**UNIVERSIDADE DE SÃO PAULO
INSTITUTO DE FÍSICA DE SÃO CARLOS**

Felipe Ferraz Morgado de Oliveira

**Growth of superconducting and ferroelectric
heterostructures**

São Carlos

2018

Felipe Ferraz Morgado de Oliveira

**Growth of superconducting and ferroelectric
heterostructures**

Dissertation presented to the Graduate Program
in Physics at the Instituto de Física de São Car-
los, Universidade de São Paulo, to obtain the
degree of Master in Science.

Concentration area: Applied Physics

Advisor: Prof. Dr. Júlio Criginski Cezar

Corrected version
(Original version available on the Program Unit)

São Carlos
2018

I AUTHORIZE THE REPRODUCTION AND DISSEMINATION OF TOTAL OR PARTIAL COPIES OF THIS DOCUMENT, BY CONVENCIONAL OR ELECTRONIC MEDIA FOR STUDY OR RESEARCH PURPOSE, SINCE IT IS REFERENCED.

Oliveira, Felipe Ferraz Morgado de
Growth of superconducting and ferroelectric
heterostructures / Felipe Ferraz Morgado de Oliveira;
advisor Julio Crigenski Cezar - revised version -- São
Carlos 2018.
94 p.

Dissertation (Master's degree - Graduate Program in
Física Aplicada) -- Instituto de Física de São Carlos,
Universidade de São Paulo - Brasil , 2018.

1. Pulsed laser deposition. 2. Hight Tc
superconductors. 3. Ferroelectricity. 4. Field-effect
devices. 5. Oxides. I. Cezar, Julio Crigenski, advisor.
II. Title.

I dedicate this work to all those who seek their professional fulfillment along with their personal pleasure.

ACKNOWLEDGEMENTS

Many people contributed to this work, so I apologize in advance in case someone is left out. In any case, I would like to express my sincere gratitude for all those people who have helped me, since each of them contributed significantly to the development of this work. Returning to the topic in matter, I would like to first thanks to my advisor Júlio Criginski Cezar immensely for the opportunity to work in the laboratory and also for the immense professional and personal support during all these years that we have been working together. There is no way I can express my gratitude for everything he has done for me and I hope that little by little I will be able to reciprocate that kindness and professionalism, and also to pass on all this knowledge.

I am eternally grateful to the researchers of the group Pedro Schio de Noronha Muniz, Thiago José de Almeida Mori, Tulio Costa Rizuti da Rocha and Wendell Simoes e Silva for the scientific discussions, professional and personal orientations, availability, professional support, many lectures and, more importantly, by the friendship developed over the years.

I would also like to thank all members of the Group of Surfaces and Interfaces of Multifunctional Materials (SIMM) of the National Laboratory of Synchrotron Light in which this work was carried out. In particular: Flavia Regina Estrada for discussions involving microscopy, for many rides to work and for a good friendship, Camili Ambrosio and Horacio Ribeiro de Moraes for the technical support, Felipe Luiz Alvares Vital for introducing me to the group and for the friendship, Anderson Hebert of Abreu Gomes, Danian Alexandre Dugato, Jeovani Brandao, Karine Silva Alcântara, Leandro Tolentino Coutrim, Lucas Capel Godinho, Maíra Dombroski Neme and Rodrigo dos Santos Rodrigues for the laughter and friendships.

I am also very grateful for my girlfriend Joseanne Cristina for being always by my side supporting me, encouraging me and being part of this my trajectory. I'm sure this route would be a lot less interesting if she was not with me.

And finally, I thank the funding agencies that have made this work possible, both directly and indirectly, such as the São Paulo Research Foundation (FAPESP) through projects 2016/14051-4, and 2012/51198-2, National Council for Scientific and Technological Development (CNPq) and the Ministry of Science, Technology, Innovation and Communications (MCTIC).

I am smart enough to know that I am dumb.

Richard Feynman

ABSTRACT

OLIVEIRA, F. F. M. **Growth of superconducting and ferroelectric heterostructures.** 2018. 94 p. Dissertação (Mestrado em Ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2018.

The phase diagram of complex oxides is very diverse due to the strong interaction between electrons in the electronic structure. It is possible to probe those interactions by changing electrostatically the carrier density, the main concept behind the Field-Effect Transistors (FET) which is the building blocks of nanoelectronics devices.¹⁻³ In the case of high- T_C superconductor copper oxides, it is possible to use this concept to switch between superconducting and insulator phases, for example using an adjacent liquid electrolyte layer to inject charges in a superconducting film.⁴ With that in mind, the objective of this work was to establish protocols to grow superconductor and ferroelectric films for future fabrication of superconducting FET devices. We optimized the deposition conditions for the growth of a single layer of superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ and the ferroelectric barium titanate on SrTiO_3 substrates by pulsed laser deposition (PLD). Several techniques were employed to study the properties of the thin films, such as X-ray diffraction, atomic force microscope, X-ray photoelectron spectroscopy, resistance vs temperature and ferroelectric hysteresis. Regarding the superconductors thin films, we observed several relations between the superconducting features and the growth parameters. For instance, lower growth temperatures contribute to the nucleation of a -axis oriented grains meanwhile higher growth temperature tends to be c -axis oriented. Regarding the frequency of the laser (proportional to the growth rate), it seems that lower frequency is related to higher surface roughness and the presence of non-superconducting contributions. As it increases, the roughness decrease and the sample presents a sharper superconducting transition. Finally, we also did the first steps towards the field effect device by growing a heterostructure thin film consisting of a superconductor and ferroelectric material. The sample grew c -axis oriented on strontium titanate substrate, though with a high value of surface roughness.

