Metal-Organic Chemical Vapor Deposition of Oxide Perovskite Films: A Facile Route to Complex Functional Systems

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1. Introduction

Over the last decades, there has been an extensive interest in perovskite systems to explore the enormous power of this class of compounds, which can be considered a potentially endless source of functionalities. The perovskite system possesses the ABX₃ structure, where A is a large ionic radius cation, B is a small cation and X is the anion, either halogen or oxygen. The number of publications on perovskites has witnessed a huge increase in the last decade, due to the pioneering work on photovoltaic properties of halide perovskites, and in particular the focus is devoted to oxide perovskite thin films on both single crystal and non-single crystal substrates through MOCVD processes. This study discusses the principles and the basic rules governing conventional, plasma-enhanced, and liquid-assisted MOCVD processes. Among a plethora of oxide perovskites, several classes of functionalities belonging to the perovskite class: from superconductors to dielectrics and giant-k dielectrics, from colossal magnetoresistance to ionic conductors, piezoelectrics and ferroelectrics, are explored in detail.

Perovskite oxide type materials exhibit a great profusion of unique functional properties and for this reason they have been named inorganic chameleons. Nevertheless, their actual applications require the availability of these systems in thin-film form synthesized through a simple, scalable, and straightforward technique. Metal-organic chemical vapor deposition (MOCVD) has been shown to be an outstanding process to prepare thin films of multi-component oxides. Herein, the focus is devoted to oxide perovskite thin films on both single crystal and non-single crystal substrates through MOCVD processes. This study discusses the principles and the basic rules governing conventional, plasma-enhanced, and liquid-assisted MOCVD processes. Among a plethora of oxide perovskites, several classes of functionalities belonging to the perovskite class: from superconductors to dielectrics and giant-k dielectrics, from colossal magnetoresistance to ionic conductors, piezoelectrics and ferroelectrics, are explored in detail.

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processes. After a brief description of the perovskite ideal structure and distorted cells related to the A and B ion radii, the work is organized into two main sections: I) MOCVD growth of perovskite films on single-crystal substrate and II) MOCVD growth of perovskites on non-single-crystal substrate.

Selected case studies will be presented, that is, cuprates, manganites, titanates, and ruthenates illustrating their main functionalities, such as conductors, dielectrics, ferroelectrics, and superconductors, and the relations between growth and texture of the materials and their properties.

2. Ideal Perovskite and Distorted Structures

Oxide materials with a perovskite-based structure have the general formula ABO$_3$, where A is an alkali, alkaline-earth, or rare-earth metal and B is a transition or main group metal. To balance the −6 charge of the three oxygen atoms, the sum of the cation charge has to be equal to +6. Table 1 reports the possible combinations of A and B cations for the ABO$_3$ structure, together with a few examples of perovskite materials.

The ideal structure consists of a compact cubic packing of oxygen and A cations, where A cations substitute 1/4 of the oxygen atoms, and B cations occupy 1/4 of the octahedral sites. Thus, the A site involves a 12-fold coordination and the B-site a sixfold coordination environment (Figure 1). In addition, by proper substitution at the A-site or B-site, or even at both sites, with alkaline-earth or with transition metals, respectively, a huge variety of possible structures, doping combination, and thus functionalities may be obtained. For this reason, perovskites have been named inorganic chameleon or a San Patrick’s well of functionalities.

Starting with the description delineated by Goldschmidt,[17] we introduce also the so-called “tolerance factor” (t), reported in Equation (1), to indicate the stability of the perovskite structures.

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)}$$  \hspace{1cm} (1)

where $R_A$, $R_B$, and $R_O$ are the ionic radii of A$^{n+}$, B$^{m+}$, and O$^{2-}$ in the structure.

Goldschmidt,[17] derived the tolerance factor formula using his own ionic radii, which were analogous to those simultaneously derived by Pauling. These radii can be assimilated to those reported in the Shannon table for the crystal ionic radii of six-coordinated ions.[18]

Actually, distortions from the cubic structure, which involve t value different from 1, are quite common and can arise from size “mismatch” of the cations and anion, thus resulting in additional perovskite structures, such as tetragonal or orthorhombic, and derived perovskite structures.[19]

Finally, perovskite ABO$_3$ represents also the base unit of complex structures, such as the high-temperature cuprate superconductors (La$_{2−x}$Ba$_x$CuO$_4$),[20] YBa$_2$Cu$_3$O$_{6.5}$ (YBCO),[21] Bi$_2$Sr$_2$CaCu$_2$O$_{8+δ}$ (BSCCO)[22] and the giant-k dielectrics CaCu$_3$Ti$_4$O$_{12}$[24] and SrRuO$_3$.

3. MOCVD Techniques Applied for the Growth of Perovskite Films

As described in the previous section, perovskites are very complex systems, hence their synthesis in thin-film form is a very challenging task. MOCVD technique is one of the most promising approaches to deposit perovskites and, actually, more variants have been applied and will be addressed within the review. One of the most commonly applied approaches is the conventional MOCVD, that is, a thermally activated deposition with the use of plain precursors. On the other hand, the liquid-assisted MOCVD approaches represent a one-step and simple process that provides an excellent film composition control and the possibility of using a huge number of metalorganic compounds as precursors. In fact, while the conventional MOCVD requires very volatile and thermally stable precursors, in the case of liquid assisted MOCVD routes, either liquid injection (LI-MOCVD)[25,26] or aerosol-assisted (AA-MOCVD),[27] even complexes showing thermal instability and low volatility may be applied, yielding pure metal oxides on a desired substrate.

Thus, in conventional MOCVD, the metalorganic complexes suitable for vapor-phase reactions should be chemically and thermally stable during the transport process in vapor phase and should possess high evaporation rates. In the case of liquid-assisted processes, instead, they must be soluble and stable in a proper solvent without the formation of precipitates. Among the different classes of precursors, the chelate compounds are

Table 1. Possible combination of A and B ions in the ABO$_3$ perovskite systems.

| A ion charge | B ion charge | Example of perovskite materials |
|-------------|-------------|-------------------------------|
| +1          | +5          | KNbO$_3$                      |
| +2          | +4          | SrTiO$_3$, BaTiO$_3$, Pb(Zr,Ti)O$_3$, SrRuO$_3$ |
| +3          | +3          | BiFeO$_3$, LaAlO$_3$, La$_2$(Sr)MnO$_3$, Pr(Ca)MnO$_3$ |

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the main candidates as MOCVD precursors especially for the alkaline-earth ions, mainly Ca, Sr, and Ba, which represent key elements in multifunctional oxide perovskites. These elements, due to their electropositive behavior, tend to form compounds with ionic bonds and low vapor pressures. The application of chelate ligands, such as β-diketones, produces very appealing compounds as MOCVD precursors due to the small intermolecular interaction energies and thus the tendency to form single and volatile adducts, which are the most applied compound class.

Plasma enhanced MOCVD (PE-MOCVD) approach has also been applied to produce functional high-quality perovskite oxide films, such as high-k dielectrics, on a variety of substrates. PE-MOCVD has several advantages over conventional CVD techniques, including the ability to operate at lower temperatures, due to the plasma-activated precursor decomposition, while maintaining comparable or even higher deposition rates. Furthermore, the thin layers formed are, usually, mechanically stress-free. Unfortunately, the plasma used to deposit layers may collide with the growing sample and, in some cases, damage the film surface.

To have better insights on the overall process, different in situ characterizations may be applied to scrutinize the gas-phase and the growth steps. One of the most used techniques to investigate the gas-phase reaction mechanisms during the epitaxial development of perovskite oxide layers is the in situ IR absorption spectroscopy. Optical methods are the most powerful and challenging approaches to monitor film growth. Among them, spectroscopic ellipsometry, reflectance difference spectroscopy, and Raman, are applied as tools to characterize the sample in growth. In some cases, X-ray methods including high-resolution X-ray diffraction, X-ray photoelectron spectroscopy, and Auger spectroscopy are used as in situ characterization techniques, crucial for understanding the thin film growth process and controlling its characteristics.

4. MOCVD Growth of Perovskite Films on Single Crystal Substrate

A huge number of perovskite and perovskite-based films have been synthesized through MOCVD techniques. In addition to the specific process and operative parameters, the substrate nature plays a crucial role in the formation of perovskite layers, and the rule like grows like applies. Thus, perovskite substrates (SrTiO$_3$, LaAlO$_3$, NdGaO$_3$, etc.) guide the deposition of perovskite films, but, various other single-crystal substrates, such as yttria-stabilized zirconia (YSZ), MgO, and Al$_2$O$_3$, have been applied as well to produce interesting films for various relevant technological applications.

MOCVD has been widely and successfully employed to produce perovskite-based superconductive oxides, such as La$_{1-x}$Ba$_x$CuO$_{3+\delta}$, YBa$_2$Cu$_3$O$_{6+\delta}$, LuBa$_2$Cu$_3$O$_{6+\delta}$, GdBa$_2$Cu$_3$O$_{6+\delta}$, SmBa$_2$Cu$_3$O$_{6+\delta}$, BiSrCaCuO$_2$, and TiBa$_2$CuO$_{6+\delta}$ on SrTiO$_3$ and LaAlO$_3$ single crystal substrates. Perovskite oxides such as CaCu$_3$Ti$_4$O$_{12}$, BaTi$_{1-x}$Zr$_x$O$_3$ (BTZ), SrTiO$_3$, LaAlO$_3$, and Pb(Mg$_{1/3}$Nb$_{2/3}$)$_2$O$_3$ (PMN) have also been synthesized as thin films through MOCVD on single-crystal substrates to be exploited in various microelectronic and optoelectronic fields due to their high dielectric constant ($\varepsilon$) values.

Perovskite conducting oxides of LaNiO$_3$ and SrIrO$_3$ are of great interest since they may be employed as bottom electrodes for the deposition of perovskite ferroelectric materials for microelectronic devices. MOCVD processes have been investigated for the deposition of these materials, which, to be applied as bottom electrodes, need to be synthesized as good-quality, highly epitaxial thin films with clean and smooth surfaces.

Lanthanum manganites or cobaltites, such as LaMnO$_3$, La$_2$Sr$_2$MnO$_5$ (LSMO), and LaCoO$_3$, well-known perovskite oxides with excellent electric and ionic conductivity, have also been grown by MOCVD. In particular, alkaline-earth doped rare-earth manganites (RE$_{1-x}$A$_x$MnO$_3$; RE: La, Pr; A: Ca, Sr) are famous for their exceptional magnetic and magnetoresistive characteristics. These materials have been developed in form of thin films and deposited as epitaxial or oriented layers on single crystal SrTiO$_3$ and LaAlO$_3$ substrates using traditional or enhanced MOCVD approaches.

MOCVD has been applied as well to fabricate ferroelectric thin films of BaTiO$_3$, PbTiO$_3$, Pb$_{0.5}$La$_{0.5}$Zr$_{1-y}$Ti$_y$O$_3$, and Pb(Nb,Ti)O$_3$ which have attracted a lot of attention over the years due to their applicability in electric and optoelectronic devices, as well as in optical integrated circuits.
In the last decade, MOCVD has been also successfully applied to the deposition of multiferroic BiFeO₃ thin films, a material that has recently attracted a lot of attention due to its appealing properties. Nevertheless, this topic is not explicitly treated within this review and the readers are invited to read the minireview published by Malandrino et al. in 2017.

Given the huge numbers of materials, we will concentrate our efforts on the perovskite categories mentioned in Scheme 2.

### 4.1. Superconductors

One year after Bednorz and Müller came upon the high critical temperature superconductor (HTcS) La₁₂₋ₓBaₓCuO₄₋₅ (LBCO). Paul Chu’s group discovered the YBa₂Cu₃O₇₋ₓ (YBCO), which displayed superconducting behavior above the critical temperature measured at 77 K. Issues with their manufacturing procedures, given the complex structure, required the use of a simple and straightforward method to produce such materials. Various MOCVD approaches were applied such as plasma-enhanced MOCVD (PE-MOCVD), liquid assisted (either pulsed injection or aerosol assisted) MOCVD, and photo-assisted MOCVD.

Single crystals of SrTiO₃, LaAlO₃, NdGaO₃, were the most frequently used substrates for the growth of epitaxial oriented YBCO in thin-film form. On the other hand, yttria-stabilized zirconia (YSZ), MgO, and Al₂O₃ were also interesting substrates for some specific applications due to their low dielectric constants. Nevertheless, the use of these substrates required the implementation of buffer layers to avoid interaction of the deposited film with the substrate and to guide the epitaxial growth.

The 2,2,6,6-tetramethyl-3,5-heptandionato metal complexes of Y, Ba, and Cu were the most frequently used precursors. In this review, since the 2,2,6,6-tetramethyl-3,5-heptandionato ligand is indicated with different acronyms in the literature, it has been chosen to use the same notation reported in the original manuscript, thus dpm, thd, tmhd acronyms and the C₁₁H₁₉O₂ formula, cited within the review, indicate the same kind of ligand.

Berry et al. are credited for being the first group describing MOCVD production of high-quality YBCO superconducting perovskite in form of thin films on MgO substrates, by using metal β-diketonates as precursors.

Chern’s group together with Zhao et al. deposited for the first-time, in 1991, c-axis oriented YBCO layers on a single crystal LaAlO₃ (100) substrate using PE-MOCVD. As yttrium, barium, and copper sources, Y(dpm)₃, Ba(dpm)₂, and Cu(dpm)₂ were employed. The epitaxially grown films exhibited mirror-like smooth surfaces and the electrical resistance and magnetic susceptibility versus temperature dependences demonstrated metallic behavior in the normal state and good superconducting transitions at 88 K.

Matsuno et al. developed a liquid-assisted MOCVD deposition of YBCO with a single solution source of Y(dpm)₃, Ba(dpm)₂, and Cu(dpm)₂ β-diketonate complexes dissolved in tetrahydrofuran (THF), with the goal of overcoming the Ba source’s instability and weak volatility. Good superconducting properties were obtained for these epitaxially grown YBCO films on a perovskite single crystal substrate, that is, the SrTiO₃(100).

Tao et al., on the other hand, used a low pressure (1 Torr) MOCVD approach to increase the vaporization rate of Y(thd)₃, Ba(thd)₂, and Cu(thd)₂ metalorganic sources, while simultaneously stabilizing their sublimation properties. It was discovered that the sublimation rate of Ba(thd)₂ decreased with time of heating at a high deposition pressure of 30 Torr, but it remained relatively constant at low pressure. The critical current density was not less than 8.0 × 10⁵ A cm⁻², according to the I-V curve measured at 77 K.

Richards et al. offered an alternative way to enhance the volatility of barium precursor in 1995. The β-diketonate [Ba(thd)₃]₄ was replaced with a fluorinated metal β-diketonate adduct coordinated with a polyether [Ba(tdfnd)₂·tetraglyme] (Htdfnd = 1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dione, tetraglyme = 2,5,8,11,14-pentaaxapentadecane), which provided a more volatile and stable complex to be successfully used in the MOCVD process for depositing c-axis oriented YBCO films on SrTiO₃.

