A Sustainable Self-Induced Solution Seeding Approach for Multipurpose BiFeO$_3$ Active Layers in Flexible Electronic Devices

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The direct integration of crystalline oxide layers into flexible electronic systems requires the development of relatively simple, low-temperature processing routes. Seeding represents a powerful strategy to reach this objective by the generation of preferential sites for the nucleation of crystalline phases with a reduced energy barrier. Here, a novel approach is reported where nanoseeds are generated in situ from a precursor solution using a solvent-engineering strategy (solvent-antisolvent). The controlled addition of an antisolvent (1,3-propanediol) to a solution of metal salts (Bi/Fe) dissolved in acetic acid results in the formation of nanocrystals (seeds) by supersaturation. The presence of such nanoseeds is also confirmed in the deposited layers, improving significantly the crystallinity of the respective BiFeO$_3$ thin films as complementary, deduced by piezoresponse force microscopy. Using this low-temperature strategy, crystalline films are directly grown on flexible polymeric substrates at only 350 °C showing a remanent polarization of 10.5 µC cm$^{-2}$ and a clear photovoltaic effect (11.7 µW cm$^{-2}$) of interest in computer memories and energy harvesters. The flexibility of the BiFeO$_3$ thin films may enlarge the number of applications of this multifunctional, lead-free material in next-generation digital and sustainable electronic devices based on a facile, low-cost fabrication method with reduced energy consumption.

1. Introduction

Crystallization is a simple but fascinating process responsible for the formation of over 70% of all solid materials produced today.[1] The significance of this process extends from pharmaceutical and food technologies to biochemistry and microelectronics. The degree of crystallinity represents the basis of a wide variety of electronic materials, since many of their functionalities (optical, magnetic, and electrical) depend directly on it. For instance, the formation of the perovskite structure (ABO$_3$) in some metal oxides is conditio sine qua non for securing physical properties such as colossal magnetoresistance, superconductivity, or ferroelectricity, and even for the appearance of the photovoltaic effect or photocatalytic activity.[2]

The past two decades have witnessed an increased interest in the low-temperature processing of metal oxide thin films with the aim of enabling their direct integration into flexible electronic systems.[3] To this end, the formation of the oxide layer must proceed below the degradation temperature of the flexible substrate, i.e., typically 350 °C for polyimide foils. Several low-temperature strategies based on solution processing have been developed to induce the crystallization of metal oxide thin films at temperatures compatible with polymer substrates.[4] Thus, the use of UV-assisted photo-annealing,[5] combustion synthesis,[6] seeding effect,[7] molecular engineering,[8] or photocatalytically assisted decomposition[9] has been previously reported. Particularly, the seeding effect has largely demonstrated its effectiveness in reducing the energy barrier required for the heterogeneous nucleation of the crystalline oxide on the surface of a different material. This surface is commonly provided by i) the growth of a seeding layer[10] on top of the substrate or ii) the introduction of seeding nanoparticles[11] into the precursor solution of the metal oxide. However, the first approach requires the previous annealing to crystallize the seeding layer and so is affected by the same temperature constraints imposed by the substrate. By contrast, one of the main advantages of the second approach (use of seeding nanoparticles) relies on their already-crystalline nature before being introduced into the precursor solution. This means that nanoparticles have to be ex situ crystallized by any other method with no thermal compromise to the thin film processing of the metal oxide. Once deposited on a substrate, nanoseeds can be incorporated homogeneously into the chemical system (e.g., BiFeO$_3$ nanoparticles into a precursor solution of BiFeO$_3$ to obtain crystalline BiFeO$_3$ films[12]) or react with it (e.g., Cu nanocrystals into a molecular vanadium precursor to obtain crystalline Cu$_2$V$_2$O$_7$ films)[13] during the thin-film processing.

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Taking advantage of the seeding effect, crystallization temperatures of several metal oxide thin films have been successfully reduced by \(\approx 100\,^\circ\text{C}\) using the aforementioned methods.\[^{[10–12]}\] However, as stated before, seeding materials must be crystallized prior to the deposition of the thin film, which increases the energy consumption and complexity of the whole fabrication process. Additionally, there is usually a need to apply some form of mechanical energy for adequate mixing of external particles (seeds) with precursor solution.

