


Low-Temperature Solution Approaches for the Potential Integration of Ferroelectric Oxide Films in Flexible Electronics

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Abstract—This technical review presents the state of the art in low-temperature chemical solution deposition (CSD) processing of ferroelectric oxide thin films. To achieve the integration of multifunctional crystalline oxides with flexible and semiconductor devices is, today, crucial to meet the demands of coming electronic devices. Hence, amorphous metal–oxide–semiconductors have been recently introduced in thin-film electronics. However, their benefits are limited compared with those of ferroelectric oxides, in which intrinsic multifunctionality would make possible multiple operations in the device. However, ferroelectricity is linked to a noncentrosymmetric crystal structure that is achieved, in general, at high temperatures, over 500 °C. These temperatures exceed the thermal stability of flexible polymer substrates and are not compatible with those permitted in the current fabrication routines of Si-based devices. In addition, the manufacturing of flexible electronic devices not only calls for low-temperature fabrication processes but also for deposition techniques that scale easily to the large areas required in flexible devices. In this regard, CSD processes are the best positioned today to integrate metal oxide thin films with flexible substrates as a large-area, low-cost, high-throughput fabrication technique. Here, we review the progress made in the last years in fabricating at low-temperature crystalline ferroelectric oxide thin films via CSD methods, highlighting the recent work of our group in the preparation of ferroelectric oxide thin films on flexible polyimide substrates.

Index Terms—Ferroelectric applications: actuators, capacitors, DRAM, Fe RAM, imaging, long wire IR thermal sensing, sensors and transducers, ferroelectric materials: composite forms, polycrystalline solids, polycrystal thin film, polymers and single crystal, integrated ferroelectrics.

I. INTRODUCTION

THE 1990's trend toward the miniaturization of functional devices driven by the microelectronic industry led to the development of thin-film materials integrated with semiconductor substrates (Si-technology), able to use their properties in micro and nanodevices with high integration densities and

low operation voltages [1], [2]. However, since the beginning of this century, the electronic industry is demanding cost-efficient, soft-portable, and high-tech devices. This has pushed the advance of Flexible Electronics, where the thin film is supported on cheap flexible substrates (e.g., polymers, paper, or textile) [3]–[5]. These substrates would also meet technological demands difficult to tackle by semiconductor substrates, such as their compatibility with roll-to-roll processing and printing technologies, making real applications not possible before (e.g., smart skin, flexible displays, photovoltaic cells, or eye-type imagers) [6]–[9].

Conventional microelectronic integration routines with semiconductor substrates use a maximum temperature limit of ~500 °C. The degradation temperature of flexible substrates is always below 400 °C [10]. Therefore, Flexible Electronics is calling for low-temperature thin-film fabrication methods in addition to materials that can be processed at these temperatures. Nowadays, organic and amorphous metal–oxide–semiconductors are the most widely used materials in Flexible Electronics [4], [5]. However, other active layers different from semiconductors are increasingly demanded before the need of enlarging the performance of the forthcoming flexible devices [1], [2], [7]. This shows as an opportunity for ferroelectric oxide thin films since their intrinsic multifunctionality (e.g., ferroelectric, pyroelectric, piezoelectric, multiferroic, or photoferroic) would make possible multiple operations in the flexible device. However, in general, high temperatures are needed to crystallize these oxide films, which can produce the noncentrosymmetric ferroelectric crystal structure, and this is usually attained by thermal treatments at high temperatures (over 500 °C). These temperatures exceed by far the thermal stability of the most favorable flexible substrate (i.e., Kapton polyimide with a decomposition temperature of ~400 °C) [7], [10] and are not even compatible with the processing temperatures permitted in Si-based devices [11], [12]. Besides, most of the ferroelectric oxide compositions contain volatile elements (e.g., lead, bismuth, and alkalis) that are partially volatilized during the thermal treatment, leading to a possible loss in the stoichiometry of the oxide and to the formation of undesired nonferroelectric phases [13], [14]. All these contribute to the damage of the ferroelectric response of the film. These handicaps could be overcome with the use of organic ferroelectrics that can be processed at relatively lower temperatures. However, they present fabrication and performance limitations [15], [16].

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It should be also taken into account that the manufacturing of flexible electronic devices not only calls for low-temperature fabrication processes but also for deposition techniques that scale easily to the large areas required in flexible devices. In general, physical deposition techniques, such as pulsed laser deposition (PLD), RF-magnetron sputtering, or atomic layer deposition, permit to attain high-quality ferroelectric oxides on single-crystal substrates. However, a relatively few numbers of articles have been published about the low-temperature preparation of ferroelectric oxide films by physical deposition techniques [17]–[22], and even scarcer are those that report the use of flexible substrates [21], [23]–[25]. Therefore, different approaches have been developed since 2010 about how to transfer high-quality crystalline films grown at high temperatures on single-crystal substrates to flexible substrates [26]. Ferroelectrics such as $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT), BiFeO_3 (BFO), [27]–[32], or even the unconventional ferroelectric oxide based on doped HfO_2 (HFO), [33], [34] have been successfully prepared on thin polymer substrates by these transferring methods. However, these procedures are far from being efficient in the fabrication of large-area, flexible arrays, and the need of complex manufacturing methods and expensive equipment. In this regard, solution deposition methods are the best positioned today to integrate metal oxide thin films with flexible substrates, as a large-area, low-cost, high-throughput fabrication technique [1], [3], [35]–[38].

The deposition of thin films from solutions usually can be carried out under mild conditions [ambient pressure and the so-called chemical solution deposition (CSD)] or under high pressures (hydrothermal and solvothermal methods). The latter makes possible the deposition of the film at low temperatures, even room temperature (not reported in the case of ferroelectric oxides), but they are difficult to apply to the large areas demanded in Flexible Electronics. In addition, hydro/solvothermal synthesis for ferroelectric oxides involves two steps: nucleation and crystal growth. They are relatively easy to be achieved on single-crystal substrates with crystal structures close to that of the oxide film. However, this does not occur on polymer (or amorphous) ones, where seed (nucleation) layers have to be previously deposited on the surface of the substrate [39]–[46]. To the best of our knowledge, only Shiraishi *et al.* [39] have reported the hydrothermal preparation of KNbO_3 (KNN) ferroelectric thin films on flexible polysulfone substrates with a remanent polarization of $P_R \sim 4.2 \mu\text{C}\cdot\text{cm}^{-2}$ [39]. In this article, a LaNiO_3 perovskite seed layer is deposited by RF-magnetron sputtering on the electroded substrate (Pt/Ti/polysulfone), before the growth of the ferroelectric perovskite. Electrochemical deposition or hydrothermal–electrochemical synthesis has also been used to prepare at low-temperature ferroelectric oxide films, but these techniques are limited to the deposition of the film on conductive substrates [47].