Keywords: Pulsed laser deposition. High- T_C superconductors. Ferroelectricity. Field-effect device. Oxides.

RESUMO

OLIVEIRA, F. F. M. **Crescimento de heteroestruturas supercondutoras e ferroelétricas.** 2018. 94 p. Dissertação (Mestrado em Ciências) - Instituto de Física de São Carlos, Universidade de São Paulo, São Carlos, 2018.

O diagrama de fase dos óxidos complexos é muito diverso devido à forte interação entre os elétrons na estrutura eletrônica. É possível sondar essas interações alterando eletrostaticamente a densidade dos portadores, o principal conceito por trás dos transistores de efeito de campo (FET), que é o elemento fundamental dos dispositivos nanoeletrônicos.¹⁻³ No caso de supercondutores de alta temperatura a base de óxidos de cobre, é possível usar este conceito para alternar entre fases supercondutoras e isolantes, por exemplo utilizando uma camada adjacente de eletrólito líquido para injetar cargas no filme supercondutor.⁴ Com isso em mente, o objetivo desse trabalho foi estabelecer protocolos para crescer filmes supercondutores e ferroelétricos para fabricações futuras de dispositivos FET supercondutores. Nós otimizamos as condições de deposição para o crescimento de uma única camada do supercondutor $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ e do ferroelétrico titanato de bário em substratos SrTiO_3 por deposição de laser pulsado (PLD). Diversas técnicas foram empregadas para estudar as propriedades dos filmes finos, como difração de raios-X, microscopia de força atômica, espectroscopia de fotoelétrons de raios-X, resistência vs temperatura e histerese ferroelétrica. Em relação aos filmes finos supercondutores, observamos várias relações das propriedades supercondutoras com os parâmetros de crescimento. Por exemplo, temperaturas de crescimento mais baixas contribuem para a nucleação de grãos orientados no eixo a , enquanto a temperatura de crescimento mais alta tende a ser orientada para o eixo c . Em relação à frequência do laser (proporcional à taxa de crescimento), há um indício que valores menores de frequência está relacionada à maior rugosidade superficial e à presença de contribuições não supercondutoras. À medida que aumenta a frequência, a rugosidade diminui e a amostra apresenta uma transição supercondutora mais nítida. Por fim, também fizemos os primeiros passos em direção ao dispositivo de efeito de campo, desenvolvendo um filme fino de heteroestrutura com um material supercondutor e ferroelétrico. A amostra cresceu orientada no eixo c em substrato de titanato de estrôncio com alto valor de rugosidade superficial.

Palavra-Chave: Deposição de laser pulsado. Supercondutores de alta temperatura. Ferroeletricidade. Dispositivos de efeito de campo. Óxidos.

LIST OF FIGURES

Figure 1 – Top: schematic of the gating device, where DEME-TFSI is the ionic liquid. Bottom: reversibility of the doping. First applied positive gate voltage (left) and then negative gate voltage (right).	24
Figure 2 – Historical plot - Resistance versus temperature of a mercury wire from 1911 experiment shows a superconducting transition at 4.2 K.	25
Figure 3 – Characteristics of a superconductor Type I. Induced magnetic field (left) and the different states diagram (right).	27
Figure 4 – Characteristics of a superconductor Type II. Induced magnetic field with the presence of H_{C1} and H_{C2} (left) and the different states diagram including a new mixed state (right).	27
Figure 5 – Phase diagram as a function of doped electrons (n) and holes (p) for high- T_C cuprate superconductors. There are three main regions: the undoped region for low electron or hole doping (antiferromagnetic), optimal doping (superconducting) and pseudogap.	28
Figure 6 – Typical hysteresis curve. Arrows indicate the polarization state of the material in the corresponding electric field. E_C means coercive electric field, P_R is remanent polarization and P_S is the spontaneous polarization. Source: extracted from D. Damjanovic.	30
Figure 7 – Cross-section of a Field-Effect Transistor. Three metallic electrodes: source, gate and drain.	31
Figure 8 – Behavior of several type of materials as function of the sheet charge density (n_{2D}). In this figure, the colossal magnetoresistive and the high- T_c copper oxides are the behavior of the (La,Sr)MnO ₃ and YBa ₂ Cu ₃ O _{7-δ} , respectively. Where AF means Antiferromagnetic, FM - Ferromagnetic, I - Insulator, M - Metal, SC - Superconductor, FQHE - Fractional Quantum Hall Effect, CMR - Colossal Magnetoresistive.	33
Figure 9 – (a) Applying a voltage between gate and source to polarize the ferroelectric material. (b) The polarization remains even without the battery applying the voltage.	33
Figure 10 – Typical phase diagram of high- T_C superconductor. AF means antiferromagnetic and T_C is the critical temperature.	34
Figure 11 – Sheet resistance as function of the temperature varying the gate voltage from 0 to 1.52 V. Inset: Details of the transition from superconductor to insulator.	34
Figure 12 – (a) Tetragonal (YBa ₂ Cu ₃ O ₆) and (b) Orthorhombic (YBa ₂ Cu ₃ O ₇) YBCO perovskite structure.	36

