	242
$(Sr,Ba)(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	MOD	toluene	$Pt/Ti/SiO_2/Si$	150, 400, 700 – 750	–	0.7 – 1.2	37	–	243
$Sr(OH)_2 \cdot 8H_2O$, $Bi(AcO)_3$, $Ta(OEt)_5$, $Ba(OH)_2 \cdot H_2O$	MOD	2-methoxyethanol, 2-ethylhexanoic acid, acetic acid	$Pt/Ti/SiO_2/Si$	650, 700	–	–	–	–	244
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(n\text{-}C_7H_{15}CO_2)_5$	MOD	toluene	$SrTiO_3$	800	–	–	–	–	245
$Sr(AcO)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	MOD	2-ethylhexanoic acid, acetic acid, 2-methoxyethanol	$Pt/Ti/SiO_2/Si$	400, 750	–	–	–	–	246, 247
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(n\text{-}C_7H_{15}CO_2)_5$	MOD	n-butyl acetate	$Pt/Ti/SiO_2/Si$	150, 400, 800	–	6.75	63	10^{12}	248
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(n\text{-}C_7H_{15}CO_2)_5$, $Nb(n\text{-}C_7H_{15}CO_2)_5$	MOD	2-ethylhexanoic acid	$Pt/Ti/SiO_2/Si$	400, 800	–	5.6 – 8.5	24.94 – 39.6	–	249
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	MOD	xylene, CF_4/Ar (plasma)	Pt/SiO_2	400, 800	–	–	–	–	250
$Sr(n\text{-}C_7H_{15}CO_2)_2$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ta(OEt)_5$	sol – gel	propane-1,3-diol, 2-ethylhexanoic acid	$Pt/TiO_2/Si$	225, 550, 650	–	11	60	10^{10}	251

[a] Hereinafter, the polarisation fatigue expressed in the number of cycles.

Table 14. Conditions of MOCVD synthesis of ferroelectric thin films of $SrBi_2Ta_2O_9$ from the gas phase and their properties.

Starting compounds	Gases and solvents	Support	T /°C	P /Torr	Properties of FETF				Ref.
					ε	P_r	E_c	Y	
$Sr(DPM)_2$, $BiPh_3$, $Ta(OEt)_5$	N_2, O_2, THF, propan-2-ol, tetraglyme	$Pt/Ti/SiO_2/Si$, sapphire	500 – 700	4 – 10	–	4.15	60	10^{10}	253
$Sr(HFA)_2 \cdot TG$, $BiPh_3$, $Ta(OEt)_5$	Ar, O_2	$Pt/Ti/SiO_2/Si$	500 – 600	–	320	15	50	10^{11}	254
$Sr[Ta(OEt)_6]_2$, $BiMe_3$	O_2	$Pt/Ti/SiO_2/Si$	500 – 750, 800	–	–	6.1	87	–	255
$Sr(DPM)_2 \cdot TG$, $BiPh_3$, $Ta(OPr^i)_4(DPM)$, $Sr(DPM)_2 \cdot PMDT$, $Bi(DPM)_3$, $Ta(DPM)(OPr^i)_4$	O_2	Pt/Ti/Si	330 – 600	2 – 10	–	12	–	10^{11}	256
$Sr[Ta(OEt)_6]_2$, $BiPh_3$	Ar, O_2	$Pt/SiO_2/Si$	300 – 800	3 – 6	–	–	–	–	257

the films strongly affects the residual polarisation and the coercitive field. Oriented films exhibit improved ferroelectric properties. In particular, for the films prepared in the absence of acetylacetone and annealed at 750 °C, the permittivity (ε), residual polarisation (P_r) and coercitive field (E_c) were equal to 119, 3.1 μC cm^{-2} and 65.1 kV cm^{-1}, respectively. For the similarly prepared film in the presence of acetylacetone, the following values of these parameters were obtained:[252] $\varepsilon = 205$, $P_r = 7.2$ μC cm^{-2} and $E_c = 53.3$ kV cm^{-1}.