CSD methods are highly flexible for the fabrication of ferroelectric oxide thin films although they have not been able to reach until now the low processing temperatures ($<250^\circ\text{C}$) achieved by hydro/solvothermal synthesis (see Fig. 1) [11], [12], [14], [39], [40], [44], [46], [48]–[73].

Fukushima *et al.* [74], Dey *et al.* [75], and Budd *et al.* [76] were among the first that demonstrated the successful fabrication of ferroelectric oxide thin films [PbTiO_3 , $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, PZT, and $(\text{Pb},\text{La})(\text{Zr},\text{Ti})\text{O}_3$] by CSD on silicon substrates, by the end of the last century. These films were annealed at temperatures over 600°C , showing P_R values higher than $20 \mu\text{C}\cdot\text{cm}^{-2}$. These studies were the basis for a rapid expansion of the research in CSD-deposited ferroelectric oxide thin films [37].

In the context of the low-temperature CSD fabrication of metal oxide thin films, important efforts are being devoted nowadays to the processing of semiconductors, looking for their successful integration with flexible, large-area, low-cost electronics [3]–[5]. Thin-film transistors of amorphous binary oxides (e.g., ZnO or In_2O_3) have been deposited directly on cheap, bendable substrates using temperatures around 250°C and showing an electrical performance comparable to the dominant amorphous–silicon semiconductor. For more complex systems, such as those based on ternary or quaternary amorphous oxides (e.g., In_2O_3 – Ga_2O_3 – ZnO), high carrier mobilities are also possible using low processing temperatures [5], [35], [77]–[81].

During the last years, the group of Prof. Calzada (female) has carried out an ambitious investigation in the field of the low-temperature crystallization of ferroelectric oxide thin films by CSD methods. We have attained for these films the 400°C integration barrier (see Fig. 1), which has given us access to the direct deposition of ferroelectric oxides on flexible polyimide substrates [11], [12], [72]. Different solution strategies have been developed in our group mostly inspired in the large knowledge accumulated in a few years in the ambit of the flexible semiconductor oxide films. However, also, we have been encouraged by the outstanding studies reported by the end of the 1990s [50], [61], [82]–[87] that were driven by the necessity of finding CSD-based paths for the integration of ferroelectric oxides with the Si-technology (see Fig. 1).

The next sections of this technical review will show the most relevant CSD approaches reported in the literature to attain ferroelectric oxide thin films at low temperatures, on a road to achieve the integration of these multifunctional oxides with Flexible Electronics.

II. CHEMICAL SOLUTION DEPOSITION OF METAL OXIDE THIN FILMS

Conventional CSD processing of crystalline metal oxide thin films involves four main steps where the film evolves through different structural stages (see Fig. 2): 1) the synthesis of the precursor solution produced by the reaction among metal reagents, solvents, and other chemicals, stage (i); 2) the deposition of this solution on a substrate by a coating technique (e.g., spin coating, dip coating, spray coating, etc.), which leads to a wet layer, stage (ii); 3) the elimination of the organic compounds from the former layer (e.g., evaporation, pyrolysis), leading to condensation among the metal compounds and densification of the first obtained amorphous metal–oxygen network, stage (iii); and 4) conversion to the crystalline metal

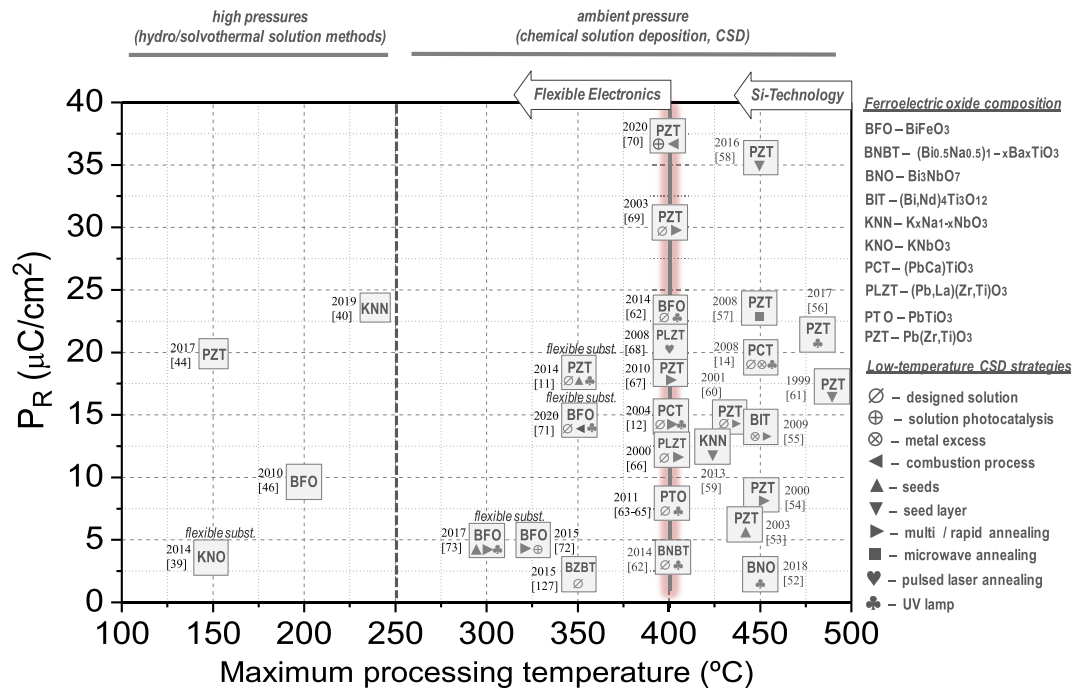


Fig. 1. Summary of the relevant results (from the point of view of the authors) reported in the literature on ferroelectric oxide thin films prepared from solutions at low temperatures. Only works including ferroelectric hysteresis behavior are referenced in this figure. The graphic shows the ferroelectric composition of the film, the processing temperature at which they were processed, and the ferroelectric remanent polarization (P_R) measured in them. The CSD strategy/strategies used for the low-temperature solution processing of the films are also shown. References of the corresponding publications together with the year of publication are included. Flexible subst. indicates that the films were directly deposited on flexible polymer substrates. Maximum processing temperature that can be used for the integration of films with Si substrates (Si-Technology) and flexible substrates (Flexible Electronics) are shown. Hydro/solvothermal methods (high pressures) have been successfully used for the preparation of ferroelectric oxide films below 250 °C. To the best of our knowledge, films with ferroelectric response (P_R) have not been attained until now at so low temperatures by CSD methods.