Figure 13 – Barium titanate perovskite structure. (a) unit cell with barium atom in the middle. (b) Shift of the Ti atom due to an electric field resulting in the polarization.	36
Figure 14 – Schematic of the pulsed laser deposition chamber. A pulsed laser will hit a target inside a controlled atmosphere chamber resulting in a plume that will condense on the substrate as a thin film.	40
Figure 15 – Schematic of an XRD experiment for a fixed X-ray tube in the Bragg-Brentano geometry.	42
Figure 16 – XRD measurement ($\theta - 2\theta$) of a thin film YBCO//STO. YBCO and STO peaks (00l) are accordingly indexed and the STO- K_β peaks are labeled as *.	43
Figure 17 – XRR measurement of Au thin film on Si substrate of thickness 5 and 20 nm.	44
Figure 18 – Schematic of an Atomic Force Microscope imaging process.	45
Figure 19 – (a) Schematic of the low temperature electronic transport chamber and (b) the current state at the laboratory.	47
Figure 20 – Illustration of the PUND method for ferroelectric hysteresis. The current is measured during the pulses P-U-N-D.	48
Figure 21 – Ferroelectric hysteresis and its respective I-V curve. Experimentally, it is expected this kind of behaviour in the ferroelectric materials.	48
Figure 22 – (a) Typical AFM topography after heat treatment of our STO substrates and (b) line profile with atomic steps of height $\approx 4 \text{ \AA}$	50
Figure 23 – X-ray diffractograms ($\theta - 2\theta$) for samples YBCO_680C (blue), YBCO_730C (dark yellow) and YBCO_780C (red). YBCO and STO peaks are indexed accordingly, STO- K_β peaks are labeled as *.	52
Figure 24 – AFM image of $10 \times 10 \mu\text{m}$: (a) YBCO_680C, (b) YBCO_730C and (c) YBCO_780C. The surface roughness for each image: (a) 30.6 nm, (b) 31.6 nm and (c) 32.8 nm. Height from 0 to 280 nm as shown in color ruler.	53
Figure 25 – Left: Scheme of a Au/Ti/YBCO/STO used to measure resistivity in four probe geometry of the YBCO thin film. Right: Resistivity-Temperature (RT) measurements of YBCO_680C, YBCO_780C and YBCO_730C.	54
Figure 26 – X-ray diffractograms ($\theta - 2\theta$) for samples YBCO_1Hz (orange), YBCO_3Hz (black), YBCO_6Hz (purple) and YBCO_10Hz (green). YBCO and STO peaks are indexed accordingly, STO- K_β peaks are labeled as * and the peak around 10° (labeled as # in the figure) is assigned to multiple diffraction peaks of the substrate.	55
Figure 27 – AFM image of $10 \times 10 \mu\text{m}$: (a) YBCO_1Hz, (b) YBCO_3Hz, (c) YBCO_6Hz and (d) YBCO_10Hz. Inset (e) AFM image $1.5 \times 1.5 \mu\text{m}$ of YBCO_10Hz. The surface roughness for each image: (a) 34.4 nm, (b) 17.1 nm, (c) 14.1 nm and (d) 16.1. Height from 0 to 195 nm as shown in color ruler.	56

Figure 28 – XPS measurement: (a) Typical survey scan of our YBCO sample to detect any impurities at the surface. The peaks are labeled with the corresponding elements. Higher resolution for each element: (b) yttrium 3d, (c) barium 3d, (d) copper 2p and (e) oxygen 1s.	58
Figure 29 – Resistivity-Temperature measurements: YBCO_1Hz, YBCO_3Hz, YBCO_6Hz and YBCO_10 Hz. Inset is the slope for each sample to get the critical temperature. All samples grown at 780 °C.	59
Figure 30 – X-ray diffractograms ($\theta - 2\theta$) for samples YBCO_1Bar (grey). YBCO and STO peaks are indexed accordingly, STO- K_β peaks are labeled as * and the peak around 10° (labeled as # in the figure) is assigned to multiple diffraction peaks of the substrate.	60
Figure 31 – X-ray reflectivity measurement and thickness analysis. (a) Linear fit and (b) Fourier transform to extract the thickness from (c) XRR data (measured and simulated).	61
Figure 32 – AFM image of $10 \times 10 \mu m$ of YBCO_1Bar sample. The extracted surface roughness was 13.6 nm. Height from 0 to 255 nm as shown in color ruler.	62
Figure 33 – Resistivity-Temperature (RT) measurement: YBCO_1Bar (6 Hz, 1 bar annealing). Inset is the slope to extract the critical temperature.	63
Figure 34 – Schematic of the studied sample: STO/YBCO/BTO/Ti/Au where Ti and Au are represented by dark gray and orange, respectively.	65
Figure 35 – (a) X-ray diffractogram ($\theta - 2\theta$) using cobalt X-rays tube ($\lambda = 1.79 \text{\AA}$) the heterostructure YBCO/BTO. All peaks from YBCO, BTO and STO are indexed accordingly.	67
Figure 36 – AFM topography of $5 \times 5 \mu m$ of YBCO/BTO sample on STO substrate. Roughness (σ_{rms}) around 25.6 nm calculated by Gwyddion.	68
Figure 37 – Electronic transport measurements of the STO/YBCO/BTO sample. Left: resistance as function of temperature measurement of the bottom electrode (YBCO) showing the superconductivity transition. Right: I-V measurement of the ferroelectric BTO with leak current features.	68
Figure 38 – Schematic of the ferroelectric hysteresis measurement using PUND and atomic force microscopy.	69
Figure 39 – Current-voltage curve of a silicon substrate with a gold thin film as electrode.	70
Figure 40 – Left: optical microscope image of the surface of the DSO / SRO(20 nm) / BFO(100 nm) / SRO(20 nm) thin film. The circles shown here are the top electrode made of SRO of $16 \mu m$. Right: I-V curve measurement on one of the SRO electrodes to probe the ferroelectric properties of the BFO film.	70

Figure 41 – Current versus voltage loop for different frequencies from 1 to 20 kHz.