Gorbenko et al. investigated the effects of changing the type of single-crystal substrate (Al₂O₃, MgO, YSZ, NdGaO₃, SrTiO₃, LaAlO₃) on the properties of MOCVD deposited YBCO films. Y(thd)₃, Ba(thd)₂, and Cu(thd)₂ were used as volatile sources of Y, Ba, and Cu. Their MOCVD procedure yielded several sets of ideal conditions for YBCO thin films, with the most promising substrates being NdGaO₃, SrTiO₃, and LaAlO₃, which had a low lattice mismatch with the YBCO layer. Typical Tc values were around 90 K and Jc ≥ 8.0 × 10⁵ A cm⁻². High-quality epitaxial YBCO films on substrates with suitable electrical characteristics, like MgO, are required for advanced devices. However, MgO and YBCO have a large lattice mismatch, resulting in the production of low-quality epitaxial films. Desisto et al. demonstrated the growth process for epitaxial YBCO films on stepped (100) MgO substrates having Tc > 88 K and Jc > 10⁶ A cm⁻². They used a commercial-scale, vertical MOCVD.
reactor within a restricted range of ideal conditions. Unfortunately, the existence of holes and defects throughout the film affected their electrical performance.\[62\]

Single crystal Al2O3 seemed particularly appealing, in terms of electrical characteristics, as a substrate for high Tc superconductors. However, the interaction between the substrate and the YBCO film at high temperatures (above 700 °C) has been a big obstacle as observed in various studies.\[63\] The introduction of buffer layers may overcome this drawback. As an example, YSZ buffer layers were deposited on silicon and c-sapphire to avoid interaction of the superconductive perovskite with the substrate.\[64\] Another extensively utilized buffer layer is CeO2. Its use on sapphire allowed the epitaxial YBCO development,\[65\] even though in some cases, given the high deposition temperatures (800–900 °C), YBCO films had some microcracks, due to the different thermal expansion coefficients, and, as a consequence, resistivity and critical current density values may have been biased.\[66\] As an alternative, a low-temperature PE-MOCVD technique, starting from a mixture of Y(thd)3, Ba(thd)2, and Cu(thd)2 powders, was applied for producing YBCO thin films directly on Al2O3 substrates utilizing plasma-activated nitrous oxide as reactant gas, thereby avoiding any sort of surface reactions.\[67\]

As established by Dubourdieu et al.,\[68\] another low dielectric constant substrate appropriate for microelectronic and microwave applications and well-matched to YBCO formation is YAlO3. On this substrate, a unique twinning geometry was observed in YBCO films deposited at 870 °C through conventional MOCVD. Only the b orientation of the substrate aligned the twinning directions of YBCO, while for films formed on MgO, SrTiO3, and LaAlO3, there were two potential orientations.\[69\] In 1997, Abrutis et al. published the findings of a similar research dealing with the YBCO film deposition on another single-crystal perovskite substrate, that is, NdGaO3 (001), whose lattice matching with YBCO is good. They adopted a vertical hot-wall injection CVD reactor in which the injector delivered micro quantities of an organic solution of Y(thd)3, Ba(thd)2, and Cu(thd)2, dissolved in THF, to manufacture high-quality superconducting YBCO films at high growth rates (0.2–1 µm min\(^{-1}\)) in order to reduce production times. Highly c-axis oriented YBCO films were obtained in the temperature range from 730 to 830 °C as confirmed by the XRD 0–2θ patterns, rocking curves, and c-scans, (Figure 2a,b). In particular, the rocking curve of the 005 YBCO reflection had a FWHM of 0.27°, indicating an excellent out-of-plane orientation, whereas the c-scans verified a strong in-plane alignment with the substrate. The resistance versus temperature curve for the produced YBCO films exhibited a high transition temperature of around 91 K, while the critical current density ($J_c$) was $\approx 4 \times 10^6$ A cm\(^{-2}\) (Figure 2c).\[70\]

Zeng et al.\[70\] presented a new photo-assisted MOCVD process that used a single liquid precursor delivery system, with a mixture of Y(thd)3, Ba(thd)2, and Cu(thd)2, dissolved in THF, to manufacture high-quality superconducting YBCO films at high growth rates (0.2–1 µm min\(^{-1}\)) in order to reduce production times. Highly c-axis oriented YBCO films were obtained in the temperature range from 730 to 830 °C as confirmed by the XRD 0–2θ patterns, rocking curves, and c-scans, (Figure 2a,b). In particular, the rocking curve of the 005 YBCO reflection had a FWHM of 0.27°, indicating an excellent out-of-plane orientation, whereas the c-scans verified a strong in-plane alignment with the substrate. The resistance versus temperature curve for the produced YBCO films exhibited a high transition temperature of around 91 K, while the critical current density ($J_c$) was $\approx 4 \times 10^6$ A cm\(^{-2}\) (Figure 2c).\[70\]

Zhao et al.\[33\] used a very fast Nd:YAG laser MOCVD approach with Y(dmp)$_3$, Ba(dpm)$_2$/Ba(mod)$_2$ (Hmod = 2,2,6,6-tetramethyl-3,5-octanedione), and Cu(dmp)$_2$ as precursors to improve the deposition rates of YBCO on single crystal LaAlO3(100) substrates. By slightly varying the deposition temperatures from about 700 to 800 °C, a-axis and c-axis oriented YBCO films were obtained. A squared grain morphology was seen on FE-SEM images of a c-axis-oriented YBCO film produced at 793 °C, with some needle-like grains spread uniformly along the boundary of the c-axis-oriented grains (Figure 2d). The deposited layer had a thickness of roughly 500 nm (Figure 2e). The c-axis-oriented YBCO pole figure revealed a fourfold pattern at $\alpha = 33°$ for the 102 reflection, while the overlap of the azimuth angles of the four pole peaks of YBCO (102) with those of LaAlO3 (001) demonstrated that the film grew epitaxial with an in-plane alignment as YBCO [0 1 0]/LaAlO3 [0 0 1] (Figure 2f). For the a-axis-oriented YBCO film, the temperature dependence of the electrical resistivity revealed a semiconducting behavior, as shown in Figure 2g, while the c-axis-oriented YBCO film showed a metallic dependence. $T_c$ values of YBCO films deposited at various deposition temperatures indicated that the $T_c$ of the a-axis-oriented YBCO films were between 20–70 K, whereas the ones of the c-axis-oriented YBCO films were around 79–90 K (Figure 2h).\[33\]

A less studied high-temperature superconductor is the parent La$_{2-x}$Ba$_x$CuO$_{4+δ}$ (LBCO), which was the first discovered HT, superconductor\[90\] and has the potential to reach a $T_c$ of 44 K. Malandrin et al.\[30\] reported a novel MOCVD approach for the deposition of c-axis oriented LBCO films on LaAlO3(100) substrate using a multi-component “single-source” mixture of Cu(thd)$_2$, La(hfa)$_3$ diglyme, and Ba(hfa)$_2$ tetranglyme. The isothermal TGA analysis revealed that mass loss was linearly proportional to vaporization time, indicating that no secondary events affecting mass transfer occurred (Figure 3a). An important point of this process is that the mixture behaves like a “single-source” precursor as indicated by the differential scanning calorimetry (DSC) curve, which shows a single endothermic peak around 75 °C, associated with melting of La(hfa)$_3$ diglyme component, and a small intensity feature around 120 °C, associated with the dissolution of the other two components in the molten La precursor (Figure 3b). LBCO films deposited at 800 °C show the best results in terms of structural data and composition. From the XRD pattern, only the LBCO (000) peaks together with the (00l) LaAlO3 ones could be identified (Figure 3c), thus implying the formation of a highly c-axis oriented LBCO structure. By recording c-scans of the LBCO/LaAlO3(100) system, the hetero-epitaxial relation between c-axis oriented LBCO film and the LaAlO3 substrate was examined. The alignment of the four peaks of the LBCO (103) pole with the (110) LaAlO3 pole confirms the epitaxial nature and the cube-on-cube growth of the LBCO films (Figure 3d). The surface morphology of some samples formed on LaAlO3 substrates consisted of grains with dimensions of roughly 400 nm as confirmed by AFM measurements (Figure 3e,f).

A summary of significant studies on applications of MOCVD techniques of YBCO and LBCO superconducting thin films is reported in Table 2. Various MOCVD approaches, including PE-MOCVD, liquid-assisted MOCVD, AA-MOCVD, thermally-activated MOCVD, and laser MOCVD, have been applied for the deposition of oriented YBCO thin films on different...
single crystal substrates. As a property to test the film quality, the critical transition temperature at zero resistance has been considered. A very low transition temperature (20 K) has been observed for the two-step ambient pressure MOCVD deposition of YBCO films on MgO substrate. When films are deposited on perovskite substrates, such as LaAlO₃ (001), SrTiO₃ (001), and NdGaO₃ (001), the film quality improves significantly with the formation of highly c-axis oriented films with Tₐ values around 90 K, independently from the applied process, that is, PE-MOCVD, photo-assisted MOCVD, and laser MOCVD. Slightly lower Tₐs are observed for films deposited on c-sapphire, or for films partially c-axis oriented on SrTiO₃ deposited through PE-MOCVD and LP-MOCVD. In the case of LBCO film deposition, a reduced-pressure MOCVD (RP-MOCVD) with a deposition temperature of 800 °C resulted in the formation of c-axis oriented films with a Tₐ value, at zero resistance, of about 27 K.

4.2. Dielectrics and Giant-k Dielectrics

Because of its outstanding dielectric constant and lack of structural change across a large temperature range, the calcium copper titanate CaCu₃Ti₄O₁₂ (CCTO) is a well-known “giant-k” dielectric perovskite material with a wide variety of possible uses. Its fabrication as thin films has been investigated for years to evaluate potentiality in device integration.[71] The earliest study on the production of CCTO in the form of thin films using chemical vapor phase processes can be traced back to Lo Nigro et al. in 2004.[40] For the CCTO film production on LaAlO₃ (001) substrates, a unique multi-element source consisting of Ti(tmhd)₂(i-Opr)₂, Ca(hfa)₂ tetraglyme, and Cu(tmhd)₂ was used. The XRD pattern in Figure 4a showed the CCTO peaks corresponding to the 00l planes, indicating that the film c-axis is perpendicular to the substrate, while from the ϕ-scan four peaks due to CCTO-{110} planes were evident and perfectly coincident with LaAlO₃-{110} positions, suggesting that the CCTO unit cell is not rotated in the plane with respect to the LaAlO₃ substrate (Figure 4b). Due to the infrared-active lattice vibrations of the CCTO layer and the substrate, the dielectric function and conductivity spectra reveal multiple rather distinct bands (Figure 4c,d).[40] If SrTiO₃ (100) single crystal is used as a substrate, the formation of pure CCTO or mixed CCTO/CTO was mostly dependent on the growth processes used, that is, one-step or two-step growth.[72] An epitaxial layer of CCTO was
Figure 3. a) Vaporization of the La–Ba–Cu combination in terms of mass percent versus time, b) DSC curves of single metal precursor and multi-component La–Ba–Cu combination; c,d) XRD, ϕ-scan of the LBCO film deposited on single crystal LaAlO3; e,f) FE-SEM and AFM images of c-axis oriented LBCO on LaAlO3. Adapted with permission. Copyright 2005, Royal Society Chemistry.

Table 2. Summary of MOCVD conditions and transition temperatures of perovskite-based superconducting materials deposited on single crystal substrates.

| Material | Substrate | MOCVD Technique | Deposition Temperature | Precursors | Structure | Tc [K] | Reference |
|----------|-----------|-----------------|------------------------|------------|-----------|-------|-----------|
| YBCO     | MgO       | Amb. Pressure Vertical MOCVD | 2-step process: a) 400 °C + b) 890 to 920 °C annealing | Cu(acac)2; Y(tmhd)3; Ba(tmhd)2 | Polycrystalline | ≈20 | [57] |
| LaAlO3 (100) | PE-MOCVD | Liquid-assisted MOCVD | 700 °C | Cu(dpm)2; Y(dpm)3; Ba(dpm)2 | c-axis oriented | 88 | [31,43] |
|          |           | Photo-assisted MOCVD | 730–830 °C | Cu(tmhd)2; Y(tmhd)3; Ba(tmhd)2 | c-axis oriented | 91 | [70] |
| SrTiO3 (100) | RP-MOCVD | Photo-assisted MOCVD | 830–880 °C | Cu(tmhd)2; Y(tmhd)3; Ba(thd)2 | c-axis oriented | 93.2 | [61] |
| NdGaO3 (100); SrTiO3 (100); LaAlO3 (100) | PE-MOCVD | Thermally-Activated MOCVD | 845–910 °C | Cu(thd)2; Y(thd)3; Ba(thd)2 | Mostly c-axis oriented | Above 88 | [64] |
| CeO2/C-sapphire | AA-MOCVD | Thermally-Activated MOCVD | 800 °C | Cu(thd)2; Y(thd)3; Ba(thd)2 | c-axis oriented | 88.5 | [66] |
| C-sapphire | PE-MOCVD | AA-MOCVD | 730 °C | Cu(dpm)2; Y(dpm)3; Ba(dpm)2 | Mostly c-axis oriented | 82 | [67] |
| NdGaO3 (100) | Hot-Wall Injection | CVD reactor | 825 °C | Cu(tmhd)2; Y(tmhd)3; Ba(tmhd)2 | Mixed a,c-axis oriented | ≈90 | [69] |
| LBCO     | LaAlO3 (100) | RP-MOCVD | 800 °C | Cu(tmhd)2; La(hfa)3 diglyme; Ba(hfa)2 tetraglyme | c-axis oriented | 27 | [30] |
successfully deposited on SrTiO$_3$ substrate using a Ca/Cu/Ti precursor combination of 1:1.3:3.2 Ca/Cu/Ti through a one-step process at a deposition temperature of 750°C, while a two-step process favored the formation of CaTiO$_3$(100) (CTO) phase. The difference was explained considering a balance between thermodynamic and kinetic contribution aided by a better lattice match between CTO and SrTiO$_3$ (misfit ≈ 2.1%) with respect to that observed between CCTO and SrTiO$_3$ (misfit ≈ 6%).[73]

A deep investigation of the dielectric and optical characteristics of epitaxial CCTO/LaAlO$_3$ films pointed to two significant absorption zones, attributed to electron transitions between valence and conduction band states, with energy values of roughly 3.6 and 4.2 eV, respectively (Figure 4e). Using a metal-insulator-metal (MIM) interdigit device, the n-type semiconducting character was assessed, and the dielectric constant value was estimated as a function of the operating frequency in the $10^2$–$10^6$ Hz frequency range, with a value of about 200 for 150 nm thick films at 1 MHz (Figure 4f). Figure 4g,h illustrate the morphology and SIM map of the deposited CCTO films. A surface depletion layer was found at the electrode/CCTO film interface, as well as an extrinsic local behavior of a high dielectric constant, according to nanoscopic SIM analysis. Indeed, the absence of the barrier at a large scale for the films thermally treated at 900°C was explained by the presence of conducting leaky patches in the films. Finally, for the sample annealed at 1000°C, the appearance of a Schottky barrier and the formation of a local colossal permittivity was recorded.[74]

SrTiO$_3$ (STO) and LaAlO$_3$ (LAO) have attracted attention in the microelectronic area for inclusion in thin-film form into devices for a range of electronic applications because of their high dielectric constants. For example, they could be employed as insulating layers in very large-scale integration (VLSI) circuits, ultra large-scale integration (ULSI) devices such as dynamic random-access memories (DRAMs), and in optoelectronic devices. Moreover, due to their close lattice matches with several superconducting materials, SrTiO$_3$ and LaAlO$_3$ have also been explored as an epitaxial insulating layer in high-$T_c$ thin-film multilayers. In 1990, the group of Feil et al.[43] published the first report on the production of STO films using the MOCVD process. They used Ti(O- iC$_3$H$_7$)$_4$ (titanium isopropoxide, TIP), Sr(dpm)$_2$, oxygen, and/or water vapor as reactants in order to minimize carbon incorporation inside the film structure. Under optimal conditions at 800°C, samples grown on (001) sapphire revealed a significant (111) SrTiO$_3$ preferred orientation.[43] To address the limitations of strontium metalorganic precursors, Fröhlich et al.[75] devised an aerosol-assisted MOCVD of STO films on (001) MgO and (001) sapphire substrates, using the Sr(thd)$_2$ and titanium n-butoxide dissolved in diglyme as precursors. According to the XRD data, STO films grown on both single crystal substrates were epitaxial in nature and could be suitable as buffer layers for the development of high-$T_c$ superconducting films.[75] Nevertheless, the Sr(thd)$_2$ had significant drawbacks, such as poor volatility and a tendency for thermally induced oligomerization during film formation, resulting in non-volatile products and transport property instability. For these reasons, Gilbert et al.[76] adopted the Sr(hfa)$_2$·tetraglyme, a “second-generation” metalorganic precursor, to increase the source vapor pressure stability. The films were deposited at...
810 °C on a single crystal LaAlO₃ substrate. According to the ϕ-scans, tetragonal distortion was seen in the epitaxial films (Figure 5a). In fact, only the four {220} and {202} reflections predicted for an a or c axis-oriented film were visible, showing that the films had the required fourfold symmetry about an axis normal to the substrate. The films were found to be pinhole-free and homogeneous across a vast region, with a granular morphology, as shown on SEM images in Figure 5b,c.[76]

Lanthanum aluminate, LaAlO₃, with a perovskite-type structure is a particularly enticing material because it has been frequently used as a substrate or insulating layer for different functional perovskite oxides. Molodyk et al.,[77] used a volatile surfactant-assisted MOCVD method starting from a solution of La(thd)₃ and Al(thd)₃ dissolved in diglyme to produce LaAlO₃ films on YSZ (100) and NdGaO₃(100) substrates in the presence of Bi₂O₃, a volatile low melting point oxide. According to EDX and RBS studies, the LaAlO₃ films produced in the presence of Bi₂O₃ did not contain bismuth. In addition, the film deposition rate of LAO films synthetized in the presence of Bi₂O₃ increased considerably when compared to films formed without Bi₂O₃.[77]

Malandrino et al. presented the first MOCVD report of epitaxial LaAlO₃ on SrTiO₃ employing a novel combination of La(hfa)₃ diglyme and Al(acac)₁ precursors in a 1:1 ratio as a “single-source” of La and Al elements.[44,78] Characterization of the molten phase through DSC confirmed a “single-source” behavior of the mixture. The gas-phase characterization of the mixed vapor precursors, obtained by recording in situ IR data, indicated that the mixture spectrum deviated marginally from the sum of the two separate precursor spectra (Figure 5d). According to the findings of thermal investigations, the linearity of the plots for all the reported IR bands indicated steady vaporization and good transport processes (Figure 5e). After growing the LaAlO₃ films at 1050 °C, morphological (SEM and AFM) characterizations revealed a smooth and grainy surface across the entire area (Figure 5f,g). The recording of XRD θ–2θ scans, rocking curves and pole figures confirmed that the in situ deposited LaAlO₃ samples were high-quality, epitaxial films.[78]

Table 3 summarizes the MOCVD procedures employed and the resulting structural characteristics of giant-k and high-k perovskite thin films. In this case, no correlation can be done on film properties versus film nature, because it is not possible to identify specific property values in the papers. Data reported in Table 3 indicate that highly c-axis oriented or epitaxial films are deposited, whatever the MOCVD technique applied.