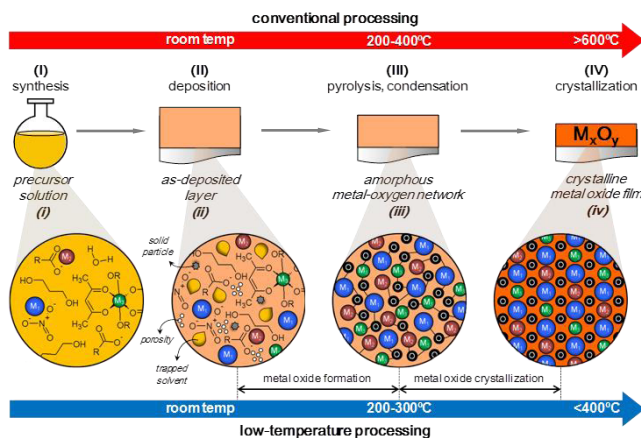


Fig. 2. Diagram showing the main steps (I–IV) of the CSD preparation of thin films. Different stages attained in the film during its conversion from the solution deposited layer to the final metal oxide crystalline film are indicated as (i)–(iv) [7]. Published with permission of the Royal Society of Chemistry.

oxide film, stage (iv), usually carried out by annealing at high temperatures (over 600 °C) (see Fig. 2) [1], [7], [37], [88].

CSD methods have the advantages mentioned in Section I over other depositions techniques, besides an accurate control of the film stoichiometry and a relatively easy preparation of complex oxide films. Major handicaps of CSD processing are related to the high temperatures that should be applied to the solution deposited layer to overcome different structural stages

indicated in Fig. 2, thus, to attain the full conversion into a crystalline film. These high temperatures hinder the CSD preparation of these films on heat-sensitive substrates.

For ferroelectric oxide thin films, these processes become more complex. While the crystallization of the ferroelectric phase mainly occurs well above 500 °C, intermediate non-ferroelectric oxides, such as pyrochlore or fluorite-type phases, are just stable below this temperature [1], [37], [89]. Therefore, low-temperature treatments of solution derived layers usually lead to films in which an incipient ferroelectric phase is immersed in an amorphous matrix that contains organic residuals and second phases. As a result, the ferroelectric response of these films is spoiled.

In the following, different CSD strategies reported in the literature for reducing the crystallization temperature of ferroelectric oxide thin films will be discussed [7], [90].

III. LOW-TEMPERATURE CSD METHODS FOR FERROELECTRIC OXIDE THIN FILMS

The interest in the preparation of ferroelectric oxide thin films at low temperatures was initially driven by the Si-technology when, at the beginning of this century, the transition to the sub-100-nm devices and the introduction of nickel silicide contacts forced the reduction of the temperature limit permitted in microelectronic routines below 500 °C (see Fig. 1). In the last decade, we have witnessed a renewed interest in the low-temperature processing of metal oxide thin

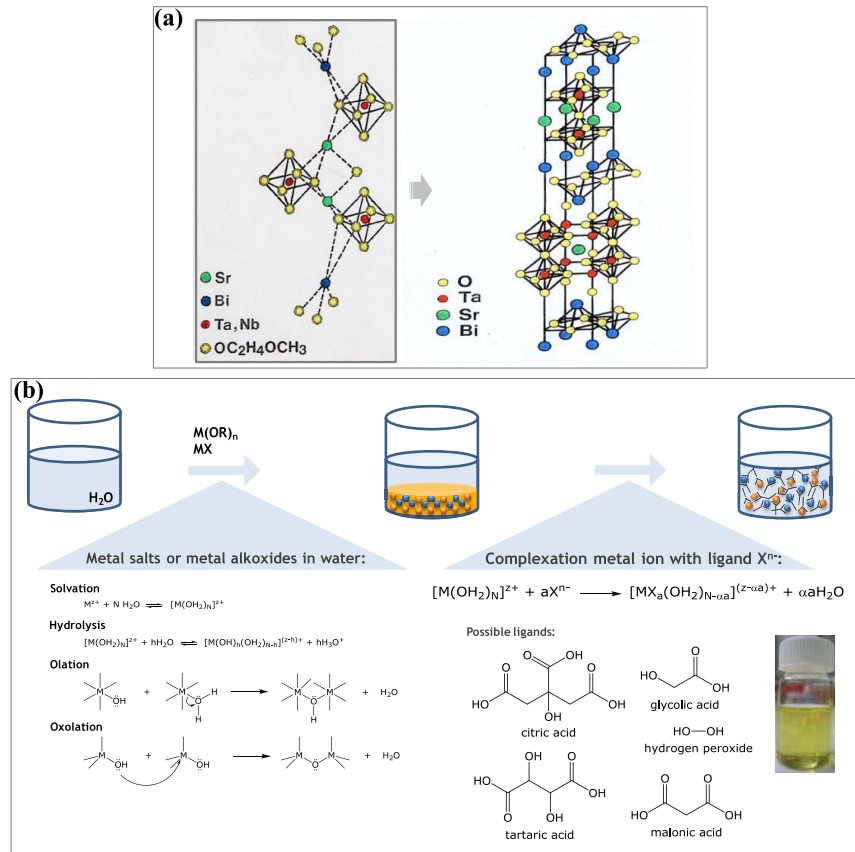


Fig. 3. (a) Proposed molecular structure of the triple metal alkoxide synthesized in the precursor solution and the crystal structure of the corresponding $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) thin films [94], [95]. (b) Aqueous solution-gel method for the synthesis of metal oxide precursor solutions [63], [98].

films because of the rapid growth of Flexible Electronics. Polyimide substrates, such as Kapton or Upilex, are the ones with the highest degradation temperatures ($\sim 400^\circ\text{C}$) [10]. Therefore, they restrain the temperature limit at which ferroelectric oxide films can be integrated with flexible devices (see Fig. 1).

In the following discussion, we consider obtaining ferroelectric hysteresis loops with measurable values of remanent ferroelectric polarization P_R as the quality control factor of the goodness of the CSD method to be applied to the fabrication of flexible systems.

A. Molecular Design of Metal Precursors in Solution

It has been proven that careful control of the chemistry of the solution can lead to an appreciable reduction in the crystallization temperature of the ferroelectric oxide layer. Two major aims are pursued following this strategy: first, increasing the homogeneity and, thus, the reactivity of the solution, stages (i) and (ii) in Fig. 2, and, second, decreasing the number of organics and, thus, accelerate their decomposition, the formation of the amorphous metal-oxygen network, and the crystallization of the oxide in the bulk film, stages (iii) and (iv) in Fig. 2.

