A SIMPLE SETUP TO OBTAIN FERROELECTRIC THIN FILMS BY DIP-COATING

UN SISTEMA EXPERIMENTAL SENCILLO PARA OBTENER CAPAS DELGADAS FERROELÉCTRICAS POR EL MÉTODO DE INMERSIÓN

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An easy, home-made experimental setup is presented to process ferroelectric thin films by using the dip-coating method. It has been used a stepper motor, a control circuit that provides electrical power to the motor, and a computer. A LabVIEW program has been developed to control all the process, including the velocities and times for the substrate's movement, which can be selected by the user. This setup allows the preparation of thin films under the same conditions than that of commercial equipment. Thin films from two systems have been obtained, $Sr_{0.70}Ba_{0.30}Bi_2Nb_2O_9$ and $(Pb_{0.980}La_{0.020})(Zr_{0.950}Ti_{0.050})_{0.995}O_3$. The corresponding structural and ferroelectric characterizations validate the experimental setup.

Se presenta un sistema de obtención de capas delgadas ferroeléctricas, por el método de inmersión, desarrollado de forma sencilla y con muy bajo costo. Se utilizó un motor de paso, un circuito para controlar el motor que a la vez provee alimentación eléctrica, y una computadora. A través de un programa desarrollado en LabView se controla todo el proceso, y es posible seleccionar la velocidad y el tiempo para el movimiento del substrato. El sistema experimental permite obtener capas con iguales condiciones que los equipos comerciales. Se obtuvieron capas de dos sistemas, $Sr_{0.70}Ba_{0.30}Bi_2Nb_2O_9$ y $(Pb_{0.980}La_{0.020})(Zr_{0.950}Ti_{0.050})_{0.995}O_3$, cuya caracterización estructural y ferroeléctrica permitió validar el sistema desarrollado.

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I. INTRODUCTION

Ferroelectric systems have attracted much attention for many years as a result of their multiple applications in non-volatile random access memories, pyroelectric devices, piezoelectric transducers, etc. [1,2]. From this point of view, considerable attention receives the processing of ferroelectric thin films. Several techniques have been developed to obtain ferroelectric thin films [3]. By using physical methods, such as sputtering and laser ablation, the stoichiometry of the films cannot be guaranteed from the original targets [3]. In addition, such as methods involve expensive equipment. Therefore, it is more common to use chemical methods [3], such as sol-gel [3–7] and polymer precursor method [8], even when these techniques have some disadvantages. Nevertheless, the processing of high-quality ferroelectric thin films and the development of simple, low cost and reproducible methods to obtain them constitutes an open topic for the scientific community.

In the present work, a low-cost, home-made experimental setup is presented in order to obtain ferroelectric thin films by using dip-coating. This setup allows getting thin films under the same conditions as those of commercial equipment. Parameters as velocity of the substrate in/out the solutions and time into the solutions are controlled by using a personal computer and LabVIEW as programming environment. Thin films from two systems were obtained, $Sr_{0.70}Ba_{0.30}Bi_2Nb_2O_9$ (SBBN-30) and $(Pb_{0.980}La_{0.020})(Zr_{0.950}Ti_{0.050})_{0.995}O_3$ (PLZT 2/95/5), which were previously studied as ceramic bulks [9–11]. X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive Spectroscopy (EDS) and Polarization-Electric Field (hysteresis loops) experiments were carried out to evaluate the thin films.

II. EXPERIMENTAL SETUP (DIP-COATING)

The experimental setup to process thin films by dip-coating was designed by using a stepper motor, a circuit to control and give electrical power to the motor, and a computer to control the process by using a LabVIEW program. Figure 1 shows the details of the interconnections of the experimental system.

The stepper motors are able to convert a sequence of voltages into discrete angular movements. Then, they can be used in situations where a certain degree of precision is required. Floppy disk readers work by using a stepper motor, which guarantees the accurate movement of the head. These motors are able to move one step at a time for each pulse that is applied.