4.3. Conductors

Among different mixed oxide perovskite materials, Sr-doped lanthanum manganite (La₁₋ₓSrₓMnO₃ or LSMO) is one of the most often utilized cathodes in solid oxide fuel cell (SOFC) systems because of its chemical stability, thermal expansion compatibility with the other parts of the cell, and high electrical conductivity at the SOFC working temperatures. Materials having high oxygen surface exchange and good diffusion coefficients are required for the catalytic reduction of oxygen at the cathode in SOFC devices. Surface exchange kinetics and ionic conductivity have been increased in manganite perovskite materials by adding strain or dislocations into the lattice. Another notable feature of these doped manganite perovskite materials is the colossal magnetoresistance (CMR) phenomenon, which occurs when an external magnetic field is applied around the ferromagnetic transition temperature, leading to their use in microelectronic devices.

MOCVD has the potential to be a very efficient and repeatable technology for rapidly producing LSMO coatings with suited thickness and composition uniformity across large areas,
since LSMO is frequently required in thin-film form for integration in such systems. The most commonly used solid electrolyte in SOFCs is YSZ. Because LaMnO₃ has a comparable thermal expansion coefficient of YSZ, it may be used in thin-film form at SOFC operating conditions. Some studies on single-crystal substrates have been carried out as a preliminary step to optimize the deposition process for a successive application on YSZ electrolytes.

Toro et al. [49] employed an in situ MOCVD process to deposit LSMO \( c \)-axis oriented films on LaAlO\(_3\) (100) substrate in order to implement a novel synthetic approach based on a multi-component source to quickly synthesize layers for use as cathodes in SOFCs. LSMO films have been deposited using La(hfa)\(_3\) diglyme and Sr(hfa)\(_2\) tetruglyme precursors in combination with the Mn as two distinct sources: the Mn(tmhd)\(_3\) or Mn(hfa)\(_2\)∙tmeda (tmeda = N,N,N,’N’-tetramethyl-ethylenediamine). Pure LSMO phase films were obtained at 1000 °C as indicated by the XRD pattern displayed in Figure 6a, which showed only two peaks of the LSMO phase related to 001 and 002 reflections, as well as the 001 and 002 reflections of the LaAlO\(_3\) substrate, suggesting that the films were highly \( c \)-axis oriented. The deposited films had smooth and homogenous surfaces with cube-like grains (Figure 6b), and a thickness of about 2μm, as shown in the SEM image (Figure 6c). Figure 6d shows the resistance versus temperature curves along two combinations in the 1 × 1 cm\(^2\) LSMO film, indicating that the resistivity trend is metallic below metallic/insulating transition temperature (\( T_P \)) and insulating above \( T_P \). [49]

Table 3. Summary of MOCVD conditions for the deposition of dielectric perovskite materials and their structural properties.

| Material | Substrate | MOCVD Technique | Dep. Temp. | Precursors | Structure | Ref. |
|----------|-----------|-----------------|------------|------------|-----------|-----|
| CCTO     | LaAlO\(_3\) (100) | RP-MOCVD | 2-step process: a) 600 °C + b) 900 °C in situ annealing | Ti(tmhd)\(_3\)∙(i-Opr)\(_2\); Ca(hfa)\(_2\) tetruglyme; Cu(tmhd)\(_2\) | \( c \)-axis oriented | [40] |
| SrTiO\(_3\) | LaAlO\(_3\) (100) | RP-MOCVD | 750 °C | TiO-(C\(_2\)H\(_5\))\(_2\); Sr(dpm)\(_2\) | \( c \)-axis oriented | [73] |
| SrTiO\(_3\) | Sapphire (001) | RP-MOCVD | 800 °C | Sr(hfa)\(_2\) tetruglyme | Preferred (111) orientation | [43] |
| MgO (001); Sapphire (001) | AA-MOCVD | 800–900 °C | Sr(thd)\(_2\); titanium n-butoxide | Preferred (001) orientation | [75] |
| LaAlO\(_3\) (100) | Low pressure Two-zone MOCVD | 810 °C | TiO-(C\(_2\)H\(_5\))\(_2\); Sr(hfa)\(_2\) tetruglyme | Tetragonally distorted epitaxial films | [76] |
| LaAlO\(_3\) | YSZ (100); NdGaO\(_3\) (100) | Single Aerosol Source MOCVD | 800–1030 °C | La(thd)\(_3\); Al(thd)\(_3\); Bi(Ph)\(_3\); Sr(hfa)\(_2\) diglyme; Al(acac)\(_3\) | Preferred (001) orientation | [77] |
| SrTiO\(_3\) (100) | Reduced Pressure MOCVD | 1050 °C | La(hfa)\(_3\) diglyme; Al(acac)\(_3\) | Preferred (001) orientation | [44,78] |

Figure 6. La\(_{0.93}\)Sr\(_{0.13}\)MnO\(_3\) film deposited on LAO substrate: a) XRD pattern of a film deposited at 1000 °C with a \( c \)-axis orientation; b,c) SEM and cross-section images of LSMO films; d) Normalized resistivity of an LSMO film as a function of temperature. Adapted with permission. [49] Copyright 2010, Wiley-VCH. LMO film deposited on STO: e) scheme of the \(^{18}\)O exchange for an LMO film deposited on STO; f,g) LMO/STO and LMO/LAO X-ray diffraction patterns; h,i) planar SEM and AFM images of LMO deposited on STO and LAO, respectively. Adapted with permission. [48] Copyright 2021, Royal Society Chemistry.
Bertrand et al. used a LP-MOCVD approach to deposit LaMnO$_3$ films on (100) YSZ at a deposition temperature of 600 °C, varying the La/Mn ratio to find the ideal composition range for fabricating good quality LMO films. Their research underlined the importance of selecting the correct chemical composition for the SOFC cathode material.

Rodriguez-Lamas et al. have looked at the ionic mass transport characteristics of LaMnO$_{3-δ}$ (LMO) as a potential oxygen electrode for SOFCs at low temperatures (500–600 °C) on two different SrTiO$_3$ and LaAlO$_3$ substrates (see scheme in Figure 6e). Pulsed injection MOCVD (PI-MOCVD) was used to produce dense thin LMO films on SrTiO$_3$ and LaAlO$_3$ single crystals using a precursor solution of La(thd)$_3$ and Mn(thd)$_2$ in m-xylene as solvent. According to the XRD analysis (Figure 6f,g), highly oriented 110 LMO films were obtained on both SrTiO$_3$ and LaAlO$_3$. SEM and AFM images of films indicated nanoscale grain sizes and remarkably smooth and homogenous surfaces (Figure 6h,i). Interestingly, they discovered that LMO films grown on SrTiO$_3$ were defect-free, whereas those grown on LaAlO$_3$ released strain by forming a dense network of extended defects that were beneficial to oxygen diffusion and surface exchange processes, resulting in higher mass transport coefficients, due to the greater film-substrate mismatch. At 500 °C, the epitaxial LMO on LaAlO$_3$ showed particularly high oxygen diffusion coefficients.

Because of its strong mixed ionic and electronic conductivity, LaCoO$_3$ (LCO) might be utilized as a cathode in solid oxide fuel cells, or as a thick ceramic membrane to separate oxygen from air. Catalano et al. reported on a simple in situ MOCVD strategy that employed a molten precursor mixture consisting of La (hfa)$_3$ diglyme and Co(tta)$_2$ tmeda at relatively high temperatures to create good quality LCO films on single crystal LaAlO$_3$ (001) substrates. Deposition temperature, in particular, has been determined to have an essential impact; in fact, films grown below 650 °C have been found to include lanthanum spurious phases, whilst films grown above 650 °C have produced good crystalline LaCoO$_3$ films.

LaNiO$_3$ (LNO) is a well-known conductive perovskite system that has notably attracted a lot of attention, as an example, LNO films have been extensively investigated as bottom electrodes for ferroelectric perovskites, good epitaxial LNO films must be fabricated.

Gorbenko and Bosak revealed in 1997 that MOCVD could be used to develop LaNiO$_3$ thin films on MgO (100) and analyzed how the structure of the films changed as the thickness increased. The films were produced at 750–850 °C on single-crystal MgO (100) substrates using a single-source MOCVD process with flash evaporation of a powder combination of volatile La(thd)$_3$, Ni(acac)$_2$ (Hacac = acetylacetone) or Ni(thd)$_2$ precursors. Two distinct stages of development were identified from the structural analyses: an initial 001 oriented LNO film with a stable in-plane alignment but a significant out-of-plane rocking curve, and another orientation, the 110 aligned in-plane, which appeared to provide strain relaxation in the film. These films did not relax completely to the bulk LaNiO$_3$ lattice parameters as a thinner film containing solely the 001 orientation.

Kuprenaite et al. used CVD reactors with three different precursor delivery systems, PI-MOCVD, atmospheric pressure MOCVD (AP-MOCVD), and a commercial direct liquid injection MOCVD, to study the effects of solvent, evaporation temperature, deposition pressure, growth temperature, and the relationship between film and solution compositions in order to optimize the composition and growth efficiency of LNO films in function of La and Ni β-diketonates. PI-MOCVD and AP-MOCVD methods employed monoglyme (1,2-dimethoxyethane) as solvent, and La(thd)$_3$ and Ni(thd)$_2$ as precursors. In the case of the commercial MOCVD, different solvents were tested. The main issue found was the high evaporation temperature and thermal instability of La(thd)$_3$, which necessitated the inclusion of an excess of La precursor in the solution, as well as the reliance of film composition on deposition parameters such as pressure and temperature. The LNO films grew epitaxially along the [012] on SrTiO$_3$ (100) and LaAlO$_3$ (012) substrates. LNO films on R-sapphire substrates, on the other hand, exhibited the lowest epitaxial quality, resulting in mosaicity and in-plane orientation dispersion. Composition deviations from stoichiometry and microstructural dispersion were the key determinants of resistivity in CVD-grown LNO films.

The used MOCVD techniques and the resultant characteristics for conducting perovskite thin films are summarized in Table 4. For the synthesis of conducting lanthanum manganites and cobaltites, such as LSMO, LMO, and LCO, metal β-diketone precursors have been prevalently applied in the MOCVD processes. In this case, the temperature of metal-insulator transition (T$_P$) and the Curie temperature (T$_C$) are specific properties for these materials. Unfortunately, T$_P$ and T$_C$ values are available only for the LSMO films, being T$_P$ and T$_C$ equal to 287 and 269 K, respectively. Due to the differences in thermal properties of the La and Ni β-diketone precursors, multiple MOCVD approaches, such as PI-MOCVD, AP-MOCVD, and direct liquid injection MOCVD, have been investigated for the LNO conducting perovskite material deposition. Only the single crystal substrate LaAlO$_3$ (011$\overline{2}$) has produced epitaxially grown LNO films among the many single crystal used substrates.

4.4. Colossal Magneto resistance

Because of its CMR properties, multi-metal manganites (RE$_{1−x}$A$_x$MnO$_3$, with RE = rare-earth trivalent ion, A = alkaline-earth divalent ion) have attracted a lot of attention since their discovery.

Snyder et al. in 1993 can be credited for one of the earliest attempts of MOCVD deposition of La$_{1−x}$Sr$_x$MnO$_3$ (LSMO) films. They used La(tmhd)$_3$, Sr(tmhd)$_2$, and Mn(tmhd)$_2$ as precursors, and oriented LSMO films deposited on a single crystal LaAlO$_3$ substrate at temperatures ranging from 600 to 800 °C. However, to generate films with adequate transport characteristics, these films needed to be post-annealed at 950 °C under oxygen atmosphere. Using the same tetramethylheptandionate precursors and a deposition temperature of 670 °C, Dahmen and Carris reported a liquid-delivery MOCVD
approach of oriented LSMO layers on MgO and LaAlO₃. They were able to deposit LSMO films with transition temperatures near room temperature by simply raising the oxygen partial pressure during the deposition process without any need for post-annealing treatments. On both substrates, the LSMO films were highly oriented, although a tiny amount of another reflection, the 220, was observed on the LSMO/MgO films, probably due to the large lattice mismatch between LSMO and MgO. Both the La/Sr ratio and the oxygen concentration in the films were shown to have a significant impact on the transition temperature and magnitude of resistivity.[83] Meda et al.[84] investigated the impact of thermal annealing on the texture of LSMO thin films produced on single-crystal substrates of LaAlO₃(001) and SrTiO₃(001). The films were fabricated by using the liquid-delivery MOCVD technique with a deposition temperature of 670 °C and a post-annealing treatment at 700–800 °C. The surface morphology was influenced by the substrate and the heat treatment.[84]

Abrutis et al.[84] described the deposition of LSMO films on LaAlO₃, SrTiO₃, and NdGaO₃ substrates at temperatures of 650–850 °C using a PI-MOCVD approach. The films were deposited using a solution of La(mthd)₃, Sr(mthd)₂, and Mn(mthd)₃ in monoglyme. Deposition temperature, solution composition, and oxygen flow had the largest influence on film properties, with the best films obtained at 825 °C on LaAlO₃. In situ or post-annealing treatments of the produced films in pure oxygen raised the temperature of the semiconductor–metal transition, but decreased the MR and the temperature coefficient of resistance.[84]

It was discovered that when manganite films are obtained with thicknesses below 100 nm, the temperature of the resistivity maximum was significantly reduced.[85] Most manganite oxides produced in ultra-thin film form on a variety of single-crystal substrates showed structural deformation and compositional inhomogeneity at the substrate–film interface. This area was discovered to contain two phases, both having a significant influence on the characteristics of ultra-thin films. Balevičius et al.[85] used a PI-MOCVD technique to study how the two-phase structure could affect the magnetic characteristics of LSMO films produced on NdGaO₃(001) substrates. They observed that the two-phase structure influenced the electric and magnetic properties, and that the Curie temperature for a 20 nm film was quite close to the resistivity peak temperature (295 K).[85]

Li et al.[86] discovered a greater MR effect around room temperature in the calcium-doped lanthanum manganite (La₀.₈Ca₀.₂)MnO₃ (LCMO) thin films. Such LCMO films were deposited through liquid-source MOCVD on (100) LaAlO₃, (110) NdGaO₃, and (100) MgO using La(tmhd)₃, Ca(tmhd)₂, and Mn(tmhd)₃ as source precursors. These films had a MR change of 200% in a 3T field, 300% in a 6 T field, and 550% in a 14 T field at 270 K.[86]

Heremans et al.[87] investigated the temperature dependence and the low field transport features of LCMO films produced on single-crystal sapphire and YSZ substrates using a liquid-delivery MOCVD approach and compared the results with films deposited on LaAlO₃ substrates. They concluded that the substrate had a significant influence on the film texture and, as a result, on its magnetoresistive properties. Indeed, growing on YSZ and sapphire substrates produced significantly more disordered films with higher resistivity and MR across a wider temperature range.[87]

Vagner et al.[88] recently employed the PI-MOCVD approach to synthesize Sr- and Co-doped lanthanum manganite films, La₁₋ₓSrₓMn₁₋₃₃Co₃O₄ (LSMCO), which is a material of interest as an active layer to make magnetic field sensors work at room temperature. The films were deposited on different single crystal substrates: LaAlO₃ and r-plane sapphire at 750 °C under different optimized conditions. Strain generation, texture, and changes in electrical transport and magnetic properties were related to substrate nature. XRD investigations of LSMCO films on single crystal LaAlO₃ substrate revealed epitaxial growth along the [001] direction (Figure 7a). The morphology reflects the orientation observed in the XRD pattern with grains of hundreds of nanometers (Figure 7b,c). In the Co-doping range of 0 < y < 0.17, epitaxial LSMCO/LaAlO₃ films showed a change in strain from tensile to compressive, whereas nanostructured films remained tensely strained. The nanostructured form of LSMCO/r-plane sapphire was impacted by the large mismatch between the a-axis parameter of LSMCO films and the substrate. According to the Volmer–Weber growth model, many growth centers were produced during the early development stage of nanostructured films, and subsequent crystalline grain growth continued in columnar structures with a specific size of crystalline grains dependent on the growth process conditions. Epitaxial films with strongly oriented crystallites were produced in the case of LSMCO/LAO, as confirmed by the pole figure measurements (Figure 7d), while a moderate texture with two preferred orientation was observed for the polycrystalline films on r-plane sapphire (Figure 7e). Furthermore, at room temperature, MR experiments demonstrated the maximum MR for

| Material | Substrate | MOCVD Technique | Dep. Temp. | Precursors | Structure | Ref. |
|----------|-----------|-----------------|------------|------------|-----------|-----|
| LSMO     | LaAlO₃(100) | RP-MOCVD        | 1000 °C   | La(tmhd)₃; Mn(tmhd)₃ | c-axis-oriented | [49] |
| LaMnO₃   | (100) YSZ     | RP-MOCVD        | 600 °C    | La(tmhd)₂; Mn(acac)₂ | –          | [79] |
| SrTiO₃(100); LaAlO₃(100) | PI-MOCVD | 800–900 °C | La(thd)₂; Mn(thd)₃ | 110 orientation | [48] |
| LaCoO₃   | LaAlO₃(100) | RP-MOCVD        | 700–900 °C| La(hfa)₁; diglyme; Co(tta)₁-tmeda | c-axis-oriented | [50] |
| LaNiO₃   | MgO(100)     | Flash MOCVD     | 750–850 °C| La(thd)₁; Ni(acim)₁; | Mixed 001 and 110 orientation | [46] |
| R-Sapphire (01T₂); SrTiO₃(100); LaAlO₃(01T₂) | PI-MOCVD(a) AP-MOCVD(b) LI-MOCVD(c) | 450–750 °C(a); 500–675 °C(b); 650–750 °C(c) | La(thd)₁; Ni(thd)₂ | Epitaxial [01T₂] grow on LaAlO₃ | [80] |
nanostructured films with Co amount of $y = 0.06$ at a magnetic field of 2T and reduced anisotropic behavior for films with Co content in the range from 0.12 to 0.17.[88] 