To attain these targets, pioneering works in the synthesis of homometallic and heterometallic molecular complexes as precursors of electronic oxides were reported by the group

of Prof. Hubert-Pfalzgraf (female) in the late 1990s and beginning of this century [91]–[93]. Based on these studies, ferroelectric oxide thin films have been prepared at relatively low temperatures by using solutions where accurate control of the chemical system was carried out. Hence, the group of Prof. Kato (female) observed the primary steps of crystallization in ferroelectric $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT) thin films at $\sim 500^\circ\text{C}$, when these films were deposited from complex metal alkoxides that contained the three metals in a single molecule [94], [95]. The molecular structure of this alkoxide has the same arrangement of metals and oxygen as the sublattice of the SBT crystal, thus facilitating the conversion of the precursor into the crystalline oxide phase [see Fig. 3(a)]. The group of Prof. Kosec (female) and Prof. Malic (female) also prepared ferroelectric Ti-rich PZT films at 400°C with considerable P_R values ($\sim 30 \mu\text{C}\cdot\text{cm}^{-2}$) from high homogeneous solutions [66], [69], [96], [97]. These were synthesized by selective modification of the Zr reagent with acetic acid that led to precursors formed by dimeric Zr organizations with bridging alkoxide groups.

The fabrication of ferroelectric oxide thin films from aqueous solution-gel methods developed in the group of Prof. Van Bael (female) and Prof. Hardy (female) also has been focused in decreasing the decomposition temperature of the solution deposited layer by the use of water as a solvent and tailored water-soluble metal complexes with a low decomposition temperature [stages (i) and (ii) in Fig. 2], which is

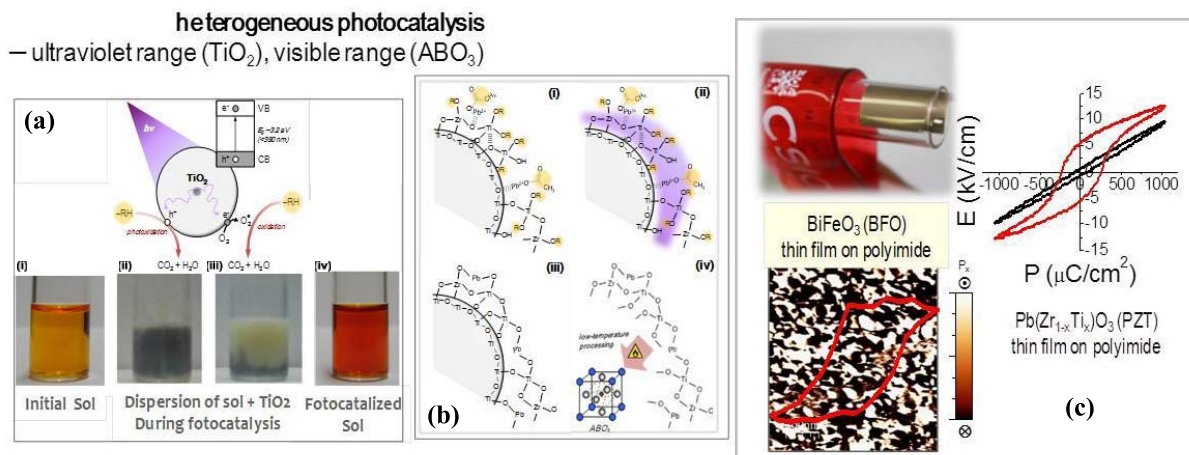


Fig. 4. Photocatalytically assisted decomposition of ABO_3 perovskite precursor solutions. (a) Photocatalytic process and images of the organic decomposition in solution: (i) initial precursor solution, (ii) and (iii) dispersions formed by the solution and the photocatalytic nanoparticles during the photocatalysis process, and (iv) photocatalyzed solution after removing the nanoparticles. (b) Steps of the photocatalysis of a PZT solution with TiO_2 nanoparticles: (i) adsorption of oligomers on the surface of the nanoparticles, (ii) degradation of organics, (iii) polycondensation, and (iv) low-temperature perovskite liquid precursor. (c) Ferroelectric PZT and BFO films deposited on flexible polyimide substrates [72]. Adapted with permission of WILEY-VCH Verlag GmbH & Co.

able to induce the film crystallization at low temperatures [see Fig. 3(b)] [63], [98], [99]. In general, the ferroelectric response of ferroelectric thin films prepared from aqueous solution–gel methods is highly improved when combined with other low-temperature solution methods [63].

These works prompted other researchers to take advantage of the molecular design of the metal precursor solution to attain ferroelectric oxide thin films at low temperatures. Some relevant publications using this strategy are collected in Fig. 1 [11], [12], [14], [60], [62]–[66], [69], [71]. In these publications, this CSD method is usually combined with other ones that will be shown in the next sections.

B. Photocatalysis-Assisted Solution Decomposition

In 2015, it was shown that low-temperature precursor solutions of ferroelectric oxides can be synthesized in liquid media after the irradiation of the dispersions resulting from the mixture of these solutions and photocatalytic nanoparticles. This idea appears from the merging of two rather distant fields in materials science, such as heterogeneous photocatalysis and low-temperature CSD.

Fig. 4 shows how precursor solutions are photocatalyzed by dispersed nanoparticles. Irradiation of the dispersions by light yields the photodegradation of the solutions, which leads, after the particles' removal, to a so-called low-temperature liquid precursor. This strategy determines the chemistry of the solution, so it can be directly connected with the stage (i) in the CSD process (see Fig. 2). Layers deposited from these solutions are converted into the crystalline films at low temperatures. These studies have been carried out on precursor solutions of PZT and the multiferroic and photo-ferroic BiFeO_3 (BFO). Ferroelectric PZT and BFO thin films have been prepared by this CSD strategy at temperatures below 350°C , which has made possible their direct deposition on flexible polyimide substrates [72]. The flexible films

showed well-defined ferroelectric hysteresis loops with values of P_R of $\sim 5 \mu\text{C}\cdot\text{cm}^{-2}$.

C. Metal Excesses

Another strategy that has been used for lowering the crystallization temperature of metal oxides is to add to the precursor solution, metals of low melting point able to form during the thermal treatment of the film [stages (iii) and (iv) in Fig. 2] liquid phases. These liquids have a behavior close to a solvent, where the diffusion of the elements is enhanced, facilitating the rearrangement of the atoms at relatively low temperatures to form the crystal oxide phase.

Due to their relatively low melting points, post-transition metals, such as Ga, In, Tl, Si, Sn, Ge, Pb, or Bi, have been used to produce metallic liquids during the synthesis of some inorganic materials, by flux synthesis [100], [101]. In ferroelectric oxide thin films, a similar phenomenon can be awaited by the addition of excesses of metals, such as Pb or Bi, which are practically present in most of the ferroelectric oxides (see Fig. 1). Traditionally, low excesses of these elements are added to the precursors of ferroelectric oxide materials to compensate for their loss by volatilization during annealing. However, the addition of large excesses of Pb (up to 50 mol%) and Bi (20 mol%) to precursor solutions of PZT and $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT), respectively, has made possible the crystallization of the corresponding perovskite films at low temperatures (between 450°C and 500°C), with values of P_R of $\sim 30 \mu\text{C}\cdot\text{cm}^{-2}$ for PZT films and $\sim 15 \mu\text{C}\cdot\text{cm}^{-2}$ for BIT films (see Fig. 1) [55], [86]. The reason behind the enhanced crystallization of these films upon metal excess addition remains unclear. Some authors point out that the metal oxide excess may not only effectively act as a flux for crystal growth but also as a network modifier facilitating the rearrangement of ions for crystallization [102]. Nevertheless, the results show that the amount of ferroelectric phase attained at a given annealing temperature increases with the metal excess amount [86].