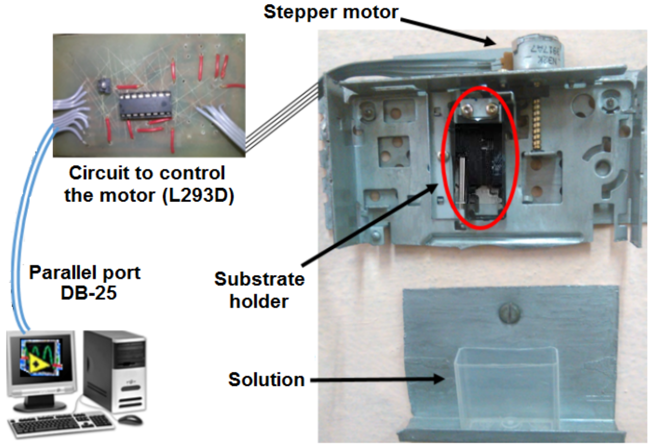

Figure 1. Experimental setup to obtain ferroelectric thin films by using the dip-coating method.

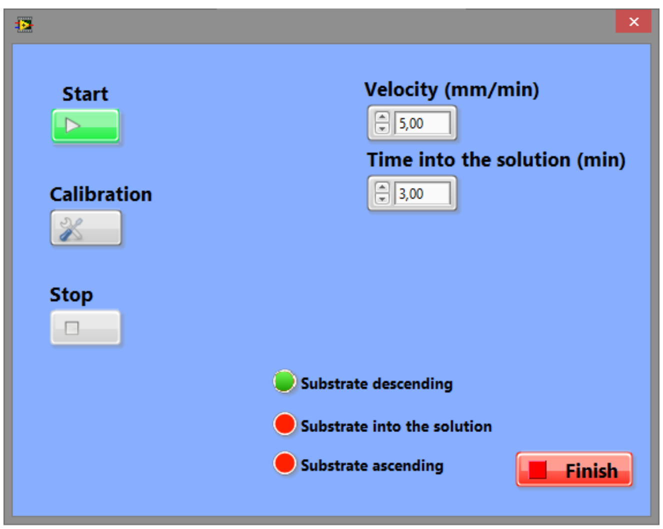

Figure 2. Frontal panel of the program, illustrating the downward motion step of the process.

The rotation's angle for each step [12] can range from 90^0 to 1.8^0. For the proposed experimental setup, it has been used a stepper motor from a discarded floppy disk, a bipolar motor of 5 volts and 8 steps lap. The pulse sequence to control bipolar stepper motors is well known [12] and only the time between steps, the parameter that defines the speed of the motor, differs between specific applications. In the present experimental system, the motor is controlled by using a L293D integrated circuit through the parallel port of the computer [13]. A LabVIEW program was developed to control all the process, including the velocities and times for the substrate's movement, which can be selected by the user, offering different conditions to process thin films. Figure 2 shows the frontal panel of the program, where the user can calibrate the system, select the velocity for downward and upward motion of the substrate, and its time into the solution, and follows all the process through three control buttons (substrate descending, substrate into the solution, substrate ascending). The figure shows the case when the substrate is descending (the corresponding control button is green).

III. THIN FILMS PROCESSING

Thin films were prepared by using a sol-gel process [4–7] The solution containing the desirable ions was prepared from SBBN-30 ceramic powders, which were obtained by conventional mixed oxides method [9,10]. The stock solution was prepared by dissolution of the powders (0.5) g in acid solution [10 % of nitric acid (HNO_3) and 90 % of distilled water]. The dissolution was optimized by heating the solution up to around 80 ^oC for 1 hour. Simultaneously, a resin was obtained by the Pechiney's method using citric acid and ethylene glycol (citric acid/ethylene glycol = 42/58 in mol %). The mixture was heated at 70 ^oC for 1 hour, when transparent resin was obtained. After that, the resin and the stock solution were mixed at 90 ^oC for 1 hour.