Legrand *et al.*[237] prepared 30 nm-thick SBN films by the sol – gel method [deposition on a support of double oxide $SrTiO_3(001)$]. The films often crystallise in the temperature range 500 – 700 °C. As a rule, this occurs at a lower temperature, between 500 °C and 550 °C. As a result, epitaxial layers (001)SBN//(001)$SrTiO_3$ and (100)SBN//(110)$SrTiO_3$ are formed.[202] The mechanism of crystallisation of the SBN films was studied in detail by Shimizu *et al.*[184]. However, SBN films with the composition 1 : 2 : 2 : 9 can hardly be applied in nonvolatile memory elements.

In addition to metal carboxylates and β-diketonates, aryl derivatives and preformed bimetallic alkoxides are used in the preparation of SBT films by the MOCVD method (Table 14). Multilayer composites with the composition $Pt/Ti/SiO_2/Si$ are typically used as supports. The temperature of the process is typically varied from 300 to 800 °C and the residual pressure, from 1 to 10 Torr. Alkyl, aryl and dipivaloylmethane bismuth derivatives deposited at 500 °C,[255] 470 °C[256] and 330 °C, respectively. The use of aryl derivatives complicates the control over the preparation of films with required compositions.[256] Final characteristics of the films are largely determined by the temperature regime of annealing; some of them are listed in Table 14.

7. Films of $Bi_4Ti_3O_{12}$

Films of $Bi_4Ti_3O_{12}$ (also referred to as BTO) are synthesised most often by the sol – gel and CVD methods (Tables 15 and 16). In the former method, metal alkoxides and carboxylates (primarily, acetates and naphthenates) are typically used. In the latter method, the availabe starting compounds are employed, *e.g.*, alkoxy or aryl derivatives or metal β-diketonates. Crackless films are produced from $Bi(NO_3)_3$, $Ti(OPr^i)_4$ and $Ti(OBu^n)_4$ dissolved in glacial acetic acid or monoglyme. This was achieved by applying solutions of the starting compounds onto platinum-coated silicon or $SrTiO_3(100)$ supports using spin-coating followed by annealing at 500 °C or 600 °C, respectively. This resulted in well-ordered films which consequently possessed good dielectric and ferroelectric properties. The films synthesised by the MOD method were additionally annealed at 700 °C and manifested the following characteristics: permittivity, 184 at a signal frequency of 100 kHz; dielectric loss tangent, 0.039; residual polarisation, 4.4 μC cm^{-2}; coercive force, 84 kV cm^{-1}; resistivity, 10^8 Ω cm at room temperature; mean leakage current density, 10^{-7} A cm^{-2} at a film thickness of 0.5 μm under an applied field of 100 kV cm^{-1}. The hysteresis loop on the polarisation curve remained unchanged over 10^{10} cycles of repolarisation.[274]

Table 15. Conditions of synthesis of ferroelectric thin films of $Bi_4Ti_3O_{12}$ from metal carboxylates and their properties.

Starting compounds	Method	Solvents	Support	T /°C	P /Torr	Properties of FETF				Ref.
						ε	P_r	E_c	Y	
$Bi(AcO)_3$, $Ti(OPr^i)_4$, $Ti(OCH_2CH_2OMe)_4$	sol – gel	acetic acid, 2-methoxyethanol	$Pt/Ti/SiO_2/Si$	128 – 135, 200, 700	–	120, 132	4	1.8	–	258
Bi,Ti naphthenates, O_2	MOD	–	–	–	4×10^5	45	1.9	23	10^7	259
$Bi(NO_3)_3 \cdot 5H_2O$, $Bi(AcO)_3$, $Ti(OPr^i)_4$	sol – gel	2-methoxyethanol, acetic acid, propan-2-ol	–	124, 300, 750	–	–	–	–	–	260
$Bi(NO_3)_3 \cdot 5H_2O$, $Bi(AcO)_3$, $Bi(n\text{-}C_7H_{15}CO_2)_3$, $Ti(OCH_2CH_2OMe)_4$	"	–	$Pt/Ti/SiO_2/Si$	550	–	105	13.5	60	–	261
$Bi(AcO)_3$, $Ti(OMe)_4$	"	2-ethylhexanoic acid, ethanol	$Pt/TiO_x/SiO_2/Si$	250, 550 – 700	–	–	–	–	–	262

Table 16. Conditions of MOCVD synthesis of ferroelectric thin films of $Bi_4Ti_3O_{12}$ and their properties.