This measurement uses the PUND waveform before the compensation (i.e. subtraction of peaks) for the 1 to 10 kHz. For the 20 kHz curve, it is calculated the PUND compensation and it is shown the ferroelectric hysteresis in red. .

LIST OF TABLES

Table 1	– Summarize of the parameters used to grow our films.	51
Table 2	– Atomic concentration in all samples extracted from CasaXPS software. . . .	57
Table 3	– Thickness determined by XRR of the YBCO thin films where YBCO_680C, YBCO_6Hz and YBCO_1Bar have 10000, 4000 and 2000 deposition laser shots, respectively.	62
Table 4	– Summarize of the parameters used to grow our films. Roughness (σ_{rms}) of the YBCO films determined by AFM images of $10 \times 10\mu m$ using the free software Gwyddion. The critical temperature (T_C) of the measured samples extracted from the peak found in the first derivative of the RT curve.	64
Table 5	– Summarize of important parameters used to grow our films.	66

LIST OF ABBREVIATIONS AND ACRONYMS

AFM	Atomic Force Microscope
BCS	Bardeen–Cooper–Schrieffer theory
BTO	Barium titanate
T_C	Critical Temperature
FET	Field-Effect Transistors
PUND	Positive Up Negative Down
PLD	Pulsed Laser Deposition
SPM	Scanning Probe Microscopy
STO	Strontium titanate
XRD	X-Ray Diffraction
XPS	X-ray Photoelectron Spectroscopy
YBCO	Yttrium Barium Copper Oxide

CONTENTS

1	ELECTROSTATIC CONTROL OF SUPERCONDUCTOR THIN FILMS	23
2	THEORETICAL FOUNDATIONS	25
2.1	Superconductivity	25
2.1.1	Fundamental properties of superconductivity	26
2.2	Ferroelectricity	28
2.2.1	Historical background of ferroelectricity	29
2.2.2	Ferroelectric properties	29
2.3	Field-effect in correlated oxide systems	31
2.3.1	Principles of the field-effect transistors	31
2.3.2	Control of transport properties of high- T_C superconductors	32
2.4	Materials	35
2.4.1	Strontium titanate	35
2.4.2	Yttrium barium copper oxide	35
2.4.3	Barium titanate	35
3	EXPERIMENTAL TECHNIQUES	39
3.1	Pulsed laser deposition	39
3.2	Characterization Techniques	41
3.2.1	X-ray diffraction	41
3.2.1.1	X-ray reflectivity	43
3.2.2	Scanning probe microscopy	44
3.2.2.1	Atomic force microscope	45
3.2.3	X-ray photoelectron spectroscopy	46
3.2.4	Low temperature electronic transport chamber	46
4	SUPERCONDUCTOR THIN FILMS ON STRONTIUM TITANATE SUBSTRATES	49
4.1	Preparation of SrTiO₃ substrates	49
4.2	Pulsed laser deposition growth	50
4.3	Group 1: growth temperature	51
4.3.1	Structural properties	51
4.3.2	Topography	52
4.3.3	Superconductivity	53
4.4	Group 2: frequency of the deposition laser	54
4.4.1	Structural properties	54

4.4.2	Topography	55
4.4.3	Chemical surface analysis	56
4.4.4	Superconductivity	57
4.5	Group 3: high pressure	60
4.5.1	Structural properties	60
4.5.2	Topography	62
4.5.3	Superconductivity	62
4.6	Partial conclusions	63
5	FERROELECTRIC THIN FILMS	65
5.1	Growth - PLD	65
5.2	Structural properties	66
5.3	Topography	66
5.4	Hysteresis measurement	67
5.5	Partial conclusions	71
6	CONCLUSIONS	73
7	PERSPECTIVES	75
	REFERENCES	77
	ANNEX	87
	ANNEX A – PARASITIC PHASES AT THE ORIGIN OF MAGNETIC MOMENT IN BIFEO₃ THIN FILMS GROWN BY LOW DEPOSITION RATE RF SPUTTERING	89

1 ELECTROSTATIC CONTROL OF SUPERCONDUCTOR THIN FILMS

The phase diagram of complex oxides is very diverse due to the strong electron-electron interaction in the electronic structure, making this kind of materials part of what is known as strongly correlated systems. Among other mechanisms, the interactions can be explained by the electrons repelling each other by Coulomb's law and by Fermi repulsion (Fermi hole) with electrons of the same spin. These interactions break the free conduction electron approximation. In the case of superconductor oxides, it is possible to probe those interactions by changing electrostatically the carrier density, in a similar way of the main concept behind the Field-Effect Transistors (FET) which are the building blocks of electronic devices.^{2,3} Basically, in these transistors it is applied a voltage across a dielectric gate to control the carrier density in the channel between the other two contacts (drain and source). Consequently, the conductivity of the channel is changed according to the gate voltage.⁵

Using superconductors based FET one could conduct a study on the superconductor-insulator transition. In addition, thin films are good candidates for this study because we can modulate its properties by changing the growth parameters. In other words, we could design a film with a controlled disorder on different length scales in order to increase the pair-breaking effects and thus exciting the transition to the insulating phase.⁶ This could potentially bring new information about the still incomplete theory on high temperature superconductivity. A similar approach has been used to study this transition in cuprate superconductors, employing electrostatic doping by means of an electrolyte in contact with the thin film. For example, Perez-Muñoz et al.⁴ used the device in Figure 1 (top) to probe the properties of $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ by applying a voltage on the ionic liquid. Figure 1 (bottom) shows the resistance-temperature curves for several gate voltages (V_g), the critical temperature reduction (increase) with larger (smaller) values of V_g , i.e. a reversible effect. The effect of the electrostatic doping on the electronic structure of the superconductor material was probed by X-ray absorption. Such approach has the potential to allow deep understanding of how the electronic structure of superconductors change with doping.