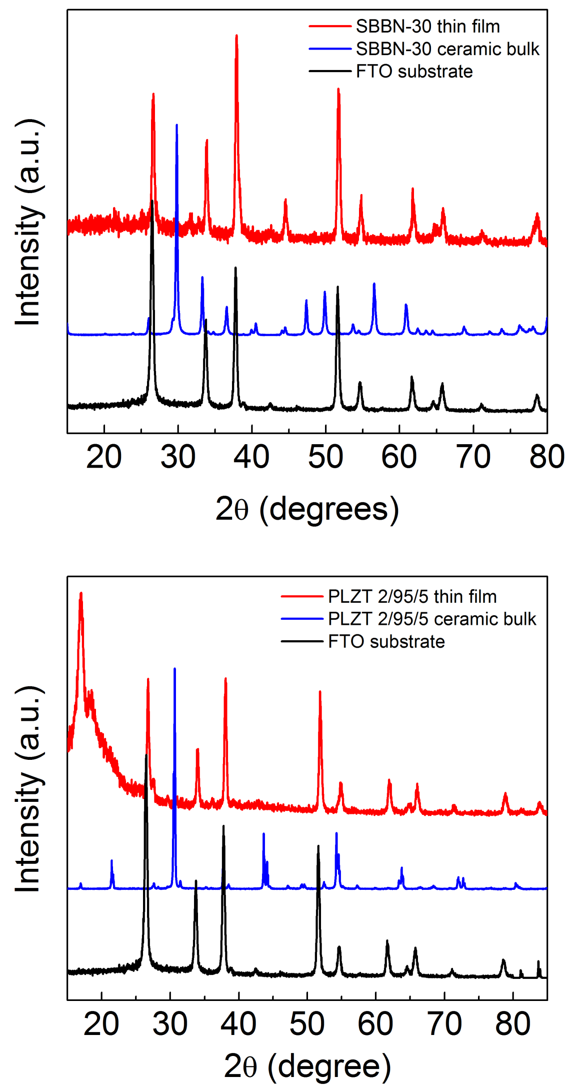

Figure 3. X-ray diffraction patterns, at room temperature, for (a) SBBN-30 and (b) PLZT 2/95/5 thin films. It has been included the corresponding results for ceramic bulk samples and the FTO substrate.

A similar way was used to prepare the solution from PLZT 2/95/5 ceramic powders, which were obtained by conventional mixed oxides method too [11]. The stock solution was prepared by dissolution of the powders (0.2) *g* in acid solution [30 % of nitric acid (HNO_3) and 70 % of distilled water]. The dissolution was optimized by heating the solution up to around 80 ^oC for 1 hour. The resin was obtained using citric acid and ethylene glycol (citric acid/ethylene glycol = 44/56 in mol %). The mixture was heated at 90 ^oC for 1. Finally, the resin and the stock solution were mixture at 90 ^oC for 1 hour.