Starting compounds	Support	Process conditions			Properties of FETF				Ref.
		T_v /°C	T_p /°C	P /Torr	ε	P_r	E_c	Y	
$BiPh_3$, $Ti(OPr^i)_4$	$Pt/Ti/SiO_2/Si$, sapphire	120–150, 35	500–750	1–5	180	0.6	13	–	263
$BiPh_3$, $Ti(OEt)_4$	$Pt/Ti/SiO_2/Si$, sapphire	165–170, 75–127	450–500	6	–	19.6	244.3	–	264
$BiPh_3$, $Ti(OBu)_4$	Si	130–140, 150–170	550	–	93	38	45	–	265
$BiPh_3$, $Ti(OPr^i)_4$	$Pt/SiO_2/Si$	140, 30	480–650	5	130	1.3	25	–	266
$BiPh_3$, $Ti(OBu)_4$	Si(100)	150–170, 130–140	450–750, 600–800	–	–	–	–	–	267
$Bi(o\text{-}C_7H_7)_3$, $Ti(OPr^i)_4$	$Pt/Ta/SiO_2/Si$, p-Si, $Bi_2SiO_5/Si/Al$	160, 50	400, 500	2–10	30	9–11	120–90	10^{12}	268, 269
$Bi(o\text{-}C_7H_7)_3$, $Ti(OPr^i)_4$	$Pt/Ta/SiO_2/Si$, BiO_x-buffer	–	400	5	–	1.9–8.2	55–90	–	270
$BiPh_3$, $Ti(OMe)_4$	$Pt/SiO_2/Si$	270	640	6	132	38	45	–	271
$BiMe_3$, $Ti(OPr^i)_4$, $La(DPM)_3$, $VO(OEt)_3$	$Ir/TiO_2/SiO_2/Si$, $Pt/Ti/SiO_2/Si$	–	600	–	–	–	–	–	272, 273

Jones *et al.*[179] accomplished deposition of films onto multilayer composite supports $Pt/Ti/SiO_2/Si$ from vapour of organometallic precursors. The $Bi_4Ti_3O_{12}$ phase proved sensitive to pyrolysis and annealing due to diffusion of titanium into bismuth titanate to yield the $Bi_2Ti_2O_7$ phase. Nevertheless, the ferroelectric properties of the resultant film were satisfactory: residual polarisation of 8.2 μC cm^{-2} and coercive force of 7 kV cm^{-1}. Malik *et al.*[275] prepared thin films of BTO on Si(100) supports from vapour of $BiPh_3$ and $Ti(OBu^n)_4$ at 550 °C and atmospheric pressure using N_2 as a carrier gas and O_2 as an oxidant. According to the X-ray diffraction study, the single-crystal films exclusively exposed (100) crystal faces. The residual polarisation and coercive force were 38 μC cm^{-2} and 45 kV cm^{-1}, respectively. Desu *et al.*[276] also used $BiPh_3$ and $Ti(OBu^n)_4$ for the same purpose; they studied the film growth as a function of the oxidant concentration. The films were deposited at 600 °C on composite supports $Pt(111)/SiO_2/Si(100)$ with buffer layers of $Bi_2Ti_2O_7$. The final films were characterised by a residual polarisation of 1.3 μC cm^{-2}, coercive force of 25 kV cm^{-1}, permittivity of 130 and leakage current density of 10^{-8}–10^{-7} A cm^{-2}.

The possibility of growing thin films of BTO from metal alkoxides by the MOCVD method at a temperature below 400 °C has been demonstrated.[268–270] The films with a thickness of 100 nm manifested good surface morphology and good ferroelectric properties: residual polarisation of 11 μC cm^{-2}, coercive force of 90 kV cm^{-1} and leakage current density of 7×10^{-9} A cm^{-2} at 3 V. The ferroelectric properties of the films with a thickness of 50 nm were satisfactory: $P = 9$ μC cm^{-2} and $E_c =$ 120 kV cm^{-1}. No polarisation fatigue of the film was observed after 10^{12} switches.