Nevertheless, the use of a liquid electrolyte hinders the use of more sophisticated electronic structure techniques, like scanning tunneling spectroscopy (STS) or angular resolved photoemission spectroscopy (ARPES). In view of this, it would be desirable to have a fully solid state device. This could be accomplished using a ferroelectric material as the gate of the FET. These ferroelectric materials possess a spontaneous polarization, which means that the electric polarization remains even after the external electric field is removed.^{2,7} Besides the potential to study the basic superconductivity science, controlling the superconductor state of a device is potentially useful to use superconductor qubits in quantum computation.⁸ For that, a ferroelectric gate can promote several advantages over the usual FETs, for example, it could

Figure 1 – Top: schematic of the gating device, where DEME-TFSI is the ionic liquid. Bottom: reversibility of the doping. First applied positive gate voltage (left) and then negative gate voltage (right).

Source: Adapted from PEREZ-MUÑOZ et al.⁴

potentially consume less energy, good scalability and non-destructive readout operation.⁹

The objective of this Master work was to obtain the good conditions to grow superconductor and ferroelectric thin films, that in the continuation could potentially be used to fabricate FET-controlled superconductor devices. To pursue such objectives, we optimized the growth of a high- T_C superconductor and ferroelectric thin films by pulsed laser deposition. The films were characterized both structurally and morphologically. In the case of superconductor films, they were also check by transport measurements as function of the temperature.

Our results are described in this dissertation in the following manner: chapter 2 recalls the basic aspects of superconductivity, ferroelectricity and the field effect in correlated oxide system. The experimental techniques used to growth and characterize the samples are discussed in chapter 3. Chapter 4 describes the results obtained for the high- T_C superconductor thin films, while in chapter 5 reports those obtained for ferroelectric layers. Chapter 6 summarizes the work and discusses future possibilities.

2 THEORETICAL FOUNDATIONS

In this chapter will be discussed briefly the theory about superconductivity, ferroelectricity and field-effect devices.

2.1 Superconductivity

The discoveries related to superconductivity were related to the advances in cryogenic technology. In 1908, Heike Kamerlingh Onnes was able to liquefy Helium gas and to perform experiments with the temperature around 4K. Three years later, the first steps were taken for superconductivity, they succeeded to measure a drop in resistivity of solid mercury beyond the sensitivities of their equipment (Figure 2).¹⁰ They also measured the same behavior for metals such as tin, lead and aluminum. Only in 1933, Meissner and Ochsenfeld showed that superconductors became perfect diamagnetic, which means that all magnetic field is excluded from entering the superconductor.¹¹

Figure 2 – Historical plot - Resistance versus temperature of a mercury wire from 1911 experiment shows a superconducting transition at 4.2 K.

Source: ONNES et al.¹²

Two years after Meissner, the London brothers proposed a theory to describe the Meissner effect. They said the magnetic field penetrates slightly into the bulk of the superconducting material instead of abruptly ending at the surface. This depth of penetration is called London penetration depth. In 1950, Landau and Ginzburg described the superconductivity in terms of

an order parameter based on experimental observations.¹³ In 1957, John Barden, Leon Cooper and John Schrieffer explained superconductivity as a purely quantum mechanical phenomenon, giving a full description and explanation of the microscopy behavior. It is known as BCS theory. It says that superconductivity occurs with Copper pairs, that is a pair of correlated electrons created by the interaction of electrons and phonons. This theory explained very well all the superconductor metals of critical temperature lower than 35 K. In 1986, Bednorz and Muller discovered a barium and lanthanum copper oxide with a critical temperature of 34 K.²

In the next years, many high- T_C superconductors were discovered. In 1987, a material with a critical temperature higher than the boiling temperature of liquid nitrogen (77 K) was discovered.¹⁴ It is composed of yttrium, barium, copper and oxygen ($\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, known as YBCO). Other copper oxides were discovered in the following years, such as $\text{Bi}_2\text{Sr}_2\text{CuO}_{6+x}$ ($T_C = 85\text{K}$),¹³ $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ ($T_C = 115\text{K}$),¹⁵ $\text{Tl}_2\text{Ca}_2\text{Ba}_2\text{Cu}_3\text{O}_{10}$ ($T_C = 120\text{K}$)¹⁶ and $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ ($T_C = 135\text{K}$).¹⁷ However, thallium and mercury-based superconductors are not as attractive as others high- T_C superconductors due to their toxic nature.¹³ Nowadays, hydrogen under high pressure is studied as high-temperature superconductor because hydrogen atoms provide strong phonon-electron interaction. It opened the possibility of superconductors with critical temperature around room temperature. For example, sulfur hydride (H_2S) under 90 GPa has a T_C of 203 K¹⁸ and a predicted T_C of 303 K under 400 GPa for yttrium hydrogen.¹⁹