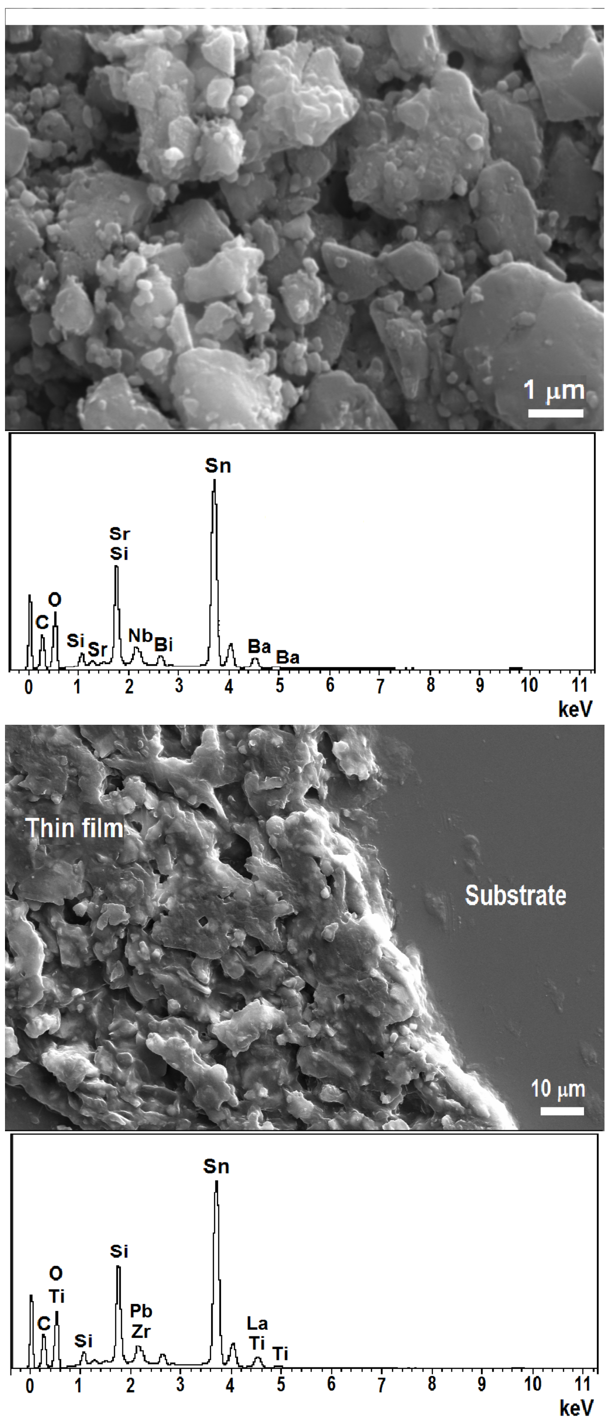

Figure 4. SEM micrographs and EDS spectra for (a) SBBN-30 and (b) PLZT 2/95/5 thin films.

Films from both solutions were deposited at room temperature on FTO substrates by using the experimental setup, which was described in section II (dip-coating method). Finally, the deposited films were submitted to a heat treatment of 450 ^oC for crystallization. Deposited films were crack-free and looked uniform on the substrates.

IV. THIN FILMS CHARACTERIZATION

X-ray diffraction (XRD) measurements were performed, at room temperature, by using a Panalytical X'Pert Pro Multipurpose (MPD) diffractometer with CuK_{α_1} radiation (λ = 1.54056 Å) and an incident angle of 1^o. The data were collected in the angular range 20^o to 60^o in 2θ and a step of 0.02 degrees. Figure 3 shows the X-ray diffraction patterns, at room temperature, for the obtained thin films. The figures also include the results for the corresponding ceramic bulks, as well as the used FTO substrate. The results did not reveal any information concerning the films, i.e. the observed diffraction lines were almost exclusively associated to the FTO substrate, because of the area of the deposited films was smaller than that of the diameter of the beam. Note that it is not a limitation of the developed experimental setup. The deposition area is selected by the user considering the size of the used substrate.

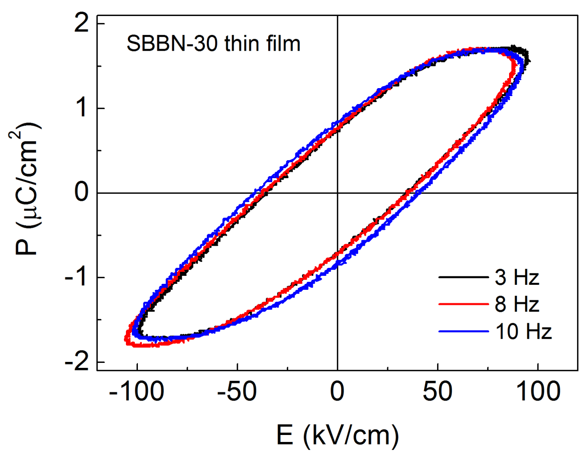

Figure 5. Hysteresis loops, at room temperature and several frequencies, for the SBBN-30 thin film.