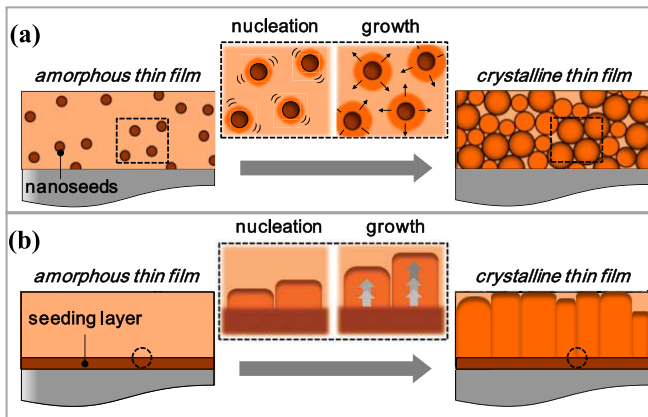


Fig. 5. Illustration showing the nucleation and growth of crystalline metal oxide thin films assisted by the seeding effect. (a) Crystalline nanoseeds previously introduced within the bulk film. (b) Crystalline seeding layer previously grown on the surface of the substrate [7]. Published with permission of the Royal Society of Chemistry.

D. Combustion Process

The combustion process has been shown to be an efficient synthesis method for producing oxide powders, ceramics, or hard alloys [103]. The group of Prof. Galassi (female) has reported the use of sol-gel combustion for the preparation of different ferroelectric oxide materials [104], [105]. However, in the case of thin films, this strategy has been mainly applied to semiconductor oxides. Here, thin-film transistors have been prepared by solution combustion on flexible polymer substrates at temperatures as low as 200 °C [81], [106]. These works make use of the localized energy supplied to the film during the reaction between some of the reagents (fuels and oxidizers) incorporated into the solution [107]. This involves a first selection/design of the chemistry of the solution in the stage (i) of the CSD method (see Fig. 2). As a result, the external application of just low-temperature heating to the film (stage (iii) in Fig. 2) is able to initiate a strong exothermic redox-based combustion that supplies to the film enough energy to produce the crystallization of the oxide film.

Our group has prepared photoferroic BiFeO₃ thin films at 350 °C directly on flexible polyimide substrates, by using this solution strategy combined with other ones discussed in this technical review. The films show ferroelectric response with values of P_R of $\sim 13 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1), besides photovoltaic and photocatalytic properties [71]. To the best of our knowledge, only another article, recently published has successfully prepared PZT thin films on silicon substrates by the use of solution combustion and 20 mol% of Pb excess. These films treated at 400 °C have high values of $P_R \sim 35 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1) [70].

E. Seeded Solutions

Crystallization of metal oxides is a nucleation-controlled phenomenon [7]. Therefore, one of the first strategies reported in the literature to enhance crystallization kinetics of ferroelectric oxide films is the seeding effect [84], by which the use of seeds in the bulk film or seeding layers on the substrate surface enhance the nucleation of the crystalline oxide films (see Fig. 5).

The group of Prof. Vilarinho (female) has been using diphasic sol-gel precursors for the low-temperature crystallization of ferroelectric oxide films [53], [108]. In these precursors, PZT nanoparticles were added to the sol to enhance the perovskite crystallization. As a result, they have prepared from these dispersions ferroelectric PZT thin films at 410 °C for long times of 30 h. The precursors are attained by the incorporation of crystalline PZT nanoparticles into the synthesized solution (stage (i) of the CSD process in Fig. 2).

The presence of these nanoparticles in the deposited layer (stage (ii) in Fig. 2) provides a large number of nucleation sites during the annealing of the film (stages (iii) and (iv) in Fig. 2). This accelerates the crystallization of the oxide phase on the surfaces of the nanoparticles [see Fig. 5(a)] because of the lower activation energy for the crystallization of the perovskite in the seeded films compared with the unseeded films, 146 and 219 kJ·mol⁻¹, respectively. These PZT films show P_R values of $\sim 8 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1) [53].

F. Seeding Layers

The crystallization kinetics of ferroelectric oxide thin films is also accelerated by the use of seeding layers on the surface of the substrate [see Fig. 5(b)]. Thus, K_xNa_{1-x}NbO₃ (KNN) thin films have been prepared by CSD at 425 °C on silicon substrates with a V₂O₅ solution deposited seed layer, also treated at 425 °C. The ferroelectric hysteresis loops show a low remanence of the polarization with values of P_R estimated by the authors below $13 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1) [59].

It has been shown that if the crystal structure of the seeding layer is close to that of the ferroelectric oxide, the resulting film grows with a strong preferred orientation [85]. On the other hand, if this seed layer has a nonferroelectric composition, a decrease in the ferroelectric response (lower P_R values and higher coercive fields E_C than fully crystallized films) should be expected since it would work like a bottom in-series interface in a planar configuration of capacitors fabricated with the ferroelectric film [1], [14], [109].

The major handicap, however, of this strategy is that this seed layer usually needs to be crystallized at a high temperature (over 500 °C). Therefore, it is difficult to apply to the preparation of films on heat-sensitive substrates.

Prof. Whatmore's group showed that seeding layers can be internally formed at relatively low temperatures during the crystallization of the oxide film (stage (iv) in Fig. 2) [61]. They prepared ferroelectric PZT thin films with $P_R \sim 16 \mu\text{C}\cdot\text{cm}^{-2}$, at 480 °C by promoting the formation between 300 °C and 400 °C of the intermetallic Pt₃Pb at the surface of the substrate. These Pt₃Pb interfaces worked as a nucleation surface for the PZT perovskite, hindering, in addition, the formation of the second pyrochlore phase, which is stabilized during the heating of the film at temperatures below 500 °C. Interfaces similar to this always appear as intermediate ones during the processing of most of the ferroelectric oxide films containing Pb or Bi. They are elements that easily diffuse toward and react with the Pt electrode [109]. However, the full crystallization of the oxide on these intermetallic interfaces always occurs at temperatures over 400 °C, not being possible the use of

this strategy for the integration of these films with Flexible Electronics.

Alternatively, seeding layers consisting of 2-D oxide nanosheets can be deposited at room temperature on any substrate. This has shown to be effective in inducing a strong preferred orientation of ferroelectric oxide thin films grown on the top of them by PLD [110]. Recently, it has been also shown the reduction of the crystallization temperature (400 °C) of KNN films prepared by sputtering on a $\text{Ca}_2\text{Nb}_3\text{O}_{10}$ nanosheet seed layer. P_R values below $5 \mu\text{C}\cdot\text{cm}^{-2}$ have been obtained in these films [18]. Our group has an ongoing work about the capability of using 2-D nanosheet layers for decreasing the processing temperature of ferroelectric PZT and BFO thin films on flexible substrates prepared by CSD [111].