Here, we have developed a novel approach for the self-induced formation of nanoseeds into precursor solutions of metal oxides. Instead of adding nanoparticles to the solution, these are generated in situ by inducing their controlled precipitation using a solvent-engineering strategy. The concept is inspired by the solution-process fabrication of next-generation solar devices based on hybrid perovskites.\[^{[13]}\] Since the introduction of the antisolvent crystallization of these materials,\[^{[14]}\] the power-conversion efficiency of the resulting cells has significantly been enhanced due to the formation of uniform and pinhole-free films. The crystallization of an intermediate phase (also called adduct or precipitate) upon the dropwise addition of a non-dissolving solvent during the deposition process is revealed as the key factor to increase the density of crystallization nuclei within the film.\[^{[16]}\] In this work, we conceived this method with a different but rather original purpose: to induce the formation of nanocrystals into a precursor solution that could be subsequently used as seeds for lowering the crystallization temperature of the corresponding thin films. To demonstrate this approach, we have selected the BiFeO\(_3\) system as a prototype of multifunctionality based on its multiferroic\[^{[15]}\] and photoferroelectric\[^{[16]}\] properties with potential application in future devices such as four state logic magnetoelectric memories or multisource energy harvesters. Figure 1 depicts the scheme that illustrates the low-temperature strategy proposed. When an antisolvent (1,3-propanediol) is added to a solution consisting of a solute (either bismuth nitrate or iron acetylacetonate) dissolved in a solvent (acetic acid), the solubility of the respective salts in the liquid medium is reduced creating supersaturation conditions at the local level.\[^{[17]}\] After a certain time, nanoseeds of crystalline nature start to nucleate by a chemical equilibrium-controlled process forming thus a detectable nanoparticle dispersion. Once deposited on a substrate, each nanoseed acts as a nucleation center, decreasing the activation energy for the crystallization of the system. Crystalline films of BiFeO\(_3\) can be therefore achieved at low-processing temperatures, making possible their direct growth on flexible polymeric substrates. In addition, the simplicity of the strategy proposed here constitutes a clear advantage over previously reported methods\[^{[7b]}\] that require the use of singular equipment such as excimer UV lamps. The ferroelectric nature of these films, together with their photovoltaic effect, may open the door to a new generation of high-tech products based on the classical properties of this material (ferro-, pyro-, and piezoelectricity) but with a wide range of novel applications enabled by its flexible nature (e.g., wearable sensors, biomedical implants or self-powered devices).

### 2. Results and Discussion

Solutions of bismuth and iron salts were prepared by dissolving the respective reagents in pure acetic acid (see Experimental Section). According to measurements carried out by dynamic light scattering (DLS), no signal was detected after the dissolution of the components (Figure 2a). This state corresponds to an undersaturated solution, namely stage A in previous Figure 1. Interestingly, the scenario completely changes once 1,3-propanediol is added to the system (Figure 2b). Detectable nucleation occurs due to the lower solubility of the solute (i.e., the bismuth and iron salts) in this solvent (hence called antisolvent). A single narrow distribution of particles sizes is now detected by DLS (\(\approx 40\,\text{nm}\)). Overall, these results mark a transition toward the early formation stages of a nanoseed dispersion, namely stage B in previous Figure 1. The supersaturation conditions imposed by 1,3-propanediol will induce the nucleation of nanoseeds until the system comes to the chemical equilibrium: a suspension composed of seeds homogeneously dispersed in a saturated solution. This state corresponds to what we have called a self-induced seeding solution, namely stage C in previous Figure 1.

![Figure 1](image.jpg)

**Figure 1.** Schematic illustration of the solvent-engineering approach used for the low-temperature processing of flexible BiFeO\(_3\) thin films, from the initial dissolution process of the metal salts to obtain an undersaturated solution (A); to the early formation stages of a nanoseed dispersion (B) after antisolvent addition; and its subsequent evolution to the self-induced seeding solution (C) that is finally deposited on a substrate.
The time-lapse required to reach this equilibrium (\(t_x\), where \(x\) stands for days) depends on several thermodynamic factors, such as the interfacial free energy of the system progressively altered by the nucleation and growth of crystals.\([17]\) This reasoning can explain the shift toward larger sizes (≈70 nm) and the broadening observed in the particle size distribution of Figure 2c measured at this stage, with a wider distribution of values.