2.1.1 Fundamental properties of superconductivity

A superconductor material exhibits a decay to zero resistivity below a certain threshold of temperature, known as critical temperature (T_C). During this superconductor state, it repels any magnetic field from its interior. In the BCS theory, the electron travels through the lattice and may create a distortion (phonons). In result, it will arrange a positive cloud around the electron that will attract other electrons with opposite spin and moment to form the Copper pairs. The energy of those pairs are slightly lower and leave a gap of 0.001eV which prevent the collision interactions that lead to usual resistivity. For temperature with less thermal energy than this gap, the resistivity of the material will be zero.¹³

The superconductivity breaks down depending on a critical magnetic field applied (H_C). The superconductors are divided into two types according to how this break down occurs. They are named Type I and Type II superconductors. The Type I superconductors are also called soft superconductors, they are well described by BCS theory and are composed mostly of metals and metalloids. In this kind of superconductor, all the magnetic flux are expelled from the material by an induced magnetic field. Figure 3 shows the transition from superconductor to normal state depending on the magnetic field applied. Before the critical magnetic field H_C , there is an induced magnetic field that cancels out the applied field (Meissner state). The material goes back to the normal state with greater values of critical magnetic field or temperature. The Type I superconductors are not very good for applications because they have a very low H_C .¹³

Figure 3 – Characteristics of a superconductor Type I. Induced magnetic field (left) and the different states diagram (right).

Source: Adapted from BEGON-LOURS²; CHINTAMANENI.¹³

Type II Superconductors, also known as hard superconductors,¹³ exhibit a smooth decay of the induced magnetic field (Figure 4, left), characteristic of what is commonly known as the mixed state that lies between the Meissner state and the normal state. In other words, the flux starts to penetrate the material and to increase continuously from H_{C1} to H_{C2} where the material goes back to the normal state. Consequently, H_{C2} can be much higher than H_C from the type I superconductors, opening the possibility of a high-field superconducting magnet.²⁰ It is worth noting that the material remains with zero resistance at the mixed state.²¹ The high- T_c cuprates and pure metals such as niobium are Type II superconductors.²

Figure 4 – Characteristics of a superconductor Type II. Induced magnetic field with the presence of H_{C1} and H_{C2} (left) and the different states diagram including a new mixed state (right).

Source: Adapted from BEGON-LOURS²; CHINTAMANENI.¹³

In the case of oxides, some become superconductors when doped with electrons, while others with holes, depending on which chemical element is changed, but in either case there

is an optimum doping value that maximizes T_C . The T_C boundary in the T vs doping phase diagram is known as superconducting dome as depicted in Fig 5. In the underdoped regime below the temperature T^* , the material presents the phase known as "pseudogap". The exact origin and its effect onto superconductivity are still unclear.²² Traditionally the doping is chemically changed, but it has been shown that in the case of very thin superconductors films, the doping can be changed by accumulating charges at their interfaces in a suitable device. This opens up the possibility to electrostatically tune the transport properties of a superconductor oxides as will be discussed in section 2.3.2.

Figure 5 – Phase diagram as a function of doped electrons (n) and holes (p) for high- T_C cuprate superconductors. There are three main regions: the undoped region for low electron or hole doping (antiferromagnetic), optimal doping (superconducting) and pseudogap.

Source: HARTINGER.²³

2.2 Ferroelectricity

Ferroelectric materials exhibit spontaneous electrical polarization, even in absence of an external electric field. This process is reversible and it is described by the ferroelectric hysteresis (described at section 2.2.2), analogous to the magnetic hysteretic behavior of ferromagnetic materials (that is the reason for the name ferro-electricity²).

2.2.1 Historical background of ferroelectricity

The ferroelectric history starts with the discovery of the electric hysteresis in Rochelle Salt in 1920.²⁴ However, it did not attract much attention because the Rochelle Salt is slightly changed by dehydration either in the vacuum or dry air. In 1935, it was discovered the low temperature (below 120 K) ferroelectric potassium dihydrogen phosphate (KDP) and the isostructural dihydrogen arsenate.^{25,26} A few years later, during the Second World War, it was the beginning of the perovskite era with the synthesis/identification of the ferroelectric perovskite barium titanate (BaTiO_3 , known as BTO).^{27,28} Before the discovery of the BTO, the ferroelectrics were more of a scientific curiosity with complex structures. Following the discovery, there was a boost in the popularity of the ferroelectricity because BTO has a more stable and simpler structure, rapidly improving fundamental understanding of ferroelectrics.²⁷

From 1950 to 1960, the number of known ferroelectrics rapidly increased. In 1950 only Rochelle salt, KDP and a few perovskite ferroelectrics were studied. In 1960, more than twenty-five ferroelectrics were well established, mostly perovskite ferroelectrics.²⁷ Perovskite oxides (name taken from the mineral perovskite CaTiO_3 ²⁹) have chemical formula such as ABO_3 where A and B are two cations atoms of different elements.³⁰ In 1951, Devonshire did some important theoretical and phenomenological work leading towards a better understanding of the ferroelectrics.³¹ It was based on previous works done by Landau and Ginzburg and it used concepts of point group symmetry and nonlinear elasto-dielectric coupled interactions with electrostriction and piezoelectric coefficients. It was named Landau-Devonshire-Ginzburg Theory (LDGT), a very important tool for understanding ferroelectrics.³²