G. Multiannealing and Rapid Thermal Processing

Related to the seeding layers method, it is the multiannealing process in which very thin layers are deposited and crystallized. Then, this crystalline layer enhances the nucleation of the oxide in further coated solution layer [54], [60], [112]. However, these seed layers need to be annealed at high temperatures (over 600 °C) to get the crystallization of the ferroelectric oxide because, otherwise, metastable nonferroelectric phases, such as pyrochlore or fluorite, are stabilized at lower temperatures. For ferroelectric perovskite films, it has been demonstrated for conventional thermal treatments that the formation rate of the perovskite is rather low and it occurs through a two-stage transition process, i.e., amorphous state to pyrochlore/fluorite phase and then to perovskite oxide (stages (iii) and (iv) in Fig. 2). However, the crystallization behavior of the films is completely different when they are crystallized by rapid thermal processing (RTP). Here, heating rates are around three orders of magnitude larger than those of conventional annealings. The major feature of RTP is that the fast heating rates avoid the nucleation and crystallization of the nonferroelectric second phases, as the films skip over the temperatures of formation of these phases (between 300 °C and 500 °C) in a very short time. When they are heated fast enough to the temperature of pure perovskite formation, a single-stage transition (from amorphous to perovskite) is realized, thus completely circumventing the formation of the second phase (see Fig. 6) [113], [114].

It is obvious that the lowest temperature limit that can be reached for the processing of ferroelectric films by this method is determined by the temperature of crystallization of the oxide. Thus, PZT films were prepared at 450 °C with values of P_R of $\sim 8 \mu\text{C}\cdot\text{cm}^{-2}$ by using this strategy alone (see Fig. 1) [54]. After this publication, only the combination of multiannealing RTP with other approaches has led to an appreciable reduction in the processing temperature of ferroelectric oxide films.

H. Microwave Annealing

Microwave annealing has shown great potential for the synthesis of inorganic materials, such as nanoparticles, nanostructures, or thin films [115]. The energy of a microwave

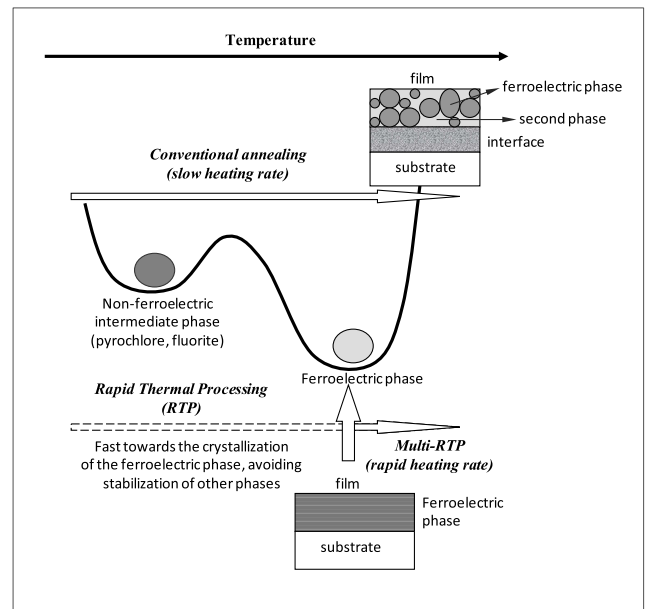


Fig. 6. Scheme showing the crystallization of ferroelectric oxide thin films by multiannealing rapid thermal processing (RTP) in comparison with conventional annealings.

photon (2.45 GHz) is not enough to produce chemical reactions but for being converted into dielectric heating within the material. This would produce selective and uniform heating in the film, which results in lower thermal budgets than those needed for the formation of the oxide in conventional heating processes. This thermal homogeneity within the bulk film during microwave annealing joined to the moderately fast heating rates (about an order of magnitude more than those reached with conventional ovens) must be among the main reasons to get the crystallization of oxide thin films at relatively low temperatures by using this type of heating [116], [117].

The number of publications on ferroelectric oxide thin films prepared by CSD and microwave annealing at temperatures below 500 °C is limited and none to temperatures compatible with flexible substrates (< 400 °C). An example is the preparation of PZT thin films crystallized at 450 °C, after a previous pyrolysis/condensation step at 400 °C. These films presented P_R values of $\sim 23 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1) [57].

I. Pulsed Laser Annealing

Pulsed laser annealing has also been used for the crystallization of complex oxide thin films [19], [118]–[122]. This annealing method is based on the irradiation of amorphous layers with excimer lasers, usually of ArF ($\lambda = 193$ nm) or KrF ($\lambda = 248$ nm), with pulse lengths of several tens of nanoseconds. Here, irradiation results in a photothermal effect because of the relatively high absorbance of metal oxides in the UV range, the high power provided by pulsed lasers (106 – $107 \text{ W}\cdot\text{cm}^{-2}$), and the small area irradiated by the high-intensity lasers. This gives rise to local temperatures over 1000 °C at the surface of the film, which can lead to the crystallization of the oxide without the need to apply treatments at high temperatures [123]. Both epitaxial and polycrystalline films have been attained by pulsed laser annealing

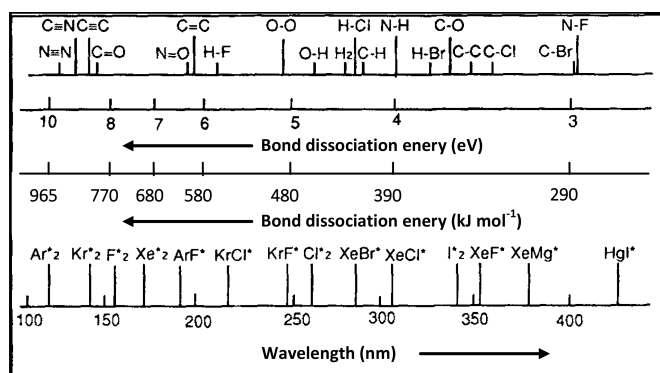


Fig. 7. Wavelengths (nm) of commercial excimer lamps with a range of irradiation from the near (354 nm) to the deep (126 nm) UV region. These UV sources are shown in comparison with the energies (eV and $\text{kJ}\cdot\text{mol}^{-1}$) of the typical chemical bonds excited at these wavelengths [126]. Published with permission of the Elsevier Science B. V.