Among the doped manganite perovskites, the Pr(1–x)Ca₀ₓMnO₃ (PCMO) manganite has been extensively studied, for its significant MR properties. Catalano et al.[51,89] proposed an MOCVD approach for the deposition of pure PCMO on SrTiO₃ (001), SrTiO₃ (110), MgO (001), and LaAlO₃ (001) substrates, using a mixture of Pr(hfa)₃ diglyme, Ca(hfa)₂ tetraglyme, and Mn(tmhd)₃ as precursors. The nature of substrate orientation is reflected in the microstructure and morphology of the deposited films. The XRD peaks were associated with 0k₀ reflections for PCMO films deposited on SrTiO₃ (001), whereas for films deposited on SrTiO₃(110) the two PCMO peaks corresponded to the 00l reflections (Figure 7f). There were no other peaks, indicating that the films did not contain any other crystalline impurity phases. The PCMO films obtained on SrTiO₃(001) and SrTiO₃(110) had a compact and homogenous morphology as shown by FE-SEM images (Figure 7g). Temperature and applied magnetic fields were also used to determine the conduction characteristics of the films (Figure 7h,i). Magnetic studies revealed the existence of a FM transition temperature, which has been linked to the film transport capabilities. No CMR effect was observed, likely due to the need for a magnetic field higher than 6 T to induce the insulant-metal transition in the studied films.[51]

Table 5 shows the employed MOCVD processes and related properties of CMRs perovskite thin films. Lanthanum and praseodymium manganites with CMRs characteristics have been deposited using liquid-assisted MOCVD and low-pressure MOCVD in the same way as prior conducting manganites. Good results have been obtained for the formation of pure or doped manganites using metal β-diketonate precursors combined in an appropriate ratio and deposited at a relatively high temperature. Single crystal perovskite substrates of LaAlO₃ (100), SrTiO₃ (100), NdGaO₃ (110), and even single crystal sapphire, are the most commonly used substrates for the formation of epitaxial films. The very different $T_c$ and $T_p$ values are related to film composition, thickness, and substrate nature.

4.5. Piezoelectric and Ferroelectric

Microelectronics and optoelectronics have sparked interest in ferroelectric thin films such as PbTiO₃ (PT), Pb(Zr,Ti)O₃ (PZT), and BaTiO₃ (BT), which take advantage of their unique dielectric, electro-optic, electric, piezoelectric and ferroelectric characteristics. MOCVD-grown PT and PZT films have been widely documented, with microstructured films ranging from random polycrystalline to highly epitaxial. Since Okada et al.[90] pioneering MOCVD deposition of PT and PZT, other researchers have continued to explore how to optimize the manufacturing of these materials.

Dorman et al.[91] for example, used an MOCVD technique with a combination of metalorganic precursors such as Pb(C₂H₅)₄ (tetraethyl-lead, TEL), and titanium isopropoxide, to explore the kinetics of the PT on SrTiO₃ substrate. They discovered that epitaxial PbTiO₃ on SrTiO₃ could be developed above 700 °C, and that the layer’s composition was unaffected by the Pb/Ti ratio at 700 °C, which varied from 0.2 to 1.7, but as the
temperature dropped below 700 °C, an increasing portion of PbO was integrated.\cite{91}

Foster et al.\cite{92} on the other hand, studied the effect of substrate on the structure and twinning of PbTiO3 thin films deposited on three different substrates: MgO (001), SrTiO3 (001), and LaAlO3 utilizing TEL and TIP as precursors, along with their LaAlO3 displayed multi-domain structure. For the films deposited on SrTiO3, the energy based on polarization and spontaneous strain could be totally absorbed by the stepped surface once the films cooled from the deposition temperature (650 °C) (Figure 8b). The PbTiO3 films on LaAlO3, the a-domains were equally and alternately c-domains to tilt away from the surface normal direction, while domain structure in the LaAlO3 substrate had a direct impact on the domain configuration of PT films.\cite{93}

Batzer et al.\cite{94} used the same deposition processes to analyze the domain structures of PT films produced on single-crystal MgO substrates, confirming the presence of both c and a domains, with a dominating c-domain population. However, such PT films were discovered to have a fourfold symmetry structure incorporating four a-domain variations, but no sign of separation was identified in the c-domain examination. This was explained by the presence of a differential thermal stress caused by the difference in thermal expansion coefficients between the PT film and the MgO substrate, which appeared to be partially released by the formation of c-domains and partially responsible for the Curie temperature change.\cite{95}

Yen et al.\cite{95} investigated the domain formation processes of PbTiO3 thin films generated by MOCVD between 550 and 700 °C applying Pb(tmhd)2 and TIP as precursors. The presence of alternating a/c/a/c domain structure on the surface of epitaxial PT films grown on LaAlO3 substrates caused the a-domains to tilt away from the surface normal direction, while domain structure in the LaAlO3 substrate had a direct impact on the domain configuration of PT films.\cite{96}

Table 5. Summary of MOCVD conditions for the deposition of CMRs perovskite materials and their CMR properties.

| Material | Substrate | MOCVD Technique | Dep. Temp. | Precursors | Structure | TC, Tp [K] | Ref. |
|----------|-----------|-----------------|------------|------------|-----------|------------|------|
| LSMO     | LaAlO3 (100); MgO (100); LaAlO3 (100) | RP-MOCVD | 2-step process: 600–800 °C + post annealing 950 °C | La(tmhd)3; Sr(tmhd)3; Mn(tmhd)2 | c-axis oriented | 360, 455 | [81] |
| SrTiO3 (011); LaAlO3 (001) | Liquid delivery MOCVD | 670 °C | La(tmhd)3; Sr(tmhd)3; Mn(tmhd)2 | c-axis oriented | –, – | [82] |
| LaAlO3 (100); SrTiO3 (001); NdGaO3 (001) | Liquid delivery MOCVD | 650–850 °C | La(tmhd)3; Sr(tmhd)3; Mn(tmhd)2 | c-axis oriented | –, 330 | [84] |
| NdGaO3 (001) | Liquid injection MOCVD | 825 °C | La(tmhd)3; Sr(tmhd)3; Mn(tmhd)2 | c-axis oriented | –, – | [85] |
| LCMO | LaAlO3 (100); NdGaO3 (101) | Liquid delivery MOCVD | 600–700 °C | La(tmhd)3; Ca(tmhd)3; Mn(tmhd)2 | c-axis oriented | 270, – | [86] |
| Single Crystal Sapphire, YSZ | Liquid Delivery MOCVD | – | – | – | c-axis oriented | 230, – | [87] |
| LSMCO | LaAlO3 (100); R-Sapphire (01T2) | PI-MOCVD | 750 °C | – | c-axis epitaxial | –360, –360 | [88] |
| PCMO | SrTiO3 (001); SrTiO3 (110); MgO (001); LaAlO3 (001) | LP-MOCVD | 800–100 °C | Pr(hfa)3 diglyme, Ca(hfa)2 tetraglyme Mn(tmhd)3 | 0k0 oriented on SrTiO3 (001), 00l oriented on SrTiO3 (110) | –, – | [51,89] |
film, separated at room temperature, approached each other on growing temperature and produced a single signal at 600 °C, whereas three spots associated with PbTiO$_3$ 202, 220, and 022 fused into one at 500 °C in a 1000 nm film.[97]

An in-depth characterization of epitaxial PbZr$_x$Ti(1–x)O$_3$ thin films is similarly critical to ascertain its fundamental characteristics. Indeed, the nucleation and growth processes of PZT thin films produced by MOCVD on MgO (100) were investigated by Wakiya et al.[98] They observed that in the early stage of development, lateral step-growth arose before 3D expansion, following the Stranski–Krastanov growth model. During this phase, the island coalesced producing 3D islands (nuclei), and the grain size distribution passed through a bimodal transition from monodispersed to the final structure.[98]

Ichinose et al.[99] reported the domain structure transition for very thin Pb(Zr$_{0.05}$Ti$_{0.95}$)O$_3$ films produced on (100) KTaO$_3$ substrates following the same pulsed-MOCVD technique at 600 °C deposition temperature. From the in-plane XRD pattern of PZT on KTaO$_3$ (Figure 8c) measured at room temperature, it was possible to discern four distinct spots at phi ≠ 0 and two spots at phi = 0, which matched in-plane tilted forms of PZT a-domains, as well as the ones of the KTaO$_3$ substrate (Figure 8d). When the measurement temperature was raised up to 500 °C, the two extra diffraction spots at phi = 0 vanished. It was feasible to examine the 3D distribution of domain structures using piezoresponse force microscopy (PFM) measurements of PZT and PT films formed on KTaO$_3$. The PFM analysis of the PZT/KTaO$_3$ heterostructure (Figure 8e) exhibited a complex domain distribution consisting of a/c-domains and a$_1$/a$_2$-domains, whose distribution is strictly related to the temperature (Figure 8f).[99]

BaTiO$_3$ possesses outstanding electrical and electro-optic characteristics, making it particularly appealing for electronic and photonic applications. Various substrates have been used: perovskite-like substrates (LaAlO$_3$ and NdGaO$_3$) were chosen to induce a specific domain growth, while MgO was used for optical applications. In fact, MgO was one of the most commonly utilized substrates due to its low refractive index, cubic crystal structure, excellent microwave properties, and modest cost.
As Ba and Ti precursors, the Ba(dpm)$_2$ and the titanium isopropoxide have been the most frequently used compounds for the deposition of BaTiO$_3$ films.\cite{100-103}

Kwak et al.,\cite{100} who produced polycrystalline BaTiO$_3$ thin films using the reactants Ba(dpm)$_2$, titanium isopropoxide, and O$_2$ as reacting gas, may be credited for being the first group to report on the MOCVD of barium titanate thin films. Deposition took place in an inverted vertical hot-wall reactor at temperatures ranging from 550 to 800 °C with reduced pressure. However, because of the high lattice mismatch and thermal expansion coefficient discrepancies between the film and the substrate, they couldn’t fabricate epitaxial barium titanate films in the investigated temperature range on Al$_2$O$_3$ (102) and NaCl (100) substrates.\cite{100}

Nakazawa et al., used a mixture of these precursors to deposit BaTiO$_3$ on (100) MgO, obtaining a-axis preferentially oriented films.\cite{101} Van Buskirk et al.,\cite{102} investigated the fabrication of BaTiO$_3$ thin films using a commercial PE-MOCVD reactor in order to reduce the deposition temperature. The BT films were deposited on LaAlO$_3$ (001) and NdGaO$_3$ (001) substrates at a temperature of 680 °C, resulting in epitaxial films on both single crystal substrates with no random oriented grains or impurity phases. Kaiser et al.,\cite{103} proposed the first standard MOCVD technique for producing BaTiO$_3$ thin films on MgO (100) at low temperatures (600 °C). They made epitaxial films with the a-axis perpendicular to the substrate surface. According to second harmonic generation statistics, however, the films showed also some c-axis-oriented domains.

To handle the limitation of the Ba(dpm)$_2$ source, other different precursors based on the fluorinated β-diketonate, Ba(hfa)$_2$, moiety were tested. In particular the second-generation Ba(hfa)$_2$tetraglyme was applied as a volatile source of barium by Wills et al.,\cite{104} Encapsulating the metal ion in a sterically saturated environment and fluorinating the ligand are two effective ways for producing precursors with high volatility and stable vapor pressure. Furthermore, the addition of neutral donor ligands, such as polyethers to the metal complex reduces the chance of oligomerization or water coordination. MOCVD deposition of BaTiO$_3$ on LaAlO$_3$ was carried out in the range 600–800 °C, employing this supply of barium and the TIP as source of titanium. The existence of an extra Ba$_2$F$_2$ phase could not be avoided if the deposition temperature was dropped further, for example to 600 or 700 °C.\cite{104}

Since low substrate temperatures are desirable in a traditional MOCVD technique for a variety of reasons, including less interdiffusion between the film and substrate and lower concentrations of undesired thermally activated defects, further studies were carried out using a two-step deposition process to produce BaTiO$_3$ on MgO for microwave applications.\cite{105} The two-stage process of nucleation and growth, using TIP and Ba(hfa)$_2$ PEB (PEB = pentaethyleneglycolethylbutylether) as precursors, included a low-temperature nucleation stage (750 °C) and a high-temperature growth stage (900 °C). Although the morphology was remarkably flat, indicating a layer-by-layer growth, residual tensile strain in the films resulted in a complex polydomain structure (a and c-oriented).\cite{105}

Table 6 outlines the MOCVD processes applied for the deposition of ferroelectric and piezoelectric perovskite thin films. Unfortunately, no specific functional property values are available in the references and only film structural characteristics are reported in Table 6. Using low-pressure MOCVD and pulsed MOCVD, epitaxial and highly oriented PT and PZT films have been effectively produced on a variety of single-crystal substrates, such as LaAlO$_3$, SrTiO$_3$, and MgO, using a mixture of Pb(C$_2$H$_5$)$_4$, titanium isopropoxide, and Zr(O-i-C$_4$H$_9$)$_4$. Improved deposition processes have allowed the production of high-quality films at lower temperatures, up to 550 °C. Single crystal Al$_2$O$_3$, LaAlO$_3$, NdGaO$_3$, and MgO substrates were used to deposit oriented BT films. Reduced pressure and PE-MOCVD with deposition temperatures in the range 600–800 °C and a combination of Ba(thd)$_2$ tetraglyme or Ba(thd)$_2$ and TIP as precursors have been applied.

5. MOCVD Growth of Perovskites on Non-Single Crystal Substrates

By pushing the physical limitations of existing technologies, the various functional characteristics of perovskite-based materials permitted the creation of new, more complex, and miniaturized integrated devices for microelectronic applications.\cite{106}

The MOCVD approach is generally a well-established technique for device integration, such as metal-oxide (MOS) transistors, DRAMs, and ferroelectric (Fe)-RAMs, opto-electronic integrated circuits (OEICs), and so on.\cite{107} For various emerging applications, perovskites are needed in thin-film form on non-perovskite substrates such as Si (100), Pt, or other kinds of bottom electrodes. Specifically, high-k dielectric and ferroelectric films need to be integrated on a range of substrates, including Si (100), Pt, and multilayers, due to their special applications in microelectronic devices, while manganites need to be deposited on YSZ electrolyte pellets.

For this type of applications, there has been a vast variety of high-k perovskite oxide thin films developed, including CaCu$_3$Ti$_4$O$_{12}$\cite{108} (Ba,Sr)TiO$_3$ (BST),\cite{109} Pb(La)TiO$_3$ (PLT),\cite{110-113} LaAlO$_3$,\cite{114} CeAlO$_3$,$^{115}$ BaHfO$_x$,\cite{116} and BaHfTiO$_3$.\cite{117} Thin films of ferroelectric perovskite-based oxides such as BaTiO$_3$,\cite{52} PbTiO$_3$,\cite{118} PZT,\cite{118} Pb(Mg$_{0.5}$Nb$_{0.5}$)$_2$O$_3$ (PMN),\cite{119} Pb$_2$La$_2$TiO$_7$ (PLT),\cite{113,119} SrTiO$_3$,\cite{121,122} NbO$_{1.6}$,\cite{123,124} SrBi$_2$Ta$_2$O$_{9}$ (SBT),\cite{125} and (K$_{0.4}$Na$_{0.6}$)NbO$_3$ (KNN)\cite{126} have been successfully deposited on a variety of substrates, including Pt(111)/SiO$_2$/Si, Pt(100)/MgO(100), Pt/Ti/SiO$_2$/Si multilayers or simple (100)-Silicon wafers.

The ferroelectric property of these materials is well known to be strongly reliant on the electrode materials. Different forms of conductive materials have also been investigated, but ruthenate oxides such as SrRuO$_3$\cite{127} and (Ba,Sr)RuO$_3$\cite{128} are unquestionably the best. Other common conductive perovskites such as LaNiO$_3$\cite{129,130} and LaCoO$_3$ or Sr-doped LaCoO$_3$\cite{131} have been studied as good electrode materials for the deposition of highly epitaxial ferroelectric and piezoelectric oxides in thin-film form.