To further confirm that the chemical equilibrium corresponds to a suspension composed of seeds dispersed in a saturated solution, a precursor solution of BiFeO₃ was prepared from the individual solutions of the metal cations mixed together at stage B (see Figure S1, Supporting Information). Time-dependence concentration studies of this solution mixture are depicted in Figure 3a, which shows a moderate decrease with time until stable values are reached at stage C. Note that this time-lapse is directly related to the level of supersaturation induced in the system, which depends on the experimental conditions specifically used. Here, the concentration of the precursor solution of BiFeO₃ decreases upon crystal nucleation from a value of 0.125 \(\text{m}\) in the initial solution mixture (\(t_0\)) to a value of 0.085 \(\text{m}\) in the self-induced seeding solution obtained after seven days (\(t_7\)). This result is supported by the thermogravimetric and differential thermal analysis (TG-DTA) characterization of the gel powders derived from the solution, showing that the weight loss measured during the thermal decomposition of the precursor is slightly larger at \(t_7\) rather than at \(t_0\) (see Figure S2, Supporting Information). It should be recalled that this concentration corresponds to the saturated solution obtained after the agglomeration and sedimentation of crystals (i.e., the supernatant of the corresponding suspension).

In Figure 2, particle size distributions by dynamic light scattering at different stages (A–C) of the chemical process followed to obtain the a) undersaturated solution, b) nanoseed dispersion, and c) self-induced seeding solution used for the preparation of BiFeO₃ thin films by the solvent-engineering approach.

In Figure 3, a) Evolution of concentration with time in a precursor solution of BiFeO₃ after the antisolvent addition (20% v/v antisolvent). Note that this concentration corresponds to the saturated solution obtained after the agglomeration and sedimentation of crystals (i.e., the supernatant of the corresponding suspension). b) X-ray patterns of the metal salts (bismuth nitrate and iron acetylacetonate) used as starting reagents to prepare a precursor solution of BiFeO₃, and the precipitate formed in this solution after the antisolvent addition under high supersaturation conditions (50% v/v antisolvent).
To gain further insight into the identity of these crystals, the nuclei formed in a solution under higher supersaturation conditions (see Experimental Section) were isolated and analyzed by X-ray diffraction (XRD). The corresponding pattern of Figure 3b denotes the crystalline nature of this compound, whose reflections cannot be assigned however to any of the constituent reagents (XRD patterns of bismuth nitrate and iron acetylacetonate are also included in the graph). Therefore, the resultant crystalline phase may correspond to an intermediate compound derived from the solution mixture, where the participation of both acetic acid and 1,3-propanediol on the basis of their coordinating properties should not be disregarded.[18]

As stated before, the nanoseeds formed in the solution by this solvent-engineering strategy are expected to remain in the corresponding layer once deposited on a substrate. Figure 4 shows the scanning electron microscopy (SEM) images of the surface of films prepared from the initial solution mixture (t0) and the self-induced seeding solution obtained after seven days (t7). When a single layer from the former (t0) is deposited and dried at 150 °C, a smooth surface with no distinctive morphological features is obtained in the respective film (Figure 4a). On the contrary, the analogou film derived from the self-induced seeding solution (t7) shows the presence of dispersed populations of agglomerates on the surface (Figure 4b). Primary particles with a size between 50–70 nm are observed to constitute such agglomerates, as inferred from the inset image. Note that these particle sizes are similar to those calculated by DLS from the corresponding solution (Figure 2c). Cross-section imaging of a thicker film counterpart corroborates the presence of dispersed populations of agglomerates on the film surface when the sample is 15° tilted (Figure 4c). A well-defined microstructure with slightly distinctive morphological features can be discerned that is attributed to the random distribution of nanoparticles over the whole film (Figure 4d). Analysis by energy-dispersive X-ray spectroscopy (EDX) confirmed the presence of both bismuth and iron elements in the agglomerates, with a marked difference in the atomic ratio between the oxygen and carbon elements (O/C = 0.99) with respect to the same area of the film without agglomerates (O/C = 0.39). This might be indicative of a less organic content present in the particles that constitute the agglomerates (see Figure S3, Supporting Information). Therefore, the presence of nanoparticles in the self-induced seeding solution strongly influences the surface morphology of the layers obtained after its deposition. The formation of agglomerates in this film may be ascribed to the permanence of nanoparticles in the deposited layer and their subsequent agglomeration by centrifugal force during the spinning process. Independently of the solution system used (initial mixture vs seeding solution), both films develop a single-phase crystalline structure after annealing at a relatively high temperature of 450 °C (Figure 4e,f). The microstructure of these perovskite films consists of round-shaped grains with a size between 80 and 100 nm. Slightly larger grains are observed in the film derived from the initial solution mixture (Figure 4e) when compared to the one obtained from the self-induced seeding solution (Figure 4f). This can be attributed to the presence of particles in the latter that increase the density of nucleation sites within the film and therefore inhibits the grain growth.[19] Note that the populations of agglomerates that were clearly visible in Figure 4b can also be inferred from the surface morphology of this crystalline film (Figure 4f), suggesting a template effect.[20] Images of higher magnification (see insets) show similar microstructures between different areas of the film that suggest the total incorporation of the initial nanoparticles into the final perovskite grains. This is complementary and supported by the absence of secondary phases in the corresponding XRD pattern.