Scanning Electron Microscopy (SEM) experiments were carried out on the thin films by using a Carl Zeiss Evo L5-15 microscope equipped with an X-ray energy dispersive spectrometer. Figure 4 shows the SEM micrographs and the energy dispersive spectroscopy (EDS) spectra for the processing thin films. Dense and uniform surfaces were observed and no micro-cracks or other microstructural defects were found. On the other hand, the EDS spectra have showed the presence of the corresponding elements for both studied systems. The spectra also included the elements, which correspond to the used FTO substrate (Sn and Si). These results validate the experimental setup for thin film preparation.

Finally, Polarization-Electric Field (P-E) dependences (hysteresis loops) were obtained by using a modified Sawyer-Tower circuit, which was previously developed by us [14]. Figure 5 shows the hysteresis loops, at room temperature and several frequencies, for SBBN-30 thin film. Typical ferroelectric loops were obtained as expected considering the same measurements for the corresponding ceramic bulk [10]. Also a similar qualitative behavior to that of previous report in systems of the same Aurivillius family was obtained [15]. On the other hand, typical antiferroelectric loops were obtained for PLZT 2/95/5 thin film. Figure 6 shows the P-E dependence at 3 *Hz*, as an example of the obtained results at several frequencies. Previous structural analysis on the ceramic bulk sample has shown the coexistence of both antiferroelectric-orthorhombic (Pbam) and ferroelectric-rhombohedral (R3c) phases; the hysteresis loops have also shown a higher stability for the antiferroelectric phase [11]. The thicknesses of the thin films were estimated by using Atomic Force Microscopy (AFM) showing a value of 150 nm.

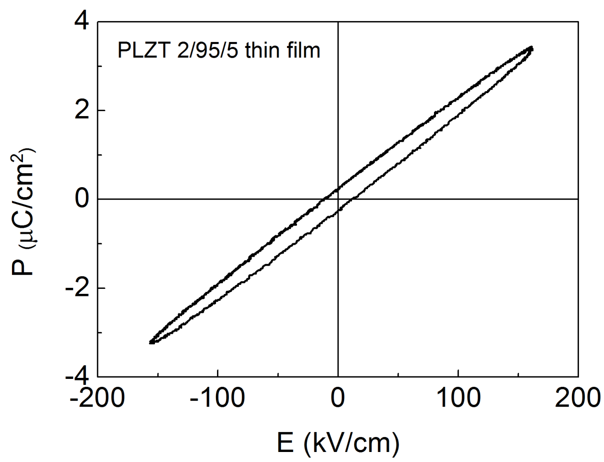

Figure 6. Hysteresis loops, at room temperature and 3 Hz, for the PLZT 2/95/5 thin film.

V. CONCLUSIONS

A low-cost, home-made experimental setup has been designed and constructed in order to obtain ferroelectric thin films by dip-coating method. It was designed by using a stepper motor, a circuit to control and provide electrical power to the motor, and a computer to control the process by using a LabVIEW program. The developed setup allows getting thin films under the same conditions than that of commercial equipment. The user can select the velocities and times for the substrate's movement, offering different conditions to process thin films. Thin films of $Sr_{0.70}Ba_{0.30}Bi_2Nb_2O_9$ and $(Pb_{0.980}La_{0.020})(Zr_{0.950}Ti_{0.050})_{0.995}O_3$ were obtained and their structural and ferroelectric behavior was studied. Dense and uniform surfaces were observed and no micro-cracks or other microstructural defects were found. The EDS spectra showed the presence of the corresponding elements for both systems. Typical ferroelectric and antiferroelectric loops were obtained, respectively, as expected. These results validate the experimental setup, which has been developed to obtain ferroelectric thin films.

VI. ACKNOWLEDGMENTS

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