Because of their significant magnetoresistance (GMR) effects and strong catalytic and electrical characteristics, lanthanum manganite and A-site and B-site doped lanthanum manganites, La$_{1-x}$A$_x$Mn$_{1-y}$B$_y$O$_3$\cite{132} are the most investigated manganites. They can be used in systems such as Solid Oxide Fuel Cells (SOFCs) as well as in the microelectronic field, in devices such as CMRs sensors or ReRAMs.
Due to the wide variety of materials, we will concentrate our efforts on the categories mentioned in the diagram below (Scheme 3).

### 5.1. Superconductors

Despite their historical importance, high-temperature superconducting materials gained a boost in applications when they began to be implemented as thin films on appropriate substrates. Several commercial applications need high-quality YBa$_2$Cu$_3$O$_7$ thin films, which have been efficiently developed on different common substrates like fused silica (SiO$_2$), polycrystalline alumina (Al$_2$O$_3$), Ag, or other technological substrates such as rolling assisted biaxially textured substrates (RABiTS) for coated conductors. In 1991, Zhao et al. reported the first effective synthesis of superconducting $c$-axis oriented YBCO thin films directly on Ag using a PE-MOCVD approach.[133]

MOCVD applications for the deposition of YBCO films on various substrates have frequently been limited by issues with substrate-film interaction. Buffer layers have been grown between the substrate and the superconducting perovskite in order to avoid diffusion between the two. By employing CeO$_2$ as a buffer layer, Studebaker group[134] developed a unique liquid delivery MOCVD process for the deposition of YBCO thin films on silver-coated stainless steel and fused silica substrates in 1995. Metalorganic Y(thd)$_3$, Ba(thd)$_2$ tetraglyme, and Cu(thd)$_2$ precursors were dissolved in an organic solvent and utilized to deposit YBCO films through a liquid delivery system, while Ce(thd)$_4$ was employed to produce CeO$_2$ buffer layer. Unfortunately, they discovered that when the film was formed at 680 °C directly on a silver-coated stainless-steel substrate, the silver tends to diffuse through the film to the surface once the YBCO deposition is completed. The oxygen backfill methodology was changed to limit silver diffusion, and this approach yielded high-quality YBCO films with no silver on the surface. At 77 K and 3 GHz, these films had an extremely low surface resistance of 110 µΩ.

On the other hand, $c$-axis oriented YBCO films were obtained on fused silica with a CeO$_2$ buffer layer generated in Table 6. Summary of MOCVD conditions for the deposition of ferroelectric perovskite materials and their structural properties.

| Material | Substrate | MOCVD Technique | Dep. Temp. | Precursors | Structure | Ref. |
|----------|-----------|-----------------|------------|------------|-----------|------|
| PT       | SrTiO$_3$ (001) | RP-MOCVD       | >700 °C    | Pb(C$_2$H$_5$)$_2$: titanium isopropoxide | $c$-axis-oriented | [91] |
| MgO (001); SrTiO$_3$ (001); LaAlO$_3$ (001) | RP-MOCVD | 700–750 °C | Pb(C$_2$H$_5$)$_2$: Ti(OC$_3$H$_7$)$_4$ | Oriented samples | [92] |
| SrTiO$_3$ (001) | RP-MOCVD | 650 °C | Pb(C$_2$H$_5$)$_2$: Ti(OC$_3$H$_7$)$_4$ | $c$-axis oriented | [93] |
| LaAlO$_3$ (100) | RP-MOCVD | 550–700 °C | Pb(thd)$_2$: Ti(OC$_3$H$_7$)$_4$ | $c$-axis oriented, alternating $a$/c/c domains | [53] |
| MgO (100); NdGaO$_3$ (110) | RP-MOCVD | – | Pb(C$_2$H$_5$)$_2$: Ti(OC$_3$H$_7$)$_4$ | $c$-axis and $a$-axis domains | [95] |
| KTaO$_3$ (001) | Pulsed MOCVD | 580 °C | Pb(thd)$_2$: Ti(OC$_3$H$_7$)$_4$ | $a$-axis oriented | [96] |
| PZT | MgO (100) | RP-MOCVD | >500 °C | PbET-POZ/Zr(dpmm)$_2$POT | $c$-axis oriented | [90] |
| MgO (100) | RP-MOCVD | 650 °C | Pb(C$_2$H$_5$)$_2$: Zr(O-i-C$_4$H$_9$)$_4$: O$_2$ | Epitaxial | [98] |
| KTaO$_3$ (100) | Pulsed MOCVD | 600 °C | Pb(C$_2$H$_5$)$_2$: Zr(O-i-C$_4$H$_9$)$_4$: O$_2$ | $c$-axis and $a$-axis domains | [99] |
| BaTiO$_3$ | Al$_2$O$_3$ (102); NaCl (100) | Vertical MOCVD | 550–800 °C | Ba(dpm)$_2$: Ti(OC$_3$H$_7$)$_4$: O$_2$ | Polycrystalline | [100] |
| MgO (100) | RP-Pressure MOCVD | 800–100 °C | Ba(thd)$_2$: Ti(OC$_3$H$_7$)$_4$: O$_2$ | $a$-axis oriented | [101] |
| LaAlO$_3$ (001); NdGaO$_3$ (001) | PE-MOCVD | 680 °C | Ba(thd)$_2$: tetraglyme; Ti(OC$_3$H$_7$)$_4$ | Mixed 110 and 100 oriented | [102] |
| MgO (100) | RP-MOCVD | 600 °C | Ba(thd)$_2$: Ti(OC$_3$H$_7$)$_4$: O$_2$ | Mixed $a$/c/c-axes | [103] |
| LaAlO$_3$ (001) | RP-MOCVD | 600–800 °C | Ba(hfa)$_2$: tetraglyme; Ti(OC$_3$H$_7$)$_4$: O$_2$ | $a$-axis epitaxial orientation | [104] |
| MgO (100) | RP-MOCVD | Two-step process: low T nucleation 750 °C, high T grow 910 °C | Ba(hfa)$_2$: PEB; Ti(OC$_3$H$_7$)$_4$ | Mixed $a$/$c$/c-axes | [105] |
two steps. At low temperatures, an amorphous layer of CeO$_2$ was deposited, followed by an oriented CeO$_2$ crystalline phase at higher temperatures.$^{[134]}$

The development of superconducting YBCO for applications in technological fields has made significant progress over the years. In particular, second-generation (2G) tapes based on biaxially textured YBCO films, attracted a lot of interest since they offered up new possibilities of manufacturing viable conductors for power applications at high magnetic fields and temperatures.$^{[135,136]}$ The YBCO deposition on technological metallic substrates (RABiTS) requires the use of buffer layers in order to avoid undesirable side reactions. Donet et al.$^{[137]}$ presented the YBCO deposition on different buffer layer architectures epitaxially grown on RABiTS by PI-MOCVD process. This approach enhanced the YBCO characteristics by optimizing different deposition parameters and the stacking order, producing the best YBCO films when deposited ex situ over Ni/CeO$_2$/YSZ/CeO$_2$ heterostructure created by co-evaporation.$^{[137]}$

Caroff et al.$^{[138]}$ on the other hand, tested the pyrochlore La$_2$Zr$_2$O$_7$ (LZO) as a buffer layer since its lattice properties better match those of YBCO and it is a highly refractory material, allowing the creation of more stable interfaces than the ones with CeO$_2$ layer. They described for the first time a single buffer layer architecture created by integrating two chemical processes: MOCVD-deposited YBCO on NiW RABiTS substrate with a single thick layer of LZO$_{MOD}$ on top.$^{[138]}$

Dechoux et al.$^{[139]}$ proposed a combination of metal-organic deposition (MOD) and reel-to-reel MOCVD deposition to fabricate analogs of YBCO coatings directly on LZO$_{MOD}$/Ni wires. Wire substrates with different diameters have been constructed by molding a flat textured substrate covered with LZO using a Nexans-developed process (Figure 9a). The reel-to-reel MOCVD reactor was the first of its kind to be designed specifically for thin film deposition on cylindrical objects. The invention of this unique rotating arrangement has resulted in an increased YBCO homogeneity around the wire. The desired orientation of YBCO along the c-axis was verified through the XRD pattern, and diffraction of both Ni (200) and LZO (004) planes was still evident despite the mechanical deformation applied to the tapes during the shaping process (Figure 9b). They also evaluated the $T_c$ and $J_c$ values on a variety of round samples, including one with a $J_c$ mean value of 0.13 MA cm$^{-2}$ at 77 K and a $T_c$ transition of 90 K. In this regard, because chemical contamination appeared to be the source of the observed low $J_c$ values, the whole buffer layer has been a critical component in preventing NiW species diffusion in the YBCO layer during the deposition.$^{[139]}$ Zhao et al.$^{[140]}$ recently disclosed a unique laser CVD process of YBCO films on Hastelloy C276 substrate multi-coated with CeO$_2$/LaMnO$_3$/MgO/Gd$_2$Zr$_2$O$_7$ with high deposition rates ranging from 10 to 55 µm h$^{-1}$. In this case, ion-beam-assisted deposition and/or PLD were used to create the CeO$_2$, LaMnO$_3$, MgO, and Gd$_2$Zr$_2$O$_7$ buffer layers. Plane views and cross-sectional SEM images of c-axis oriented YBCO films are shown in Figure 9d–g. This orientation was seen to be preserved as the deposition rate increased; however the microstructures of the YBCO films formed at $R_{dep} = 10–32$ µm h$^{-1}$ were different, with a flat surface having some outgrowth grains scattered throughout.

The ratio between the c-axis-oriented grains and the a-axis-oriented grains, in needle-like shape, was nearly half to
half as the deposition rate was increased to 38 µm h⁻¹. Figure 9h,i shows the detailed epitaxial growth mechanism for these a-axis- and c-axis-oriented grains. Finally, the effect of the deposition rate on the $T_c$ and $J_c$ (Figure 9j,k) indicated a decrease of both terms on increasing the deposition rate, with the highest $T_c$ (87–91 K) and $J_c$ (2.2–2.4 MA cm⁻²) at the lowest deposition rate.[140]

The $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ (LBCO) superconducting perovskite has garnered relevant interest among other superconducting cuprates. However, the MOCVD method for LBCO deposition has been given limited attention, with just a few studies focusing entirely on single-crystal perovskites. The possibility to grow the superconducting LBCO system was also developed as homogeneous nanotube arrays through an MOCVD template route on anodized aluminum oxide (AAO) membrane, following an approach similar to that previously used for the deposition of binary oxides.[141,142] Over the past decades, the field of nanotube research has advanced to the stage that materials of essentially any composition can be made into nanotubes with desired sizes and aspect ratios. In this context, the AAO membranes are attractive candidates for use as templates in several applications due to their outstanding characteristics, including stability, transparency, and biocompatibility.[143] To grow uniform LBCO coatings on nanostructured substrates through MOCVD, a homogeneous mixture of La(hfa)₃ diglyme, Ba(hfa)₂ tetraglyme, and Cu(tmhd)₂ has been used as a multicomponent single source, as reported in our previous work for the synthesis of thin films.[10] LBCO nanotubes on AAO membranes have been deposited by using a reduced pressure MOCVD approach and a deposition temperature of 800 °C. The LBCO layer conformally covered the whole nanostructured surface as can be seen in the FE-SEM images (Figure 10a,b) following the morphologies of the nanotubes membrane, reported in the AFM images (Figure 10d,e). The EDX mapping (Figure 10c) confirms the presence of all the components and the homogeneous distribution of the elements in the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ phase. This synthetic approach has a lot of potential for MOCVD deposition of functional films on nanostructured and complex surfaces.

Table 7 depicts the MOCVD procedures employed for the deposition of superconducting perovskite thin films produced on various substrates. PI-MOCVD and, more recently, laser MOCVD have enabled the fabrication of polycrystalline or oriented YBCO thin films on a variety of substrates, ranging from simple silica to technological metallic substrates. In the case of PI-MOCVD, the precursors used for the deposition of such films are generally single metal β-diketonates dissolved in an appropriate solvent and combined in a proper molar ratio.

![Figure 10. $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ deposited on AAO membranes: a,b) FE-SEM images at different magnitudes; c) EDX mapping of the elements composing the LBCO phase; d,e) AFM images of the AAO membranes.](image-url)
Tc values achieved for YBCO thin films are relatively high and comparable to those found for epitaxial films formed on single-crystal substrates.

5.2. Dielectrics and Giant-k Dielectrics

The calcium-copper-titanate CaCu3Ti4O12 (CCTO), discovered by Subramanian et al. [108] in the early 2000s, is now well recognized as one of the perovskites with the greatest dielectric constant, above 10^5 at 1 kHz, that remains almost unaltered until 300°C, deserving it the nickname “giant-k”. The group of Lo Nigro et al. developed for the first time an MOCVD approach for the fabrication of high epitaxial CCTO thin films on single crystal LaAlO3, and then on industrially relevant substrates, such as the SiO2/Si, Si3N4/Si and the Pt/TiO2/SiO2/Si(100) multilayer stack, which is extensively used as a bottom electrode for dielectrics. The CCTO films were grown in two steps: 1) an MOCVD deposition process using a multi-component source of Ca(hfa)2 tetraglyme, Cu(tmhd)2, and Ti(tmhd)2(O-iPr)2 precursors in a 1:1:3 stoichiometric ratio; 2) a post-annealing process that resulted in the formation of polycrystalline film on Pt/TiO2/SiO2/Si(100) substrate. The development of the pure CCTO phase without impurities was confirmed by the XRD pattern (Figure 11a), while the FE-SEM images (Figure 11b) indicated a homogeneous morphology over the surface for a 750°C deposition temperature. The dielectric constant was measured by fabricating a planar metal-insulator-metal (MIM) capacitor with an upper Pt electrode sputtered on the CCTO layer and a photolithographic lift-off technique to finish the device. The values of the dielectric constants at 1 MHz remain unchanged across a large temperature range, rising significantly beyond 350 K, as shown in Figure 11c. In any case, the total values for the CCTO-as-dep and CCTO-annealed

| Material         | Substrate                        | MOCVD Technique       | Dep. Temp. | Precursors                              | Tc [K] | Ref. |
|------------------|----------------------------------|-----------------------|------------|-----------------------------------------|--------|------|
| YBCO             | Ag                               | PE-MOCVD              | 700°C      | Cu(dpm)2; Y(dpm)3; Ba(dpm)2             | 85     | [133]|
| CeO2/silver-coated stainless steel; CeO2/fused silica | Liquid-delivery MOCVD | 680°C | Cu(thd)2; Y(thd)3; Ba(thd)2 tetraglyme | >90    | [134]|
| RABITS            | Liquid-delivery MOCVD            | 680°C                  | Cu(thd)2; Y(thd)3; Ba(thd)2 tetraglyme | >90    | [134]|
| La2Zr2O7/Al2O3    | PI-MOCVD                         | 775–810°C             | Cu(tmhd)2; Y(tmhd)3; Ba(tmhd)2 | =89    | [137]|
| LZO               | PI-MOCVD                         | 800°C                  | Cu(tmhd)2; Y(tmhd)3; Ba(tmhd)2 | 91     | [138]|
| Hastelloy C276    | Nd:YAG Laser MOCVD               | 600°C                  | Cu(dpm)2; Y(dpm)3; Ba(dpm)2 | 87–91  | [140]|
| CeO2/LaMnO3/MgO/Gd2Zr2O7 | PI – reel-to-reel MOCVD  | 800°C                  | Cu(tmhd)2; Y(tmhd)3; Ba(tmhd)2 | 90     | [139]|

Figure 11. a) XRD pattern of CCTO deposited on Pt/TiO2/SiO2/Si(100) multilayer substrate; b) FE-SEM image of the film annealed at 750 °C; c) C–V measurement on a Pt/CCTO/[Pt/TiN/SiO2/Si(100)] at 1 MHZ as a function of temperature. Adapted with permission. [72] Copyright 2006, American Chemical Society. d) Composition of the Ba and Ti ion ratio as a function of the temperature for the formation of BST films; e) XRD pattern of BST film before and after annealing at 700 °C under Ar and O2; f) Cross-sectional SEM images of BST films deposited at 400 °C. Adapted with permission. [141] Copyright 2001, The Electrochemical Society.
MOCVD production of (Ba,Sr)TiO₃ (BST) films on various substrates with a variety of morphologies, spanning from amorphous to nanocrystalline, is well documented in the literature. Thin films of BST have become one of the most widely used ceramic materials as well as dielectric substrates for integration in microelectronic devices (ULSIs, DRAMs, etc.), due to its high dielectric constant, ease of integration into device processes, low leakage current, and lack of deterioration over time. In the MOCVD manufacturing of BST thin films, high deposition temperatures have typically been used, and throughout the course of the years, a range of metal diketonate precursors have been explored to improve the film characteristics. For instance, the group of Gao et al. [146] in the early 2000s, had successfully fabricated BST thin films on Ir/Si and Pt/Si multilayer substrates at 650–700 °C by using two different sets of precursors. Because the first set of Ba(tmhd)₂, Sr(tmhd)₂, and Ti(tmhd)₃ precursors have comparable reactivities, the final precursors. Because the first set of Ba(tmhd)₂, Sr(tmhd)₂, and Ti(tmhd)₃ precursors have comparable reactivities, the final film composition is almost equivalent to the original mixture. The second set, which included Ba, Sr, and Ti β-diketonates with different reactivities, required more Ti precursors to get stoichiometric BST. This fact also impacted the overall step coverage, which for the latter did not surpass 50%. The microstructure and morphology of the films were also affected by the nature of the substrate. In fact, films on Pt/Si substrates displayed good crystalline quality and low surface roughness, but on Ir/Si substrates, the issue of Ba and Sr segregation resulted in nonuniform surface composition. Nevertheless, the previously mentioned high-temperature MOCVD deposition of BST caused several challenges, particularly when it came to integrating these systems, particularly into DRAM devices. As a result, research groups began to explore low-temperature MOCVD approaches, first facing some processing issues such as the existence of amorphous films, contaminants, compositional irregularities, and so on. The group of Hwang et al. [147] effectively fabricated for the first time BST thin films, starting from a mixture of Ba(methd)₂, Sr(methd)₂ (Hmethd = methoxyethoxytetramethylpentanedione), and Ti(mdp)(thd)₃, (dpd = methylpentanedioxy), on SiO₂/Si and Pt/SiO₂/Si wafers at low temperatures (420–470 °C). The dome MOCVD reactor used in the study, allowed to regulate both wafer and wall temperatures, resulting in an identical composition of BST on both the wafer and even on a patterned substrate. With the same precursors, Lee et al. [148] deposited BST films on Pt/SiO₂/Si wafers by a liquid injection MOCVD (LI-MOCVD) process, using methanol as solvent. However, as mentioned before, while Ba(methd)₂, Sr(methd)₂ exhibits a comparable reactivity and volatility, the titanium precursors may not completely dissolve from the ligands, suggesting a possible negative effect on the film structure, with the formation of humps or a hazy appearance (Figure 11d). The films were deposited at 440 °C, however, only after annealing at 700 °C under Ar and O₂ gases, the crystallinity of the BST film was somewhat improved (Figure 11e). The cross-sectional SEM image of the BST films on the trench pattern with an aspect ratio of 3.5 confirmed a good deposition conformity (Figure 11f).