IV. Metal and metal oxide electrodes, prepared from organometallic precursors, for thin-film capacitors

Thin films of ferroelectrics can be used as electrode-separating dielectric layers in the manufacture of capacitors for the memory elements of SLIC. With this regard, the issue of polarisation fatigue of the capacitors due to ageing of the ferroelectric material becomes of key importance.

Both metals, such as platinum, gold, ruthenium, iridium and titanium, and highly conductive metal oxides, such as RuO_2, IrO_2, $SrRuO_3$, $CaRuO_3$, $LaNiO_3$ and $(La,Sr)CoO_3$, are used as the electrode materials. These can be produced by vapour deposition from the following organometallic precursors: $Pt(acac)_2$,[277,278] $MeCpPtMe_3$,[279–284] $Au(HFA)Me_2$,[285,286] $Me_2Au(TFA)$ (TFA is 1,1,1-trifluoropentane-2,4-dione), $Me_2Au(HFA)$, $Me_2Au(acac)$,[287] $AuR(CN)R'$ (R = Me, Ph, vinyl, prop-1-ynyl, 3,3-dimethylbutyl; R' = Me, Et, Pr^i, Bu^t, Ph),[288] $Ru(EtCp)_2$, $[RuC_5H_5(CO)_2]_2$,[289] $Ru_3(CO)_{12}$,[282] $Ir(acac)_3$, $Ir(acac)Cl_2$,[290] $(EtCp)Ir(COD)_2$ (COD is cyclooctadiene).[291,292]

The starting compounds and selected technological parameters of the film deposition on supports are given in Table 17. For the preparation of RuO_2 films, $RuCp_2$, $Ru(DPM)_2$ and $Ru(EtCp)_2$ are most commonly utilised, whereas iridium cyclopentadienyl complexes and their derivatives are applied to the synthesis of IrO_2. Double oxides $SrRuO_3$ and $LaNiO_3$ can be prepared from β-diketonates of the respective metals, *e.g.*, $Sr(DPM)_2 \cdot (C_8H_{23}N_5)_x$, $La(DPM)_3$, $Ni(DPM)_2$ or $Ni(acac)_2$. Films of $YBa_2Cu_3O_7$ prepared from yttrium, barium and copper dipivaloylmethanates are sometimes employed.[313,314]

* * *

Studies conducted over the last 15 years have clearly demonstrated the possibility of using the effect of spontaneous polarisation in ferroelectric materials for the creation of the nonvolatile memory elements. The requirements to such materials have been formulated.

Among chemical methods used for the preparation of ferroelectric thin films, the MOCVD method has become the most popular. Over the last few years, this method has been widely applied, in particular, for high-temperature coatings and superconductors.[318] Ferroelectric thin films manifesting the lowest polarisation fatigue have been synthesised, for which the maximum number of recirculation cycles reaches 10^{11}–10^{12}. Among the oxide films considered above, the following materials that are promising as ferroelectrics can be distinguished: Ta_2O_5, $YMnO_3$, $BaTiO_3$, $SrTiO_3$, $(Ba,Sr)TiO_3$, $PbTiO_3$, $Pb(Zr,Ti)O_3$, $Pb(Sr,Ti)O_3$, $Bi_4Ti_3O_{12}$, $SrBi_2Ta_2O_9$. An analysis of the temperature regimes of the preparation of oxide films shows that it is the annealing step that is of key importance. Control over this step can enable preparation of films with a layered perovskite-type structure. A systematic consideration of the methods for the synthesis of ferroelectric thin films with the emphasis placed on diverse chemical methods suggests the priority of the CVD

Table 17. Characteristics of oxides used as electrodes for ferroelectric thin films.