depending on the substrate on which the film is grown. Among ferroelectric oxides, the literature shows the preparation of PbTiO_3 (PTO) thin films deposited from solutions, heated at 300°C , and annealed with an ArF excimer laser. The group of Prof. Trolhier-McKinstry (female) also crystallized PZT films and $(\text{Pb}, \text{La})(\text{Zr}, \text{Ti})\text{O}_3$ (PLZT) films with a KrF excimer laser, maintaining the substrate temperature $\sim 400^\circ\text{C}$ during the growth of the perovskite [68], [122]. While the former was deposited by PLD, the PLZT films were prepared by CSD on silicon substrates, showing well-defined ferroelectric hysteresis loops with P_R values of $\sim 20 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1) [68]. However, the small diameter of the laser spot (in the range of 2–8 mm) restricts the application of this technique to the deposition on large-area flexible substrates. Local crystallization of ferroelectric PZT and PTO thin films on any substrate withstanding processing temperature of $\sim 250^\circ\text{C}$ was carried out by a conceptually similar technique to pulsed laser annealing, which is thermochemical nanolithography. In this case, a resistively heated atomic force microscope (AFM) tip is brought in contact with the precursor to form the crystalline phase at a temperature $\geq 550^\circ\text{C}$ [124]. This approach makes possible the crystallization at a low temperature of nanometric areas in the film surface; however, it is difficult to transfer this process to the crystallization of the large area thin films demanded in Flexible Electronics.

J. UV Excimer Lamps

The penetration of UV light is limited to the surface region of condensed matter, typically below 200 nm. Therefore, UV irradiation is very effective for inducing chemical changes in thin film materials. The irradiation with pulsed lasers shown in the previous section mainly induces thermal excitation (photothermal effect). In contrast, electronic excitation is dominant when using UV irradiation lamps. Despite having UV excimer lamps much lower power (10^{-2} – $10^{-1} \text{W}\cdot\text{cm}^{-2}$) than lasers, they can irradiate over large areas under controlled atmospheres, minimizing thermal excitation, and enhancing photochemical reactions in the irradiated surface [125]. Fig. 7 shows the emission wavelengths of commercial UV sources

TABLE I

TYPES OF CHEMICAL BONDS USUALLY FOUND IN THE AS-DEPOSITED LAYERS DERIVED FROM PRECURSOR SOLUTIONS OF METAL OXIDES [125]. PUBLISHED WITH PERMISSION OF WILEY-VCH VERLAG GMBH & CO

Chemical Bond	Dissociation Energy		Wavelength λ (nm)
	$\text{kJ}\cdot\text{mol}^{-1}$	eV	
N=N	941	9.75	127
C=O	805	8.34	149
N=N	631	6.54	190
C=C	607	6.29	197
O=O	498	5.16	240
O-H	464	4.81	258
H-H	436	4.52	274
C-H	413	4.28	290
N-H	393	4.07	304
C-O	358	3.71	334
C-C	347	3.60	345
C-N	305	3.16	392
O-O	204	2.11	586
N-O	201	2.08	595
N-N	160	1.65	748

together with the type of chemical bonds that can be excited by them [126].

Ferroelectric oxide thin films prepared by CSD are excellent systems for inducing in them photochemical reactions by light since the synthesis of the precursor solutions always involves reagents and solvents that absorb light. Table I shows the types of chemical bonds usually found in solution deposited layers and the irradiation wavelength necessary to provide the energy needed for the dissociation of these bonds [125].

The irradiation with UV excimer lamps during the preparation of thin films by CSD is known as photochemical solution deposition (PCSD). Our group has been working on the low-temperature preparation of ferroelectric oxide films by PCSD since the beginning of this century, first driven by the interest in the introduction of high-performance ferroelectrics in microelectronic devices [12] and second by the outbreak of Flexible Electronics since 2010 [4].

However, the simple combination of UV-irradiation and CSD methods has not made possible to decrease the processing temperature of ferroelectric oxide thin films much lower than 500°C .

Yue *et al.* [56] reported the crystallization of PZT thin films at 480°C by the deposition of precursor solutions containing Ti(IV) and Zr(IV) alkoxides modified with acetylacetone (AcAcH) and irradiation with UV excimer lamps with a wavelength of 185 and 254 nm. The films showed a ferroelectric response with P_R values of $\sim 21 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1).

The group of Prof. Trolhier-McKinstry (female) fabricated Bi_3NbO_7 (BNO) ferroelectric thin films by the deposition

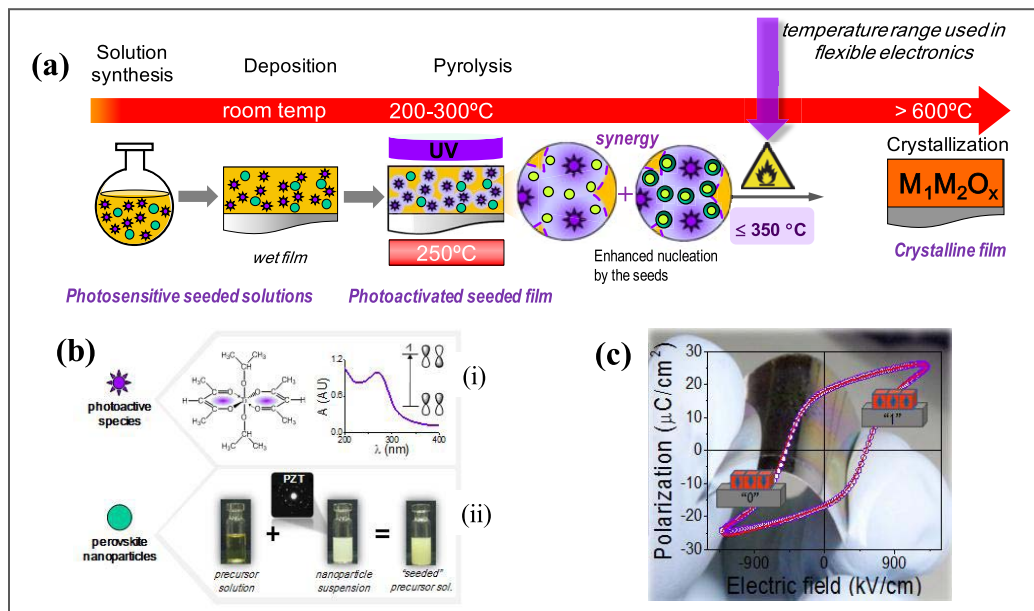


Fig. 8. (a) Schematic showing the mechanisms for the low-temperature processing of ferroelectric oxide thin films, using precursor solutions containing photosensitive species and nanocrystalline seeds. (b) Dispersions used for the deposition of the amorphous films on flexible polyimide substrates: (i) absorption in the UV range of PZT precursor solutions containing titanium alkoxides modified with β -diketone and (ii) photograph of the seeded photosensitive solutions obtained after mixing the precursor solution and the nanoparticle suspension. (c) Photograph of the resulting PZT thin film on polyimide and the ferroelectric hysteresis loop measured in it (this film was heated at 350 °C) [11], [128].

of solutions made by a modified Pechini's method [127], irradiation with a UV lamp of 260 nm, and annealing on the hot plate at 450 °C (see Fig. 1). These BNO films showed low values of P_R ($\sim 3 \mu\text{C}\cdot\text{cm}^{-2}$); however, they achieved stored energy densities of $\sim 39 \text{ J}\cdot\text{cm}^{-3}$ at room temperature, 10 kHz, and with an applied electric field of $3.6 \text{ MV}\cdot\text{cm}^{-1}$, which is of interest for their use in high-energy-density capacitors [52].