The MOCVD processes used to make giant-k and high-k perovskite thin films on various substrates are shown in Table 8. No specific functional property values are available in the references and given the variety of film structural characteristics no data are included in Table 8. In order to manufacture higher quality films, reduced pressure MOCVD techniques with a single step or two different phases of annealing have been used to make CCTO and BST thin films on various heterostructure substrates. For the deposition of BST layer on such technical heterostructures, lower deposition temperatures are necessary. Thus, low-temperature MOCVD and liquid injection MOCVD were used to reduce the deposition temperature to 420 °C. However, because such films are basically amorphous, a subsequent annealing step at a higher temperature is always required to crystallize them.

### 5.3. Conductors

Manganites are unquestionably the most notable of the several ceramic compounds with conducting characteristics. Because of its excellent electrical conduction and good ionic oxide transport, strontium-doped lanthanum manganite, La₁₋ₓSrₓMnO₃ (LSMO), has been investigated as a promising cathode material in solid oxide fuel cell (SOFC) systems, since it is stable at high working temperatures and has improved catalytic activity for hydrocarbon combustion. It has a comparable thermal expansion coefficient as the most widely used solid yttria-stabilized zirconia (YSZ) electrolyte, allowing it to be directly deposited as thin film. In this regard, Wang et al. [149] devised a PE-MOCVD process of LSMO on YSZ, starting with a mixed aerosol of La(NO₃)₃, Sr(NO₃)₂, and Mn(NO₃)₂ as precursors. They added glycerine as an additive to the initial nitrate solution, which helped the nitrate decomposition and allowed

### Table 8. Summary of MOCVD conditions for the deposition of high-k perovskite materials.

| Material       | Substrate | MOCVD Technique   | Deposition Temperature | Precursors | Reference       |
|----------------|-----------|-------------------|------------------------|------------|-----------------|
| CCTO           | SiO₂/Si; Si₃N₄/Si; Pt/TiO₂/Si; SiO₂/Si(100) | RP-MOCVD | 2-step process: a) 600 °C + b) 900 °C in situ annealing | Ti(tmhd)₂; [Op]t; Ca(hfa)₂; tetracylglyme; Cu(tmhd)₂ | [144,145] |
| (Ba,Sr)TiO₃    | Ir/Si; Pt/Si | Low pressure Hot-wall MOCVD Reactor | 650–700 °C | Ba(tmhd)₂; Sr(tmhd)₂; Ti(tmhd)₁ | [146] |
| SiO₂/Si; Pt/SiO₂/Si | Low temperature MOCVD | | 420–470 °C | Ba(methd)₂; Sr(methd)₂; Ti(mdp)(thd)₁ | [147] |
| Pt/SiO₂/Si     | LI-MOCVD   | | 440 °C | Ba(methd)₂; Sr(methd)₂; Ti(mdp)(thd)₁ | [148] |
the creation of pure LMSO phase on the YSZ substrate.\textsuperscript{[149]} Toro et al.\textsuperscript{[150]} later established a simple and low-cost method for depositing La\(_{1-x}\)Sr\(_x\)MnO\(_3\) thin films on YSZ pellets, represented in Figure 12a, using a mixture source of the La(hfa)\(_3\) diglyme, Sr(hfa)\(_2\) tetraglyme, and Mn(tmhd)\(_3\) precursors. The FE-SEM images, reported in Figure 12b–d, showed a homogeneous morphology of LSMO films deposited on YSZ pellet. The very large grains (a few \(\mu\)m wide), visible in the low magnification image under the nanostructured grain (hundreds of nanometers) distribution, were due to the YSZ grains. An accurate tuning of the deposition conditions allowed to play with the nucleation and growth processes, thus favoring growth versus nucleation and resulting in the production of thick, porous and homogeneous layers, essential characteristics for SOFC electrode applications. In particular, depositions with lower oxygen flows produced a limited number of nucleation centers with very small grains which grew to produce a porous network. The XRD pattern of an as-deposited sample on YSZ electrolyte is shown in Figure 12e. The pattern confirms the presence of monoclinic La\(_{0.8}\)Sr\(_{0.2}\)MnO\(_3\) phase reflections. The low cost and simplicity of the synthetic method make this technique intriguing as a production pathway for LSMO films, which might be used as cathode in SOFCs.\textsuperscript{[150]}

Dense membranes, made from materials with mixed electronic–ionic conductivity (MIEC) that work without an external electrical field, have a significant potential for technological application in oxygen separation. They are typically constructed of extremely porous ceramic supports on which catalytic layers can be deposited to improve reaction kinetics. The group of Abrutis et al.\textsuperscript{[151]} made the first attempt to employ La(Sr,Ca) MnO\(_3\) manganites as catalytic layers for MIEC compounds. They produced relatively thick layers of different perovskite oxides such as the LSMO or LCMO on different porous commercial substrates using PI-MOCVD at different deposition temperatures and starting with a mixture of metal \(\beta\)-diketonate precursors. However, early testing revealed that building completely gas-tight membranes of these perovskite materials on basic porous alumina substrates was quite difficult.\textsuperscript{[151]}

Manganites have also attracted a lot of attention as a memristive material because of their outstanding switching responsiveness. However, integrating them into CMOS-compatible substrates like silicon wafers is difficult. Rodriguez-Lamas et al.\textsuperscript{[48,152]} recently developed three different growth strategies to control the oxygen content (\(\delta\)) and Mn oxidation state of the active LaMnO\(_{3+\delta}\) material and to tune its transition from an orthorhombic to a rhombohedral phase. They deposited LMO films on commercial platinized silicon using PI-MOCVD approach, with a solution of La(thd)\(_3\) and Mn(thd)\(_3\) dissolved in m-xylene. Transmission electron microscopy (TEM) images were taken for samples deposited with a single-step strategy at temperatures ranging from 650 to 700 °C, as well as samples deposited with a two-step strategy, which...
included a first deposition step at a lower temperature followed by a second deposition step at 750 °C. Both films crystallized satisfactorily, however for the double-step strategy, the cross-section revealed more irregular columns, which was likely due to the difference in growth temperature between the two phases (Figure 12f). The XRD patterns of LMO films produced using these diverse deposition processes, shown in Figure 12g, indicate that all diffraction peaks may be attributed to the polycrystalline LMO perovskite phase. The fabrication of the MIM device, obtained by evaporating squared Au electrodes and reported in Figure 12h, allowed validation of the LMO films through resistive switching cycles (Figure 12i), thus confirming their applicability in ReRAM devices.[152]

The application of perovskite metal oxide materials with ferroelectric or superconductive properties, such as PbTiO3, Pb(Zr,Ti)O3, or YBCO, to Si-based microelectronics has been extensively studied. It is well known that the ferroelectric property of the lead titanate films is highly dependent on the electrode material. SrRuO3 is an electrically conductive metal oxide with a perovskite structure that has attracted a lot of interest as a buffer layer and, at the same time, bottom electrode for ferroelectric and superconducting materials. Breitkopf et al.[153] published the first report on the MOCVD of SrRuO3 on Si (111) and α-alumina in 1997, starting with a mixture of Sr(tmhd)2 as a source of strontium and bis(2,4-dimethylpentadienyl)ruthenium as a source of ruthenium. Unfortunately, the resulting film was made up of three distinct phases: SrRuO3, Sr2RuO6, and RuO2, with a relatively high resistance.[153] A few years later, Okuda et al.[127] explored the idea of improving the composition control by using different metalorganic precursors of Sr and Ru, Sr(tmhd)2 (tetraethylenepentamine)2 and Ru(tmhd)3 for the deposition of SrRuO3 prepared using a cold-wall CVD reactor. They discovered that the Ru/(Ru+Sr) ratio had a significant impact on the resistivity of films deposited at 750 °C.[127]

A method suggested by Lee et al.[154] in which SrRuO3 films deposited on (100) Si were created by sequential deposition of ruthenium oxide and strontium oxide starting from Sr(thd)2 and Ru(C5H5)2, might be used to better regulate the composition. By depositing its component oxides individually, the molar ratio of Sr and Ru can be regulated, and the two oxides can then react at high temperatures.[154] A few years later, Minamidate et al.[155] used a conventional MOCVD approach to deposit SRO layers on Ru/SiO2 substrates by using the same precursors proposed by Okuda et al.[127] They looked at the effect of composition, specifically the Sr/(Sr+Ru) ratio, on the crystallinity, surface roughness, and electrical properties of MOCVD grown PZT films deposited on them and discovered that, in the case of Ru-excess, the SRO films were essentially made of RuO2, and then the Pt/PZT/Sr–Ru–O/Ru capacitor had the greatest leakage. Although the film displayed the presence of the SrRuO3 phase in the case of Ru-deficiency, the capacitor realized with stoichiometric SRO layers had larger remanent polarization and low leakage characteristics, demonstrating that the best bottom electrode for 3D capacitors is a stoichiometric grown SrRuO3 film.[155]

Table 9 describes the MOCVD techniques exploited to deposit conductive perovskite thin films on various substrates. PE-MOCVD, reduced-pressure MOCVD, and PI-MOCVD have been used to create polycrystalline LSMO and LMO films on a range of technical substrates, including polycrystalline YSZ and pellets. The deposition temperature necessary to generate such crystalline films is rather high; it mostly relies on the used MOCVD process utilized. In the case of PE-MOCVD, lower deposition temperatures (570–650 °C) are sufficient to obtain polycrystalline LSMO films with excellent ionic conductivity. Reduced pressure and PI-MOCVD, on the other hand, necessitate a higher temperature, mostly between 650 and 900 °C.

Reduced pressure MOCVD has also been applied for the deposition of oriented SRO conducting layers on various heterostructures, such as (111)Pt/InO3/SiO2/Si, or single (100)Si substrates, at deposition temperatures in the 400–800 °C range.

### 5.4. Colossal Magnetoresponse

Multimetal manganites (La1−xAlxMnO3, A = alkaline-earth ion) have drawn special attention since their discovery because of their CMR characteristics, in addition to their ionic conductivity. Fabrication of manganites on various substrates, such as Si, YSZ, or MgO, is very desirable for hybrid integration in view of an application perspective. Indeed, the growth of an oriented or polycrystalline film is strongly reliant on the type

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**Table 9. Summary of MOCVD conditions for the deposition of conducting perovskite materials.**

| Material | Substrate | MOCVD Technique | Dep. Temp. | Precursors | Ref. |
|----------|-----------|-----------------|------------|------------|------|
| LSMO     | Polycrystalline YSZ | PE-MOCVD | 570–650 °C | La(NO3)3; Sr(NO3)2; Mn(NO3)2; glycerine | [149] |
|          | YSZ pellets | RP-MOCVD | 880–980 °C | La(hfa)3 diglyme; Sr(hfa)2 tetraglyme; Mn(tmhd)3 | [150] |
| Different porous substrates | Platinized silicon | PI-MOCVD | 650–700 °C | La(thd)3; Mn(thd)3 | [151] |
| SrRuO3   | Si (111); α-alumina | RP-MOCVD | 650–700 °C | Sr(tmhd)2; bis(2,4-dimethylpentadienyl) ruthenium | [152] |
|          | (111)Pt/InO3/SiO2/Si | cold-wall CVD | 750 °C | Sr(tmhd)2 (tetraethylenepentamine)2; Ru(tmhd)3 | [127] |
|          | (100) Si | RP-MOCVD | 550–800 °C | Sr(tmhd)2; Ru(C5H5)2 | [154] |
|          | SiO2/Si | RP-MOCVD | 400 °C | Sr(tmhd)2 (tetraethylenepentamine)2; Ru(C5H5)2 | [155] |
of used substrate; for example, using a non-oriented substrate causes the film to grow randomly, whereas using an oriented substrate causes the film to grow along a preferred orientation. It was discovered that the type of substrate may also influence the temperature range at which significant values of MR may be observed. Dobourdieu et al. published a study on the relationship between the La$_{1-x}$Sr$_x$MnO$_3$ (LSMO) manganite polycrystalline film structure and its magneto-transport properties. The polycrystalline films were prepared at deposition temperatures ranging from 500 to 750 °C on Si/SiO$_2$ substrates. Magnetization and resistivity curves of polycrystalline and epitaxial LSMO samples showed a very different transport behavior, while the Curie temperature ($T_C$) was nearly comparable for both microstructures ($T_C$ of 340 K for epitaxial films and $T_C$ of 325 K for polycrystalline films). Furthermore, the nature of the interfaces, rather than the grain size, appears to be the most critical factor in determining low-field MR.

Integration of manganites in silicon-based technology necessitates the use of low deposition temperatures, which are limited, for a thermally activated process like conventional MOCVD, by precursors decomposition temperatures and the potential formation of undesirable phases. Nevertheless, Dubourdieu et al. tested the possibility to grow functional manganite at temperatures below 500 °C, by using the PI-MOCVD technique. The β-diketonates La(thmd)$_3$, Sr(tmhd)$_3$, phen (phen = 1,10-phenanthroline), and Mn(tmhd)$_3$ were dissolved in monoglyme. Unfortunately, only amorphous films were obtained at 450 °C, so several post-annealing treatments (ranging from 650 to 900 °C) were experimented to accomplish crystallization and recover magnetoresistive characteristics. Zero-field cooled and field-cooled (0.05 T) magnetization measurements, performed on an amorphous film, indicated that the film was in a spin-glass-like state at low temperature with an irreversibility temperature of 120 K (Figure 13a). It was observed that by modifying the post-annealing process, the resistivity could be decreased by two orders of magnitude (Figure 13b), while maintaining a low-field MR on the order of 20% (at 22 K under 0.2 T).