In recent years, several deposition technologies have been developed improving and increasing a new field of study, ferroelectrics thin films. Using this kind of technology is possible to grow very thin ferroelectric devices with different or similar properties from bulk ferroelectrics. These advances helped to increase the number of applications such as the incorporation of ferroelectric as capacitors, sensors and actuators on silicon devices.³³

2.2.2 Ferroelectric properties

As mentioned before, a ferroelectric material exhibits a spontaneous electrical polarization, which means that it has a remaining polarization even if the external electric field is turned off. This behavior is described by the ferroelectric hysteresis that is the polarization as a function of the electric field (Figure 6). There are two or more of those polarization states and it is possible to switch between them using an external electric field. For small values of the electric field (region A-B of Figure 6), the polarization varies linearly with the electric field and it is not sufficient to change the polarization state. As the electric field increases, the electric polarization is aligned with the electric field (segment B-C) until it reaches the saturation (segment C-D). If the electric field is decreased to zero after reaching saturation, the polarization will be non-zero

(remanent polarization, P_R), characteristic behavior of ferroelectric materials. Decreasing even more the electric field, it is possible to reverse the electric polarization to zero (coercive electric field, E_C) and to reach a new saturation in the opposite direction (segment F-G). Lastly, it is possible to complete the hysteretic cycle by increasing the electric field.

Figure 6 – Typical hysteresis curve. Arrows indicate the polarization state of the material in the corresponding electric field. E_C means coercive electric field, P_R is remanent polarization and P_S is the spontaneous polarization.

Source: DAMJANOVIC.³⁴

The hysteresis is a typical and unique behavior of ferroelectric materials. However, it only exists below a certain temperature named Curie Temperature in analogy with the magnetic case. Most ferroelectric materials undergo a structural phase transition from ferroelectric to paraelectric above the Curie temperature and in this case, the polarization varies linearly with the electric field. There is no remanent polarization for the paraelectric phase.³⁰

There are two mechanisms that explain the ferroelectric/paraelectric transition. In the paraelectric phase, the mean polarization is zero if no electric field is applied because the orientation is random. Below the Curie temperature, a disorder-order transition occurs changing the symmetry of the unit cell and it is more energetically favorable for the dipoles to align in the same direction and orientation of their neighbors.² In the other mechanism, the paraelectric phase is cubic and the barycenter of the positive and negative charges is merged. When the disorder transition occurs, the barycenter of the positive and negative charges is displaced from each other giving rise to a dipolar momentum in the cell.

Ferroelectric applications increased considerably since the discovery of the barium titanate material during World War II. For instance, the sonar detectors used in the War, infrared detection and phonograph pickups. Around 1990, there was a wide range of applications giving by the improvement of the quality of the samples (thin films) such as memories, radio frequency and microwaves devices, pyroelectric and piezoelectric sensors and actuators, a photovoltaic device, etc. More recently, the research on ferroelectric is present on several research areas such

as nonlinear optics, mixed ionic-electronic conductors, artificial photosynthesis, ferroelectric diodes, advanced passive components (memristors) and ferroelectric random access memories (FRAM).^{28,35–42}

The barium titanate (BaTiO_3) is the first and most widely studied ferroelectric material. It was intentionally synthesized during World War II due to lack of the material mica, principal dielectric used at the time in capacitors. It has a perovskite structure and it is ferroelectric up to 120°C where the structure changes from tetragonal to cubic. BTO materials also have higher dielectric permittivity compare to other dielectrics which are attractive for many applications.^{43,44}

2.3 Field-effect in correlated oxide systems

Almost everyone is daily surrounded by semiconducting field-effect transistors (FETs) since it is extensively used in different electronic devices. Basically, a FET works as changing the carrier density of a thin semiconducting channel using an electric field and consequently changing the resistance of the device. This relatively simple idea open the possibility to experiment with correlated electron systems whose properties highly depend on carrier concentration.¹ For example, the plastic electronics is a successful technology that originates from those kinds of experiments.⁴⁵

2.3.1 Principles of the field-effect transistors

A field-effect transistor is composed of three metallic electrodes referred to as source, drain and gate, a very thin insulating film (barrier layer) and a semiconductor n or p-type channel that connects the source and drain electrodes (for illustration purposes, see Figure 7). The idea behind a conventional FET is to control the conductivity of the channel using a voltage between source and gate (V_{GS}). This voltage will induce a charge accumulation along the channel near the interface, creating a conductive path for the current between source and drain (increasing the conductivity).

Figure 7 – Cross-section of a field-effect transistor. Three metallic electrodes: source, gate and drain.
Source: LU et al.⁵

In the case of a strongly correlated oxide channel, using the same principle as FET, it is possible to change the conductivity and the ground state of the material.² Figure 8 shows a few examples of the influence of the charge density in some materials. For example, consider the high- T_C copper oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ illustrated below, it is possible through an electric field to switch between superconducting and insulator phases. In the case of the Colossal Magnetoresistance (CMR) manganites, the material may switch between an antiferromagnetic-insulator and ferromagnetic phases.

This charge modulation is only possible within a certain thickness in the channel. In 1960, Glover and Sherrill were capable of changing the critical temperature of indium and tin in an extremely small range,⁴⁶ both materials have a small penetration length of about 1 Å. To get larger effects, the penetration depth needs to be bigger and the superconductor must be thin on the same scale. It is also preferable that the insulator that separates the metal electrode gate from the superconductor has a high dielectric constant, which will result in a bigger induced charging. In the case of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, the penetration depth is around tens of Angstrom.⁴⁷ The equation that describes this characteristic is given below²:

$$\lambda_{TF} = \left(\frac{\epsilon_S \epsilon_0}{e^2 \eta_{eff}} \right)^{\frac{1}{2}}, \quad (2.1)$$

where ϵ_S and ϵ_0 are the permittivity in the superconductor and in the vacuum, respectively, e is the elementary charge and η_{eff} is the effective density of electrons that screen the applied field.