Conductive oxide	Synthesis method	Starting compounds	Solvents, oxidant gases	Support	Process conditions		ρ /μΩ cm	Ref.
					T /°C	P /Torr		
RuO_2	CVD	$Ru(DPM)_3$	O_2, N_2	$Pt/Ti/SiO_2/Si$	450	4	34 – 40	293
	CVD	$RuCp_2$	O_2	SiO_2/Si	200 – 350	3	75 – 138	294
	CVD	$Ru_3(CO)_{12}$	O_2	$Ru/SiO_2/Si$	250	2	–	295
	CVD	$RuCp_2$	O_2	$LaAlO_3$, MgO	–	–	40 – 50	296
	MOD	$Ru(OC_8H_{17-n})_4$	xylene, pentanol	Si(100)	300, 550	–	–	297
	CVD	$RuCp_2$	–	Si	500 – 600	10^{-2}	–	298
	CVD	$Ru(DPM)_2(CO)_2$	–	Si	450	4.5	–	299
	CVD	$Ru(DPM)_2(COD)$	O_2	Si	250 – 500	1 – 10	200	300
	CVD	$Ru(EtCp)_2$	O_2, N_2	$Ru/SiO_2/Si$	120, 355	–	17 – 120	301, 302
	CVD	$Ru(DPM)_3$	–	Si	250 – 450	–	45 – 60	303
	sol – gel	$Ru(NO)(NO_3)_3$	Me_4NOBu^n, ethanol, Pr^iOH	Si	600	–	–	304
	"	$RuCl_3 \cdot x\,H_2O$	propan-2-ol, citric acid, ethylene glycol	Si	130, 250, 450	–	–	305
IrO_2	CVD	Ir(MeCp)(COD)	–	Si	350 – 450	0.005	–	298
$SrRuO_3$	MOD	$Ru(n\text{-}C_7H_{15}CO_2)_4$ $Sr(n\text{-}C_8H_{17})_2$	xylene, butanol	$SrTiO_3$	300 – 750	–	–	297
$SrRuO_3$, $CaRuO_3$	CVD	$Sr(DPM)_2 \cdot (C_8H_{23}N_5)_x$, $Ca(DPM)_2 \cdot (C_8H_{23}N_5)_x$, $Ru(DPM)_3$	–	$SrTiO_3$	750	–	300, 200	306, 307
$LaNiO_3$	CVD	$La(DPM)_3$, $Ni(DPM)_2$ $Ni(ôcôc)_2$	–	MgO	750 – 850	8 – 10	–	308
	MOD	$La(NO_3)_3$, $Ni(C_4H_5O_2)_2$	citric acid	–	300 – 800	–	–	309
	sol – gel	$La(NO_3)_3$, $Ni(AcO)_2 \cdot 3\,H_2O$	–	$SrTiO_3$, $LaAlO_3$	–	–	–	310
	MOD	$La(NO_3)_3$, $La(n\text{-}C_7H_{15}CO_2)_3$, $Ni(AcO)_2 \cdot 4\,H_2O$, $Ni(n\text{-}C_7H_{15}CO_2)_2$	water, acetic acid	Si(100)	450 – 650	–	760	311
$YBa_2Cu_3O_7$	CVD	$Y(DPM)_3$, $Ba(DPM)_2$, $Cu(DPM)_2$	O_2/N_2O	$SrTiO_3$	150, 270	3.5	–	312, 313
$(La,Sr)CoO_3$	sol – gel	La_2O_3, $Co(NO_3)_2 \cdot 6\,H_2O$, $Sr(NO_3)_2$	citric acid, ethylenediamine	–	–	–		314
	MOD	$La(NO_3)_3 \cdot 6\,H_2O$ $SrCl_2 \cdot 6\,H_2O$, $Co(NO_3)_2 \cdot 6\,H_2O$	2-methoxyethanol	$SrTiO_3$	110, 500, 800	–	10 – 13	315
	MOD	$La(NO_3)_3 \cdot 6\,H_2O$, $Sr(NO_3)_3$, $Co(NO_3)_2 \cdot 6\,H_2O$	glycine, citric acid, $C_2H_6O_2$	CeO_2, MgO	80	–	–	316
	CVD	$La(DPM)_3$, $Sr(DPM)_2$, $Co(DPM)_2$	–	$LaAlO_3$, MgO	–	–	0.85×10^3	317

processes. Mixed-ligand complexes based on metal β-diketonates as are mainly used as the starting compounds. Metal and conductive oxide layers have been proposed for the manufacture of capacitors based on ferroelectric thin films and their effects on polarisation fatigue properties have been studied.

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