The effect of the self-induced seeding solutions on the crystallization process of the BiFeO3 thin films is clearly demonstrated in Figure 5. Whereas perovskite films from the initial solution...
mixture \((t_0)\) are obtained at a minimum temperature of 400 °C, this temperature is further reduced to 375 °C \((t_1)\) and even to 350 °C \((t_7)\) in the course toward reaching the chemical equilibrium of the self-induced seeding solution. We must point out that crystallization below this thermal limit (350 °C) was not observed in the films derived from this solution system after longer times \((t_{14}, \text{not shown})\). The formation of nanoparticles in the self-induced seeding solution and their permanence in the deposited layers is responsible for decreasing the crystallization temperature of the films based on the seeding effect.\(^4\) This can be attributed to the fact that the activation energy for the perovskite crystallization is reduced on the surface of such nanoparticles, which promotes the heterogeneous nucleation of the oxide phase in the film. The homogeneous distribution of seeds in the solution induced by in situ generation provides a high density of nucleation sites in the corresponding film, which finally translates into a lower processing temperature. As a result, a reduced thermal budget is needed for the crystallization of the BiFeO\(_3\) thin films. This achievement provides significant benefits in terms of sustainability to the manufacturing process of advanced materials based on reduced energy consumption and lower CO\(_2\) emissions contributing to a greener worldwide economy.\(^{21}\) Additionally, the method can in principle be applied to other materials based on metal oxides, demonstrating the general validity of the self-induced solution seeding approach. Preliminary results have shown that the minimum crystallization temperatures of Bi\(_4\)Ti\(_3\)O\(_{12}\) and LaFeO\(_3\) thin films prepared by this solvent-engineering strategy are effectively reduced in the course toward reaching the equilibrium from the initial solution mixture of precursors \((t_0)\) to the self-induced seeding solution \((t_7)\) (see Figure S4, Supporting Information). These promising findings open the possibility of using this low-temperature method to integrate new candidate materials in flexible polymeric substrates for next-generation electronics.

The presence of particle agglomerates in the deposited layers may affect the surface characteristics of the BiFeO\(_3\) thin films of this work, which in turn could influence some of their physical properties (e.g., electrical). Scanning force microscopy (SFM) was used to analyze the topography of the crystalline films obtained at 450 °C from the initial solution mixture \((t_0)\) and the self-induced seeding solution \((t_7)\). Reflections out from the shaded areas (not indexed) correspond to secondary phases either from BiFeO\(_3\) (Bi\(_2\)Fe\(_4\)O\(_9\), Bi\(_{25}\)FeO\(_{39}\)) or from the substrate.
of the crystalline film derived from the self-induced seeding solution displays piezoresponse in its entire area (Figure 6d). Since piezoelectricity is directly related to the formation of a (non-centrosymmetric) crystalline structure, the much larger percentage of regions showing the piezoelectric response of this latter film (100%) is indicative of the higher degree of crystallinity achieved in the system when nanoseeds are present. This agrees with the previous results shown in Figure 5, where the films derived from the self-induced seeding solution showed a more advanced crystallization state (i.e., crystallization occurs at an earlier stage) when compared to films prepared from the initial solution mixture. Complementary, the PFM images in Figure 6 also corroborates the previous SEM study on the different mechanism of nucleation developed in the films. The isolated piezoelectric regions observed in Figure 6c are ascribed to the homogeneous nucleation of perovskite grains from a few isolated nuclei, which radially grow with temperature within an amorphous matrix-forming typical rosette-like structures.\[23\] On the other hand, the high density of fine-size piezoelectric active regions covering the whole surface of the film, as observed in Figure 6d, would arise from the heterogeneous nucleation of perovskite grains over the surface of the nanoseeds introduced in the system. From these results, we can conclude that perovskite BiFeO₃ thin films with a higher degree of structural order and a fine-grained microstructure are therefore obtained from the self-induced seeding solutions of this work.