Žurauskiene et al. devised a similar PI-MOCVD technique for the deposition of La$_{1-x}$Ca$_x$MnO$_3$ (LCMO) films, with lower $T_C$ than LSMO, that can be used in sensors operating at cryogenic temperatures. For the films with different composition, the starting precursor mixture was made up with a solution of La(thd)$_3$, Sr(thd)$_3$, Ca(thd)$_2$, and Mn(thd)$_3$, and deposited on polycrystalline lucalox (99.9% Al$_2$O$_3$ + 0.1% MgO) substrates. It was shown that LCMO films had greater MR values and lower relative residual resistivity than LSMO films at low temperatures (80–100 K), while the latter possessed the highest MR values at room temperature. The same group recently published an article on the PI-MOCVD deposition of polycrystalline LSMO on unique disordered glass-ceramic substrates, describing how to tune their resistivity and MR by varying the film characteristics or the deposition conditions. The experimental procedure involved the use of La(thd)$_3$, Sr(thd)$_3$, and Mn(thd)$_3$ as precursors, dissolved in toluene. It was shown that the thicknesses and deposition temperatures affected the shape and microstructure of the LSMO films, as well as their CMR properties, demonstrating that these nanostructured films, due to their disordered grain boundaries, behave as superparamagnetic materials with reduced magnetic properties. More specifically, the resistivity and MR plots for films of various thicknesses (Figure 13c) and deposition temperatures (Figure 13d) reveal that these factors have a significant impact on the film properties. The electrical characteristics of a thin film are strongly influenced by its thickness at a given transition temperature, with a thinner film having the lowest metal–insulator transition temperature and the highest resistivity. Furthermore, unlike epitaxial films, which have strong MR values only near

Figure 13. LSMO films: a) magnetization (after field cooled and zero-field cooled) measured as a function of temperature for a film deposited at 450 °C on silicon; b) Resistivity measured as a function of temperature for manganite amorphous films crystallized under different conditions. Adapted with permission. Copyright 2002, AIP Publishing. c,d) Temperature dependences of resistivity and MR for LSMO films of various thicknesses and produced at different temperatures; e,f) Dependence of MR on magnetic flux density for films of various thicknesses and produced at different temperatures. Adapted with permission. Copyright 2018, Springer.
the metal-like to insulator transition ($T_m$), such nanostructured films have substantial MR values over a wide temperature range down to very low temperatures, with the highest MR values at lower temperatures being obtained for the thinnest and amorphous films. Because of the higher metal–insulator transition temperature, thicker films exhibit higher MR values at high temperatures, although the MR decreases drastically below the transition temperature $T_m$. Actually, the resistivity and MR dependences for 400-nm-thick manganese films produced at various deposition temperatures are comparable to the dependences on film thickness. Figure 13e,f demonstrates the MR dependence on magnetic flux density.

The greatest MR values may be achieved at room temperature ($T = 290$ K) by using films with the highest metal–insulator transition temperatures (i.e., samples prepared at 750 °C with a thickness of 280 nm). One of the most striking features of film dependence upon applied magnetic field was that MR did not achieve saturation until 20 T. This may be explained by the fact that much stronger magnetic fields are necessary to align the magnetic moments of the Mn ions in a disordered material. The possibility to construct CMRs LSMO films with B-site doping was also studied. Žurauskienė et al. in 2017[154] reported the results of a room temperature MR analysis of nanosynthesized Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ (LSMO) films with varied cobalt content, comparing them to the LMSO films. The presence of Co as a B-site dopant ion causes the ferromagnetic order of Mn to be destroyed, resulting in changes in the magnetic and electrical properties of the manganite. A solution of La(tmhd)$_3$, Sr(tmhd)$_3$, Mn(tmhd)$_3$, and Co(tmhd)$_3$ in monoglyme, was employed in the PI-MOCVD technique for the fabrication of LSMCO films on Al$_2$O$_3$ substrate. It was discovered that at the transition temperature $T_m$, the resistivity versus temperature dependences for all examined films showed a change from a metal-like to an insulator-like state. The $T_m$ lowered as the Co content increased, whereas the resistivity maximum tends to increase.[155]

Another intriguing manganite is the Pr(1–$x$)Ca$_x$MnO$_3$ (PCMO) phase, which has the property of having a significant resistance shift when an electric pulse is applied and might be utilized for the next-generation resistive non-volatile memory (ReRAM). The MOCVD fabrication of PCMO films with the desired atomic composition was reported by Nakamura et al.[156] The feasibility of developing PCMO films at low temperatures was examined since hybrid integration of such perovskite material on silicon demands low deposition temperatures. The precursors Pr(dpm)$_3$, Ca(dpm)$_2$, and Mn(dpm)$_3$, dissolved in THF, were employed as source materials in the liquid-assisted MOCVD process. In PCMO-based devices, the resistance variation was influenced by the film composition and the type of metal electrodes used.[157] Later, the same group proved that in PCMO-based systems, the metal electrode plays an essential role in resistance switching, thus for applications of PCMO in ReRAM devices the best metal electrodes need to be selected. Indeed, DC current–voltage measurements and AC impedance spectroscopy were used to investigate the electrical characteristics of PCMO-based devices with Ni and Al electrodes. In the Ni-based devices, current changed linearly with applied voltage, but I–V curves for Al-based devices showed nonlinear behavior. The discrepancy in I–V characteristics is thought to be due to the work function of the electrode metals.[158]

It is critical to monitor reactions that occur in the gas phase in an MOCVD process, especially if done at low temperatures, and even more so for the deposition of complex films. Nakamura et al.[159] had more recently demonstrated the possibility to study in situ via infrared spectroscopy the PI-MOCVD process for the deposition of Pr(1–$x$)Ca$_x$MnO$_3$ films on Si substrates. They were able to evaluate the thermal decomposition of rare-earth and manganese precursors in the gas phase, finding that the rate of decrease in infrared absorbance of the Pr(dpm)$_3$ remained practically constant even when Mn(dpm)$_3$ was introduced, while the thermal decomposition of La(dpm)$_3$ was accelerated in the presence of Mn(dpm)$_3$. The current findings on rare-earth precursor gas-phase behavior may be useful in interpreting the complicated development mechanism of rare-earth manganite films.

The MOCVD procedures used to make CMRs perovskite films on various substrates are described in Table 10, together with related properties, if available in the original papers. Alkaline-earth doped lanthanide manganites, having CMR, have been produced on a variety of substrates, including SiO$_2$/Si, lucalox, and polycrystalline Al$_2$O$_3$. The MOCVD procedures employed to make these films are predominantly PI-MOCVD, in which an appropriate solvent is used to dissolve a mixture of single metal β-diketonate precursors in a proper ratio, and the resulting solution is then delivered within the reactor zone. Typical deposition temperatures are about 750 °C. To produce PCMO films on SiO$_2$/Si substrate a liquid-assisted MOCVD with a deposition temperature of 480 °C has been employed. $T_c$ and $T_p$ values are mainly correlated to the doping amount and not to the applied deposition technique.

| Material | Substrate | MOCVD Technique | Dep. Temp. | Precedors | $T_c$, $T_p$ [K] | Ref. |
|----------|-----------|-----------------|-----------|-----------|----------------|-----|
| LSMO     | SiO$_2$/Si| RP-MOCVD        | 500–750 °C| La(tmhd)$_3$, Sr(tmhd)$_3$, Mn(tmhd)$_3$ | 323, 230 | [157] |
|          | SiO$_2$/Si| PI-MOCVD        | 450 °C + annealing (650 to 900 °C) | La(tmhd)$_3$, Sr(tmhd)$_3$, phen; Mn(tmhd)$_3$ | –, – | [158] |
|          | Special glass ceramic substrate | PI-MOCVD | 750 °C | La(tmhd)$_3$, Sr(tmhd)$_3$, Mn(tmhd)$_3$ | –, 235 | [160] |
| LCMO     | lucalox   | PI-MOCVD        | 750 °C | La(thd)$_3$, Sr(thd)$_3$, Ca(thd)$_3$, Mn(thd)$_3$ | –, 220 | [159] |
| LSMCO    | polycrystalline Al$_2$O$_3$ | PI-MOCVD | 750 °C | La(thd)$_3$, Sr(thd)$_3$, Ca(thd)$_3$, Mn(thd)$_3$, Co(thd)$_3$ | –, 275 | [161] |
| PCMO     | SiO$_2$/Si| Liquid assisted MOCVD | 480 °C | Pr(dpm)$_3$, Ca(dpm)$_2$, Mn(dpm)$_3$ | –, – | [29a,162,163] |
5.5. Piezoelectric and Ferroelectric

Lead-based perovskites PbTiO$_3$ (PT) and Pb(Zr,Ti)O$_3$ (PZT) were among the first ceramic ferroelectrics to be developed for use in microelectronic and optoelectronic circuits. These materials must have strong structural and electrical properties in order to be used in such devices and the choice of the substrate is critical since a suited, well-matched substrate is required for device integration and epitaxial growth. In fact, it is important to note that the electrical characteristics of functional ferroelectrics are directly connected to the epitaxial quality of films. Unfortunately, the epitaxial quality of ferroelectric oxide films grown on Si semiconductors is extremely difficult according to the large misfit between the two materials.\textsuperscript{[164]} In addition, a bottom electrode is needed, thus Pt/Ti/SiO$_2$/Si and RuO$_2$/SiO$_2$/Si are the most used substrates. These Si-based substrates require low deposition temperatures to avoid any degradation problems at the interface between the substrate and the film-forming material. Most MOCVD techniques for producing PT films were based on high-temperature processes till the early 2000s. The first MOCVD deposition of PT and PZT using a mixture of metalorganic precursors such as Pb(C$_2$H$_5$)$_4$ (TEL), Zr(O-$t$C$_4$H$_9$)$_4$, and Ti(O-$i$C$_3$H$_7$)$_4$ (TIP), was published in 1988 by the group of Okada et al.\textsuperscript{[90]} A few years later, in 1994, with the introduction of $\beta$-diketonate precursors, Hendriks et al.\textsuperscript{[165]} employed for the first time Ti(OEt)$_4$, as a titanium source, and Pb(eth)$_2$, as a source of lead, which, in contrast to the liquid TEL precursor, had the benefit of being less toxic and rather stable at ambient temperature. Unfortunately, due to the high film conductivities, most film electrical characteristics were found to be quite weak, with some hysteresis loops, occasionally observed, that did not appear to be fully saturated.\textsuperscript{[165]}

By following the procedure of deposition developed by the group of Okada,\textsuperscript{[90]} epitaxial film of PT and PZT were deposited on Pt(111)/SiO$_2$/Si and Pt(100)/MgO(100) multilayers by Shimizu et al.\textsuperscript{[118]} The resulting films were epitaxial and their crystalline structure was strongly dependent on composition, which can be mainly controlled by adjusting the ratio of precursors supplied to the chamber.\textsuperscript{[118]} Particularly, Roessinger et al. have proven that at temperatures greater than 650 °C, the [Pb]/[Ti] ratio in the films approaches unity, while remaining independent of the [Pb]/[Ti] gas phase composition.\textsuperscript{[166]}

Nevertheless, lower deposition temperatures are mandatory to avoid any degradation problems at the interface between the substrate and the film-forming material. For example, utilizing the $\beta$-diketonate Pb(eth)$_2$ and TIP as precursors, Kim et al. reported a low-temperature MOCVD procedure for depositing PbTiO$_3$ on p-InP substrates. The films deposited at 320 °C revealed a polycrystalline PT structure, however, epitaxial domains were found near the PbTiO$_3$/p-InP (100) heterointerface.\textsuperscript{[165]} Wang et al. deposited a partially crystalline phase of PT at slightly higher deposition temperatures (400 °C) on a (111)-Pt/Ti/SiO$_2$/Si and a well-oriented a- and c-axis PbTiO$_3$ films on (200)-Pt/SiO$_2$/Si using different Pb/Ti ratios. In fact, the microstructure of polycrystalline PT samples was totally reliant on the initial composition of the Pb and Ti precursors, due to the favored absorption of the lead species at the first stage of film formation.\textsuperscript{[168,169]} In some cases, an annealing treatment was required to improve the quality of the films, as for the process which described an aerosol-assisted CVD (AA-CVD) method for depositing PbTiO$_3$ films onto (001) Si substrate, starting with an equal mixture of Pb-acetate(II) trihydrate and Ti(IV) oxacetylacetonate in methanol. Amorphous samples were deposited up to 400 °C, but an annealing treatment at high temperatures (800 °C) produced excellent quality and homogenous PbTiO$_3$ thin films with a perovskite-type structure.\textsuperscript{[170]}

Ferroelectricity in PT and PZT have been proved to be influenced by their grain size. It is feasible to assess the relationship between spontaneous polarization and grain size/film thickness. In fact, it has been demonstrated that the polycrystalline PbTiO$_3$ had preferential 90° domains with a tetragonal phase, exhibiting simple lamella twinning across grains that could have spontaneous polarization.\textsuperscript{[171]} This hypothesis was supported by a research conducted by Shimizu et al.\textsuperscript{[172,173]} on the growth mechanism of PT and PZT on various substrates. According to the piezoresponse measurements, they discovered that the Volmer–Weber growth mode was the main growth mechanism for samples deposited on (111)-Pt/SiO$_2$/Si, and that PT and PZT islands with dimensions less than 100 nm possessed ferroelectricity even before coalescence to form films.\textsuperscript{[172,173]}

Since MOCVD has been shown to be a good deposition technique for PT and PZT films, attention has lately moved to synthesize novel precursors in order to produce a single molecule that is both volatile and contains all of the required components for creating the appropriate phase. For instance, Veith et al.\textsuperscript{[174]} synthesized two single-sources of lead/ titanium and lead/zirconium, the [Et$_3$Pb(OtBu)Zr(OtBu)$_4$] and the [Et$_3$Pb(OtBu)Ti(OtBu)$_4$], with similar physical characteristics and complement miscibility, which they applied as a mixture to obtain a quasi-single-source precursor allowing PZT depositions on Pt/Ti/SiO$_2$/Si at low temperatures followed by a post-annealing treatment at 650 °C. Under these conditions, smooth (100) oriented PZT perovskite films (Figure 14a), with residual polarization of 20 μC cm$^{-2}$ (Figure 14b) were obtained.\textsuperscript{[174]} Manoor et al.\textsuperscript{[175]} on the other hand, produced a single heterobimetallic precursor, that is, the [PtTi($t$-$O$)$_3$CCF$_3$]$_2$(THF)$_2$[$\mu$-$t$-$O$]$_2$ complex, tested to deposit PT films with an AA-CVD process at 500 °C on FTO-coated glass substrates. They obtained crystaline PbTiO$_3$ with a bandgap of 3.69 eV, which may be employed for a variety of future technological purposes.\textsuperscript{[175]}

Kim et al.\textsuperscript{[176]} recently developed a set of lead (IV) precursors with phenyl ligands, such as Ph$_3$Pb, Ph$_5$Pb(bts)$_2$ (bts = bis(trimethylisilyl)amide), and Ph$_5$Pb(eth)$_2$, to make ferroelectric Pb(Zr$_{0.53}$Ti$_{0.47}$)O$_3$ thin films at 550 or 700 °C on a Si wafer (Figure 14c). Ph$_5$Pb(eth)$_2$ was chosen because of its increased volatility and stability. The PZT thin film deposited at 550 °C, (Figure 14d) showed a surface with very tiny grains, while the thin film prepared at 700 °C was found to be more crystalline (Figure 14e).\textsuperscript{[176]}

Another very interesting material that needs to be synthesized as an epitaxial layer on Si substrate is the BaTiO$_3$ perovskite phase. Reinke et al.\textsuperscript{[52]} devised an interesting approach for obtaining epitaxial ferroelectric BT films on Si substrate for integrated metal-oxide–semiconductor (CMOS) manufacturing, which comprised a high vacuum (HV)-CVD approach with low deposition temperatures (400 °C), using Ba($t$Pr$_3$Cp)$_2$, TIP, and water or oxygen as reactants.
The XRD pattern (Figure 15a) showed that they were able to deposit epitaxial BaTiO$_3$ films with the same orientation of the MgO and SrTiO$_3$ buffer layers grown on Si substrate when water was used as reactant gas; while when oxygen was used as reactant gas no crystalline barium titanate was formed. Reciprocal space mappings for the (002) out-of-plane, (200) in-plane, and asymmetrical (103) reflections aided in determining overall BaTiO$_3$ layer quality and comparing depositions on various buffer layers, leading to the conclusion that BaTiO$_3$ on MgO layer had significantly greater mosaicity than the ones grown on the SrTiO$_3$ substrate (Figure 15b). The silicon-barium titanate interface, which consists of an amorphous silicon oxide layer and a crystalline strontium titanate buffer layer, is shown in Figure 15c. Years later, using the same deposition method, Borzì et al.$^{[177]}$ investigated the effect of the Ba and Ti organic precursor flow rates and ratios on the microstructure of the BT film. The layers stack is represented in Figure 15d, and it consisted of a silicon substrate on which a SrTiO$_3$ buffer layer was placed using MBE and epitaxial BT films were grown on top of it using the HV-CVD method. Particularly, the Ba(Pr$_3$Cp)$_2$ and TIP flux ratio, was the most affecting parameter and ensured the finest crystalline quality of epitaxial BaTiO$_3$ thin films on SrTiO$_3$-buffered Si substrates. As illustrated in Figure 15e, the samples showed a single phase with only (k00) orientation from the films, with a shoulder on the BT (200) reflection (Figure 15f), most likely due to the superposition of the SrTiO$_3$ (002) reflection from the buffer layer. Therefore, BT films were strongly out-of-plane oriented along the a-axis. The Williamson–Hall plot approach was used to determine the tilt mosaicity of the BT crystalline domains (Figure 15g), and the average value of the rocking curves was compared finding a good match between these two estimations. As a consequence, the W–H plot method (often used for polycrystalline materials) was demonstrated to work with these epitaxial films.$^{[177]}$

Table 11 lists the MOCVD processes used to deposit piezoelectric and ferroelectric perovskite thin films on various substrates. Over the years, plain silicon and a range of technical multilayer substrates, including Pt(111)/SiO$_2$/Si, (111)-Pt/Ti/SiO$_2$/Si, and RuO$_2$/SiO$_2$/Si, have been used to produce polycrystalline or oriented PT and PZT films. Different MOCVD techniques, such as reduced-pressure MOCVD and AA-MOCVD have been used at low deposition temperatures in order to prevent any degradation at the interface between the substrate and the material. Nevertheless, although the deposition temperatures used in these processes are lower than 500 °C, post-annealing treatments are, in certain cases, applied to crystallize the formed amorphous layer. The AA-MOCVD process has been employed to increase the volatility of metalorganic precursors of Pb, Ti, and Zr. The functional properties of these materials such as the coercitive field ($E_c$) and residual polarization ($P_r$), reported in Table 11, are strictly related to the composition more than to the applied deposition process.
6. Conclusions and Outlook

This review reports a wide summary of MOCVD approaches to fabricate perovskite thin films with various functional properties: superconductors, CMR materials, high-k and giant-k dielectrics, conductors, piezoelectrics, and ferroelectrics.