By the synthesis of photosensitive metal compounds in solutions, our group has attained ferroelectric oxide thin films [e.g., PTO, (Pb Ca)TiO₃-PCT, and (Bi_{0.5}Na_{0.5})_{1-x}Ba_xTiO₃-BNBT] at crystallization temperatures of 400 °C, by previous irradiation of the amorphous layers with an excimer UV lamp of 222 nm [12], [62]–[65].

K. Complementary Combinations of Low-Temperature CSD Methods

The results shown in the previous sections indicate that single low-temperature CSD approaches fail to lower the temperature sufficiently to allow ferroelectric thin films to be prepared on flexible substrates (see Fig. 1). We think that to achieve this goal, strategies must be directed toward a smart combination of the former methods and an intelligent design of the thin film material, as well as foresee opportunities in other research areas.

The group of Prof. Trolrier-McKinstry (female) reported in 2015 the preparation of Bi_{1.5}Zr_{0.9}Nb_{1.35}Ta_{0.15}O_{6.9} (BZNT) thin films at only 350 °C on polyimide substrates [127]. These were nanocomposite films formed by a nanocrystalline δ -Bi₂O₃ fluorite matrix and crystalline BZNT. This concept is very close to the ferrons model reported by the group of Prof. Mackenzie early this century [89]. Although the ferroelectric response of these nanocomposite BZNT films is

low ($P_R \sim 3 \mu\text{C}\cdot\text{cm}^{-2}$) (see Fig. 1), they are easily prepared on flexible substrates with low degradation temperatures and have interest in appealing areas today, such as flexible energy storage applications.

Our group has also managed to prepare ferroelectric PZT and BFO perovskite thin films at 350 °C, directly on flexible polyimide substrates by a novel CSD strategy that accelerates the degradation of the organics in the solution by a photocatalysis-assisted method explained in Section III-B (see Fig. 4) [72].

The combination of seeded precursor solutions and UV irradiation of the deposited layers has allowed us to attain ferroelectric thin films at temperatures suitable for their direct preparation on flexible polymer substrates.

Photosensitive species were synthesized in these solutions so that irradiation of the coated layers produces an acceleration of the decomposition of the organic compounds present in the system. The energy required afterward for the nucleation and growth of the ferroelectric phase is lowered by the presence of nanoparticles (seeds) with the same composition and crystal structure as that of the ferroelectric thin film (see Fig. 8) [128]. This has allowed us to successfully achieve ferroelectric PZT and multiferroic BFO films on flexible polyimide substrates at temperatures ≤ 350 °C, with P_R values of ~ 17 and $\sim 5 \mu\text{C}\cdot\text{cm}^{-2}$, respectively (see Fig. 1).

Finally, we have recently developed a threefold approach that combines the synthesis in the solution of metal precursors specifically designed to fulfill the next points: 1) to have a molecular structure resembling the crystal structure of the ferroelectric oxide, making easy the amorphous to crystalline conversion; 2) to absorb a large amount of UV-light, inducing photochemical reactions that accelerate the formation

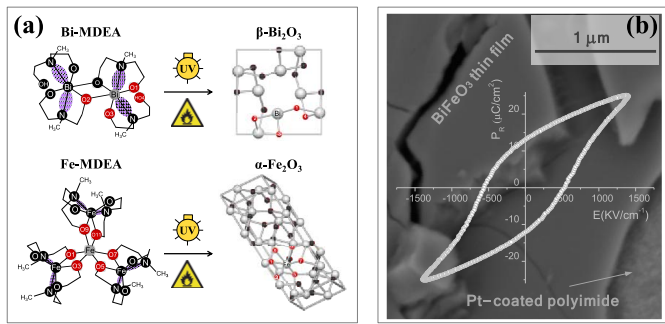


Fig. 9. (a) Molecular structure of the Bi-MDEA and Fe-MDEA complexes synthesized in the precursor solution, showing chemical features such as a suitable molecular structure, photosensitivity, and internal combustion reactants to induce the crystallization of BiFeO₃ thin films at low temperature. (b) BiFeO₃ thin film prepared from the former precursor solutions at 350 °C on Pt-coated flexible polyimide substrates and their corresponding ferroelectric hysteresis loop (measured at 128 K and 1 kHz). Adapted with permission of WILEY-VCH Verlag GmbH & Co.

of the metal–oxygen network; and 3) to produce internal combustion reactions that result in localized energy, being only needed low-temperature heating to give rise crystalline films. By using this approach, we have prepared ferroelectric BFO thin films on polyimide substrates at temperatures ≤ 350 °C with $P_R \sim 15 \mu\text{C}\cdot\text{cm}^{-2}$ (see Fig. 1) [71]. The cornerstone of this CSD method is the synthesis of a photosensitive metal complex formed among the metal cations and an alkanolamine ligand. These metal complexes have a molecular structure close to that of the crystal oxide (see Fig. 9). In addition, the nitrate groups and the amine ligands work as oxidizing and reducing agents, triggering combustion reactions in the film during heating at low temperature.

IV. CONCLUSION AND OUTLOOK

In this article, we have shown the most relevant CSD strategies reported in the literature for the low-temperature preparation of ferroelectric oxide thin films, highlighting the contribution of our group in the attempt to integrate these films with flexible polyimide substrates at low temperatures. Different CSD single approaches have been shown to reduce the crystallization temperature of ferroelectric oxide thin films (i.e., molecular design of the precursor, the addition of metal excesses, combustion process, seeded solutions and seeding layers, multiannealing, rapid thermal, microwave and pulsed laser annealing, and film irradiation with UV excimer lamps). However, for decreasing as much as possible the crystallization temperature, a deep knowledge of the mechanisms involved in these CSD methods should be addressed. This will allow us to open our mind to novel CSD strategies outside the conventional ones that will probably make possible to overcome the thermodynamic and kinetic barriers that inhibit the crystallization of the ferroelectric oxide at low temperature. Hence, the combination of some of these individual strategies has been demonstrated to be very efficient in reducing the processing temperature of these films, but possible synergies sought among them, for sure, will allow us to find new CSD pathways for a successful integration of ferroelectric oxides in emerging and disruptive technologies, such as Flexible Electronics.

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