Finally, the low-temperature strategy described in this work made possible the direct growth of BiFeO₃ thin films on flexible polymeric substrates at a temperature of only 350 °C (see Experimental Section). Reflections ascribed to the perovskite phase are detected in the X-ray pattern of Figure 7a, together with some peaks and background coming from the polymeric substrate that may hinder the proper observation of some perovskite reflections. Therefore, a sample counterpart prepared on rigid silicon under the same processing conditions is also included for the sake of comparison. Secondary non-ferroelectric phases (either Bi-rich or Fe-rich oxides) derived from the metastability of single-phase BiFeO₃ are not detected by X-ray diffraction.\[24\] The reliability of the self-induced solution seeding approach made it possible to obtain different samples of BiFeO₃ on plastic with high reproducibility (see Figure S6, Supporting Information). To support its potential application in next-generation electronics, the ferroelectric properties of the flexible thin-film were measured through the corresponding polarization-electric field (P-E) loop depicted in Figure 7b. A remanent polarization of 10.5 µC cm⁻² and a coercive field of 530 kV cm⁻¹ are obtained at room temperature after the compensation of the experimental hysteresis loop by subtracting the non-switching contributions (capacitance, resistance, and nonlinear conduction) using a simulation model.\[25\] As expected, polarization values are moderately lower than those that can be achieved in BiFeO₃ thin films prepared at conventional temperatures (over 600 °C) on rigid silicon substrates.\[26\] However, they compare favorably with most ferroelectric thin films (mainly organic) processed at low temperatures and with the values requested for the fabrication of ferroelectric devices.\[27\]
In addition, the value of remanent polarization obtained in this BiFeO₃ thin film is among the highest ones obtained for metal oxide thin films directly integrated into a flexible plastic.[7b,c,9,28] This demonstration brings the application of inorganic ferroelectrics as data storage elements in non-volatile memories much closer to emerging technologies such as wearable electronics and future smart and sustainable electronic systems. To minimize the detrimental contribution of the leakage current typically associated with undoped BiFeO₃, ferroelectric hysteresis loops were also measured in this film at a temperature of 150 K (see Figure S7, Supporting Information) yielding a value of 17.5 μC cm⁻². This result suggests that the ferroelectric response of the flexible BiFeO₃ thin film at room temperature could be further improved by tuning the leakage current behavior via chemical doping.[59] Complementary values of the same order were obtained in the film counterpart prepared on rigid silicon (see Figure S8, Supporting Information), which supports the reliability of the solution method proposed here to integrate BiFeO₃ active layers on different types of systems (semiconductor, polymer, glass, or metal substrates).