From the presented overview, we can derive the following conclusions:

a) MOCVD is a powerful technique for the deposition of complex oxides containing from two to four, or even more, different elements;

b) Table 11. Summary of MOCVD conditions for the deposition of piezoelectric perovskite films and their functional properties.

| Material | Substrate | MOCVD Technique | Dep. Temp. | Precursors | E_c [kV cm\(^{-1}\)] | P_r [\mu C cm\(^{-1}\)] | Ref. |
|----------|-----------|------------------|------------|------------|----------------------|----------------------|-----|
| PT/PZT   | Pt/Ti/SiO\(_2\)/Si; RuO\(_x\)/SiO\(_2\)/Si | RP-MOCVD | 550 °C | Ti(O\(_2\)Et\(_2\)); Pb(thd)\(_2\) | 45, 1.1 | [165] |
| Pt(111)/SiO\(_2\)/Si; Pt(100)/MgO(100) | RP-MOCVD | 530–670 °C | Pb(C\(_2\)H\(_5\))\(_4\); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\) | – | [118] |
| Pt/Ti/SiO\(_2\)/Si | RP-MOCVD | 650 °C | Pb(C\(_2\)H\(_5\))\(_4\); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\) | – | [166] |
| p-InP     | Low temperature MOCVD | 320 °C | Pb(tmhd)\(_2\); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\) | – | [167] |
| (111)-Pt/Ti/SiO\(_2\)/Si; (200)-Pt/SiO\(_2\)/Si | RP-MOCVD | 400 °C | Pb(tmhd)\(_2\); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\) | – | [168,169] |
| (001) Si  | AA-MOCVD | 400 °C + post annealing treatment 800 °C | Pb-acetate(II) trihydrate; Ti(IV) oxacetylacetone | – | [170] |
| (111)-Pt/SiO\(_2\)/Si | RP-MOCVD | 340–450 °C | Pb(C\(_5\)H\(_5\)O\(_2\)J\(_2\)); Zr(O\(_3\)C\(_3\)H\(_7\))\(_4\); | 63, 4.2 | [172,173] |
| Pt/Ti/SiO\(_2\)/Si | RP-MOCVD | 350–500 °C + post annealing 650 °C | [Et\(_3\)Pb(O\(_3\)Bu)Zr(O\(_3\)Bu)\(_2\)]; [Et\(_3\)Pb(O\(_3\)Bu)\(_2\); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\); | 250, 15–20 | [174] |
| FTO-coated glass | AA-MOCVD | 500 °C | [PbTi\(_2\)(O\(_3\)CCF\(_3\))(THF)]\(_2\); [PbTi\(_2\)(O\(_3\)Bu)\(_2\); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\); | – | [175] |
| Si       | RP-MOCVD | 500–700 °C | Pb\(_2\)Pb; Pb\(_2\)Pb(bta)\(_2\); Pb\(_2\)Pb(thd)\(_2\); Zr(O\(_3\)OPr); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\) | – | [176] |
| BT       | Si       | HV-CVD | 400 °C | Ba\(_2\)(P\(_2\)Cp)\(_2\); Ti(O\(_3\)C\(_3\)H\(_7\))\(_4\) | – | [52,177] |
b) Precursor nature plays a pivotal role in the success of described MOCVD processes, either conventional or liquid assisted (pulsed injection or aerosol assisted);
c) Perovskite layers are easily grown on perovskite or other kinds of single-crystal substrates, being the film/substrate match and the deposition temperature the driving forces of the process;
d) An accurate optimization of the deposition procedure, either through a two-step route or using a suited buffer layer, allows the fabrication of perovskite films on Si and on non-single-crystal substrates;
e) An accurate optimization of the different deposition processes is required to produce highly oriented or epitaxial films for certain applications into electronic devices based on silicon technology.

In perspective, MOCVD represents a key approach in the wide landscape of oxide perovskite synthetic methodologies. Based on the current literature data, the reported chemical vapor deposition approaches pave the way for their massive use both in industrial applications, in which the CVD processes are already a well-established technology for the fabrication of metal and oxide materials in form of thin film, and in the academic community, in which the possibility to modulate perovskite features in terms of structure and composition, and, in turn, functional properties represents a main advantage of the MOCVD approach.

In general, we can conclude that whatever the material, even the most complex in terms of metal composition, may be grown through MOCVD; the quality of the layer can be finely tuned playing with the used metalorganic precursors, the operational parameters, and overall, the process optimization. In fact, the possibility of further implementation, in terms of synthesis of more complex systems, such as multi-doped perovskite-based materials at the A and B sites, and the possibility of extending the MOCVD approach to other oxide perovskites such as BiFeO₃, NaNbO₃, KNbO₃, and (Na,K)NbO₃ systems, represents the most challenging future direction in this research field. In fact, the BiFeO₃, NaNbO₃, KNbO₃, and (Na,K)NbO₃ perovskite thin films are among the most appealing and innovative systems in the current scientific panorama of lead-free piezoelectric and ferroelectric materials.

In this context, an accurate engineering and thermal property investigation of novel metalorganic precursors would provide a further step in the MOCVD technology of complex systems. In fact, currently, one of the main bottlenecks of the process is represented by the need for novel and suitable metalorganic compounds, which fit the CVD requirements and conditions.

In summary, this review provides an important reference for the MOCVD fabrication of perovskite films and presented data confirm the huge potentiality of the technique in growing this type of layers on single-crystal substrates and non-single-crystal substrate

**Conflict of Interest**

The authors declare no conflict of interest.

**Keywords**

multifunctional materials, perovskites, single-crystal substrates, thin films, tolerance factor

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**References**

[1] C. Moure, O. Peña, *Prog. Solid State Chem. 2015*, 43, 123.

[2] a) A. Kojima, K. Teshima, Y Shirai, T. Miyasaka, *J. Am. Chem. Soc. 2009*, 131, 6050; b) N. Wang, W. Liu, Q. Zhang, *Small Methods* 2018, 2, 1700380; c) P-Y. Gu, N. Wang, C. Wang, Y Zhou, G. Long, M. Tian, W. Chen, X. W. Sun, M. G. Kanatzidis, Q. Zhang, *J. Mater. Chem. A* 2017, 5, 7339.

[3] J. P. Atfield, *Cryst. Eng. 2002*, 5, 427.

[4] M. Shaikh, A. Fathima, M. J. Swamyndhan, H. Das, S. Ghosh, *Chem. Mater. 2021*, 33, 1594.

[5] E. A. R. Assirey, *Saudi Pharm. J. 2019*, 27, 187.

[6] M. Choi, I. A. M. Ibrahim, K. Kim, J. Y. Koo, S. J. Kim, J.-W. Son, J. W. Han, W. Lee, *ACS Appl. Mater. Interfaces 2020*, 12, 21494.

[7] T. Chen, R. Ramachandran, S.-M. Chen, G. Anushya, S. D. Rani, V. Mariappan, P. Elumalai, N. Vasimalai, *Nanomaterials* 2021, 11, 1006.

[8] A. A. Demkov, J. E. Ortmann, M. Reynaud, A. K. Hamze, P. Ponath, W. Li, *Phys. Status Solidi B 2021*, 258, 2000497.

[9] R. W. Schwartz, *Chem. Mater. 1997*, 9, 2325.

[10] R. John, B. M. S. M. D. Bath, B. Lukowiak, W. Strek, A. Zarkov, A. Kareiva, *J. Sol-Gel Sci. Technol. 2020*, 93, 650.

[11] H. Wu, X. Zhu, *Perovskite Materials – Synthesis, Characterization, Properties, and Applications* (Eds: L. Pan, G. Zhu), IntechOpen, London, UK 2016.

[12] F. Weiss, M. Audier, A. Bartasyte, D. Bellet, C. Girardot, C. Jimenez, J. Kreisel, S. Pignard, M. Salaun, C. Ternon, *Pure Appl. Chem. 2009*, 81, 1523.

[13] D. M. Mattox, *Handbook of Physical Vapor Deposition (PVD) Processing*, 2nd ed., Elsevier, Amesterdam NL 2010.

[14] a) *Chemical Vapor Deposition: Precursors, Processes and Applications* (Eds: A. C. Jones, M. L. Hitchman), Royal Society of Chemistry Publishing, London 2009; b) H. O. Pierson, *Handbook of Chemical Vapor Deposition Principles, Technology and Applications*, 2nd ed., Elsevier, Amesterdam NL 1999.

[15] R. J. D. Tilley, *Perovskites: Structure-Property Relationships*, John Wiley & Sons Inc., Chichester, West Sussex, UK 2016.

[16] A. R. West, *Solid State Chemistry and its Applications*, John Wiley & Sons, Chichester, West Sussex, UK 2014.

[17] M. Goldschmidt, *Naturwissenschaften 1926*, 4, 1477.

[18] R. D. Shannon, *Acta Crystallogr., Sect. A: Found. Crystallogr. 1976*, 32, 751.

[19] S. Li, J. T. S. Irvine, *Solid State Ionics 2021*, 361, 115351.

[20] J. G. Bednorz, K. A. Muller, Z. Phys. B 1986, 64, 189.

[21] K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, C. W. Chu, *Phys. Rev. Lett. 1987*, 58, 908.

[22] H. Kumakura, K. Togano, *Solid State Ionics 1990*, 64, 125.

[23] H. A. J. T. W. Jong, *Appl. Phys. Lett. 1968*, 54, 2064.

[24] Z. Z. Sheng, A. M. Hermann, *Nature 1988*, 332, 55.

[25] C. C. H. N. T. Vogt, S. M. Shapiro, S. Awamoto, A. P. Ramirez, *Science 2001*, 293, 673.
[25] C. Dubourdieu, I. P. Senator, F. Weiss, Crystal Growth in Thin Solid Films: Control of Epitaxy (Eds.: M. Guillon-Viry, A. Perrin), Research Signpost, Kerala, India 2002, pp. 169–206.

[26] J. Wright, M. J. Crosbie, P. A. Lane, D. J. Williams, A. C. Jones, T. J. Leedham, H. O. Davies, J. Mater. Sci.: Mater. Elect. 2002, 13, 671.

[27] L. G. Hubert-Pfalzgraf, H. Guillou, Appl. Organomet. Chem. 1998, 12, 221.

[29] Q. Micard, A. L. Pellegrino, R. Lo Nigro, A. Bartasyte, G. Condorelli, G. Malardino, J. Mater. Chem. C 2020, 2020, 8, 16168.

[a] T. Nakamura, Phys. Status Solidi C 2015, 12, 958; b) C. Tsakonas, M. Dimitropoulos, A. C. Manikas, C. Galliot, Nano尺度 2013, 13, 3461.

[30] G. Malardino, L. M. S. Perdicaro, G. Condorelli, I. L. Fragalà, A. Cassinese, M. Barra, J. Mater. Chem. 2005, 15, 4718.

[31] C. S. Chern, J. Zhao, Y. Q. Li, P. Norris, B. Kear, B. Gallois, Z. Kalman, Appl. Phys. Lett. 1991, 58, 183.

[32] O. Y. Gorbenko, A. R. Kaul, I. V. Pogosova, S. N. Polyakov, E. V. Kolosova, S. A. Pozigun, V. I. Scritny, Mater. Sci. Eng. 1998, 19, 157.

[33] P. Zhao, A. Ito, R. Tu, T. Goto, Appl. Surf. Sci. 2011, 257, 4317.

[34] S. V. Samoylenkov, O. Y. Gorbenko, I. E. Graboy, A. R. Kaul, Y. D. Tretyakov, J. Mater. Chem. 1996, 6, 623.

[35] T. Nakamura, R. Kita, O. Miura, A. Ichinose, K. Matsumoto, Y. Yoshida, M. Mukaida, S. Horii, Phys. C 2008, 468, 1542.

[36] K. Endo, P. Badica, J. Itoh, Phys. C 2003, 386, 323.

[37] K. Endo, S. Arisawa, T. Kaneko, I. Tsuyomoto, Y. Tateno, P. Badica, IEEE Trans. Appl. Supercond. 2016, 26, 1.

[38] G. Malardino, D. S. Richeson, T. J. Marks, D. C. DeGroot, J. L. Schindler, C. R. Kannewurf, Appl. Phys. Lett. 1991, 58, 182.

[39] G. Malardino, L. M. S. Perdicaro, I. L. Fragalà, A. M. Testa, D. Fiorani, Chem. Mater. 2004, 16, 608.

[40] R. Lo Nigro, R. G. Toro, G. Malardino, M. Bettinelli, A. Speghini, I. L. Fragalà, Adv. Mater. 2004, 16, 891.

[41] T. Tohma, H. Masumoto, T. Goto, Jpn. J. Appl. Phys. 2003, 42, 6969.

[42] I. M. Kuzmina, A. Alikhanyan, D. Tsymbarenko, K. Lyssenko, O. Kreinin, G. Shuster, E. Lakin, E. Zolotoyakbo, Chem. Vap. Deposition 2009, 15, 342.

[43] A. Feil, B. W. Wessels, L. M. Tonge, T. J. Marks, J. Appl. Phys. 1990, 67, 3858.

[44] G. Malardino, P. Scardi, I. L. Fragalà, Chem. Mater. 1998, 10, 3765.

[45] H. Funakubo, S. Okamato, S. Yokoyama, S. Okamoto, J. Kimura, H. Uchida, J. Materiomics 2015, 1, 188.

[46] O. Y. Gorbenko, A. A. Bosak, J. Cryst. Growth 1998, 186, 181.

[47] A. Sumi, Y. K. Kim, N. Oshima, K. Akiyama, K. Saito, H. Funakubo, Thin Solid Films 2005, 486, 182.

[48] R. Rodríguez-Lamas, C. Pirovano, A. Stangl, D. Pla, R. Jönsson, L. Rapenne, E. Sarigiannidou, N. Nuns, H. Roussel, O. Chai-Pluchery, M. Boudard, C. Jiménez, R. Vannier, M. Burriel, J. Mater. Chem. A 2021, 9, 12721.

[49] R. G. Toro, G. Malardino, L. M. S. Perdicaro, D. M. Florito, A. Andreone, G. Lamara, I. L. Fragalà, Chem. Vap. Deposition 2010, 16, 143.

[50] M. R. Catalanino, R. G. Toro, A. Gulino, G. Malardino, Surf. Coat. Technol. 2013, 230, 174.

[51] M. R. Catalanino, G. Cucinotta, E. Schillirò, M. Mannini, A. Caneschi, R. Lo Nigro, E. Smecce, G. Condorelli, G. Malardino, Chemistry-Open 2015, 4, 523.

[52] M. Reineke, Y. Kuzminykh, F. Eltes, S. Abel, T. LaGrange, A. Neels, J. Fompeyrine, P. Hoffmann, Adv. Mater. Interfaces 2017, 4, 1700116.

[53] B. M. Yen, H. Chen, J. Appl. Phys. 1999, 85, 833.

[54] H. Chen, J. Lin, K. Tan, Z. Feng, B. Kwak, A. Erbil, MRS Online Proc. Libr. 1997, 493, 493.

[55] T. Matsuzaki, H. Funakubo, J. Appl. Phys. 1999, 86, 4559.

[56] M. R. Catalanino, G. Spedalotto, G. G. Condorelli, G. Malardino, Adv. Mater. Interfaces 2017, 4, 1601025.

[57] A. D. Berry, D. K. Gaskill, R. T. Holm, E. J. Cukauskas, R. Kaplan, R. L. Henry, Appl. Phys. Lett. 1998, 52, 1743.

[58] J. Zhao, P. Norris, Thin Solid Films 1991, 206, 122.
Fluorides, using MOCVD or solution routes, for energy harvesting and energy conversion.

She is currently a Ph.D. student in Materials Science and Nanotechnology under Prof. I. L. Fragalà’s supervision. Her research focuses on the synthesis, engineering, and characterization of lanthanide-doped fluoride thin films for energy conversion processes, hybrid organic-inorganic systems, and inorganic perovskites as active materials in photovoltaics and characterization of Metal-Organic Frameworks doped with luminescent ions.

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