The potential of BiFeO₃ for photovoltaic devices has attracted considerable attention in the past few years due to its relatively narrow bandgap (2.2–2.7 eV) as compared to the rest of ferroelectric oxides.[10b] Figure 7c shows the current–voltage (J–V) characteristics of the flexible BiFeO₃ thin film under different conditions of illumination and poling state. Without poling, the film exhibits some photovoltaic effect at room temperature under illumination (at 0.6 Sun), yielding a relatively small output photocurrent density (30 μA cm⁻²). This behavior can be ascribed to the self-polarization usually found in ferroelectric thin films due to strain gradients generated in the perovskite cell by substrate clamping, which induces a preferred orientation of ferroelectric dipoles and hence a net polarization in the system.[31] Both short-circuit current density and open-circuit voltage considerably increase with poling, reaching maximum values of 90 μA cm⁻² and 0.13 V. These data suggest the strong remanence of the ferroelectric dipoles obtained after polarization even at low voltages during the course of the photovoltaic measurement. From the former results, a power output of 11.7 μW cm⁻² is calculated (extrapolated to a value of ~20 μW cm⁻² at 1 Sun) which is one order of magnitude higher than that corresponding to the non-polarized sample. The built-in electric field generated by the formation of ferroelectric domains in the thin film is directly responsible for the photovoltaic effect observed, where each domain boundary acts as a classical p–n junction separating the photogenerated electrons and holes giving rise to improved properties in the device upon illumination.[32] Higher applied voltages (>10 V) led to a critical resistance degradation in the capacitor that accounts for the null photovoltage measured, despite some photocurrent being present. Under dark conditions, however, no photovoltaic effect is initially observed in the flexible film. Clearly, the ferroelectric nature of the flexible BiFeO₃ thin film has a strong effect on the photoinduced response of the device. This confirms the interesting coupling phenomenon between electrical polarization and the photovoltaic effect anticipated for the so-called photoferroelectric materials, such as BiFeO₃.[33]

Whereas the power output obtained for the flexible BiFeO₃ thin film is relatively low for an application of energy conversion (e.g., in a solar cell), this value would satisfactorily meet the requirements demanded by self-powered devices (micropower operation) based on energy harvesting from light.[34] This result acquires special relevance in the next ubiquitous technology of the Internet of Things (IoT), where tens of billions of connected devices will require a power source to work properly in the coming years. The economic load of this huge challenge could be significantly alleviated by the incorporation of multi-source energy harvesters based on multifunctional materials (e.g., photovoltaic, piezoelectric, pyroelectric, electrostrictive, magnetostrictive) integrated into low-cost, lightweight, and flexible substrates (e.g., plastic) to allow operations at remote locations.[35]

3. Conclusion

The development of a low-temperature strategy based on a solvent-engineering approach has made possible the crystallization of BiFeO₃ thin films at only 350 °C on flexible polymeric substrates. Self-induced seeding solutions are obtained upon
the addition of an antisolvent (1,3-propanediol) to a solution (a Bi/Fe salt dissolved in acetic acid) that leads to the formation of nanocrystals by supersaturation. The corresponding nanoparticles present in the deposited layer induce a seeding effect, thus increasing the density of nucleation sites and lowering the activation energy required for the crystallization of the perovskite phase. The flexible BiFeO$_3$ thin films show a remanent polarization of 10.5 μC cm$^{-2}$ and power output under the illumination of 11.7 μW cm$^{-2}$ that support their potential application in next-generation devices such as flexible computer memories and flexible energy harvesters. In addition to the reduced thermal budget achieved, with a positive impact on global sustainability, the simplicity of the solution method proposed would facilitate its implementation into the sustainable development of electronic devices and systems ever more demanded today.

4. Experimental Section

Synthesis of Precursor Solutions: The flow chart of the synthesis route leading to the precursor solutions of this work is shown in Figure S1 (Supporting Information). Bismuth (III) nitrate pentahydrate (Bi(NO$_3$)$_3$ · 5H$_2$O, ≥99.9% trace metals basis, Sigma–Aldrich), iron (III) acetylacetone (Fe(C$_5$H$_7$O$_2$)$_3$, ≥99.9% trace metals basis, Sigma–Aldrich), acetic acid (glacial, 100% anhydrous, Supelco–Sigma–Aldrich), and 1,3-propanediol (HO(CH$_2$)$_3$OH, 98%, Sigma–Aldrich) were used as metal precursors and solvents. Volume ratios of acetic acid to 1,3-propanediol of 1:1 or suspensions (seeding solutions), respectively. The concentration of the precursors solution of BiFeO$_3$ ranged from 0.125 m (initial mixture or suspensions (seeding solutions), respectively). The concentration of the precursor solution of BiFeO$_3$ ranged from 0.125 m (initial mixture at $t_0$) to 0.085 m (stable equilibrium at $t_j$) after the sedimentation of crystals (calculated from the supernatant of the corresponding suspension). A volume ratio of acetic acid to 1,3-propanediol of 1:1 was used to induce higher supersaturation conditions resulting in large precipitation of crystals.

Processing of Thin Films: Layers from precursor solutions (unseeding and seeding) were deposited on rigid Pt/TiO$_2$/SiO$_2$/(100)Si (Radiant Technologies Inc.) and flexible Pt/NiCr/Pt (75 μm thick, UPLEX-S polyimide, UBE Industries Ltd.) substrates by spin-coating (2000 rpm for 45 s). Wet films were dried at 150 °C for 5 min and pyrolyzed at 250 °C for 5 min on hot-plates. The amorphous films thus obtained were crystalized at different temperatures for 10 min by rapid thermal annealing (JIPYELC JetStar 100T Processor) under an oxygen atmosphere. The temperature at this step was controlled by an external thermocouple located on the film surface. Additionally, coatings on test samples (e.g., bare substrates) from liquid temperature lacquers (Omegaalq, Omega Engineering Inc.) were used to guarantee that the processing temperature applied is not surpassed and to maintain reproducibility. The studies showed a temperature variation of less than ±5 °C. To obtain samples of different thicknesses, deposition, drying, pyrolysis, and crystallization steps were successively repeated. For the rapid thermal annealing of the flexible films, a homebuilt sample holder maintaining the sample under tensile stress was used in order to avoid the mechanical deformation of the film due to the heat shrinkage of the polymeric substrate (see Figure S9, Supporting Information).

Characterization: Dynamic light scattering was used to determine the particle size distribution of the precursor solutions (Zetasizer Nanoparticle Analyser, Malvern Instruments Ltd.). The concentration of the precursor solutions was calculated by thermogravimetric analysis of the gel powders obtained from aliquots of the solutions dried at 110 °C overnight and calcined at 550 °C for 1 h in a furnace. Aliquots from the seeding solutions (suspensions) were taken from the supernatant. Gel powders were also subjected to thermogravimetric and differential thermal analysis (Q600, TA Instruments). X-ray diffraction was used to detect the presence of crystalline phases in the thin films and to study the nature of the crystals formed in the seeding solution (D8 ADVANCE instrument, Cu K$_\alpha$ radiation, Bruker). Scanning electron microscopy was used to observe the surface morphology of the thin films (Nova NanoSEM 230 instrument, FEI Company). Topographies of the film surfaces were also acquired by scanning force microscopy (WSxM software Nanotec Electrónica S.L.). Images of piezoelectric force microscopy were obtained with an AC voltage of 3.5 V of amplitude at 50 kHz between the film samples and conductive Pt/Ir-coated tips (PPP-NCH Pt probes, Nanosensors) on cantilevers with force constant of 42 N m$^{-1}$. Ferroelectric hysteresis loops were measured under sinusoidal excitation (2–100 V amplitude, 0.1–20 kHz frequency) using a virtual ground system composed by a pulse generator (33220A Arbitrary Waveform Generator, Agilent), a power amplifier (High-Voltage Amplifier 9100, Tabor Electronics), a current amplifier (428-PROG Programmable Current Amplifier, Keithley), and an oscilloscope (TDS 520, Tektronix). To that end, a planar array of discrete capacitors was fabricated by sputter deposition of top Pt electrodes (=10 nm thick, electrode transmittance of 0.38) on the film surface through a shadow mask. Charge loops were obtained by numerical integration from the respective current loops. The photovoltaic response was analyzed by measuring the variation of the current density with voltage in the dark and under illumination with different conditions of poling state using an electrochemical interface (PalmSens4, PalmSens) and a solar simulator (HAL-C100, Asahi Spectra) coupled to a telecentric lens that results in a homogeneously illuminated area of 25 × 25 mm$^2$. The light intensity on the measured BFO capacitor was 0.6 times the sun intensity. The same electrode configuration used for the electrical characterization (10 nm Pt/150 nm BiFeO$_3$/20 nm Pt/20 nm NiCr/75 μm PI) was adopted for the measurement of the solar cell device (active area of 0.008 mm$^2$, thickness of 150 nm).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are openly available in DIGITAL.CSIC at https://doi.org/10.20350/digitalCSIC/14500, reference number 260797.

Keywords

electronic devices, flexible thin films, multifunctional oxides, seeding effect, solution processing

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