In the case of using a ferroelectric as the insulator of the gate, there are a few advantages over a regular dielectric material. First, ferroelectric materials have a high spontaneous polarization which means that it could allow a very high charge transfer. Since they have a remanent polarization, it is possible to maintain the state of the channel/material without voltage once the polarization is set (Figure 9).

2.3.2 Control of transport properties of high- T_C superconductors

Most of the high- T_C superconductors present the phase diagram described in Figure 10. The phase diagram shows the relation between the temperature and the doping of different states of the material. For example, for a low level of doping the cuprates are antiferromagnetic insulators. At higher levels, the material becomes a superconductor and the critical temperature has a characteristic dome shape.²

Doping can be accomplished by chemical substitution of elements (e.g. partial substitution of La for Sr, $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ becomes $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$), oxygen concentration (e.g. $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$) or small change in the carrier concentration using an electric field. The advantage of electrostatic charging is that it does not change the structure of the material such as chemical doping and it is reversible.⁴⁸

Figure 8 – Behavior of several type of materials as function of the sheet charge density (n_{2D}). In this figure, the colossal magnetoresistive and the high- T_c copper oxides are the behavior of the $(\text{La,Sr})\text{MnO}_3$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, respectively. Where AF means Antiferromagnetic, FM - Ferromagnetic, I - Insulator, M - Metal, SC - Superconductor, FQHE - Fractional Quantum Hall Effect, CMR - Colossal Magnetoresistive.

Source: AHN et al.¹

Figure 9 – (a) Applying a voltage between gate and source to polarize the ferroelectric material. (b) The polarization remains even without the battery applying the voltage.

Source: BEGON-LOURS.²

One example of this feature is given by Xiang Leng et al.⁴⁹ However, in this case, they used ionic liquid instead of ferroelectric material. The ionic liquid gate may induce carrier concentration charges up to $8 \times 10^{14} \text{ cm}^{-2}$ in materials such as YBCO. The superconductor with such high carrier concentration may have a shift of critical temperature of around 50 K. This shift is presented in Figure 11, where they increased the gate voltage at the ionic liquid gate resulting in a transition between superconducting and insulator.

Figure 10 – Typical phase diagram of high- T_C superconductor. AF means antiferromagnetic and T_C is the critical temperature.

Source: BEGON-LOURS.²

Figure 11 – Sheet resistance as function of the temperature varying the gate voltage from 0 to 1.52 V. Inset: Details of the transition from superconductor to insulator.

Source: XIANG LENG et al.⁴⁹

2.4 Materials

Most of the materials used in this work have the perovskite structure. The perovskite materials have a general formula that usually is derived or similar to the composition ABX_3 , where A is a large cation, B is a medium-size cation and X is an anion. Some perovskites chemical formula are more difficult to reconcile with the general ABX_3 , but usually, their structures are built up of fragments of perovskite-like structures.⁵⁰

The next subsections describe specifically each material of this work.

2.4.1 Strontium titanate

As substrate to grow the thin films of this work, we used the strontium titanate ($SrTiO_3$ or STO). It has an idealized perovskite structure (cubic) at room temperature with a lattice parameters of $a = 3.905 \text{ \AA}$ and it is a paraelectric insulator. There are phase transitions at 105 and 65 K where it becomes a tetragonal ($\frac{c}{a} = 1.00056$) and orthorhombic ($\frac{c}{b} = 1.0002$ and $\frac{c}{a} = 0.9998$).

2.4.2 Yttrium barium copper oxide

High- T_C superconductors usually have a layered-perovskite structure. In the case of the $YBa_2Cu_3O_{7-\delta}$ (YBCO), the stacking sequence of layers along c -axis is CuO - BaO - CuO_2 - Y - CuO_2 - BaO - CuO . The YBCO unit cell (Figure 25) is composed of CuO_2 planes that are very important to the superconducting properties. The carriers only move along these planes and the other components act as charge reservoirs that influence in the charge density of the CuO_2 planes.¹³ Nevertheless, each unit cell has one yttrium in the middle of two planes of CuO_2 planes sandwiched with BaO layers and lastly, CuO chains (charge reservoirs).

YBCO presents two possible symmetries, tetragonal or orthorhombic, depending on the amount of oxygen in the CuO chains. Considering the formula $YBa_2Cu_3O_{7-\delta}$, if δ is close to zero the material presents an orthorhombic structure which is superconducting. If δ is greater than 0.63 the material is tetragonal and behaves as an antiferromagnetic insulator. A YBCO fully oxygenated has a critical temperature of 93 K with $a = 3.82 \text{ \AA}$, $b = 3.88 \text{ \AA}$ and $c = 11.68 \text{ \AA}$.^{51–53}

2.4.3 Barium titanate

The unit cell of the $BaTiO_3$ (BTO) is presented in Figure 13(a). The barium atoms are surrounded by twelve oxygen ions and the titanium atoms by six oxygen ions. At room temperature Ti atom is displaced along the c axis relative to the surrounding oxygen octahedra. This leads to a high bulk electrical polarization and high dielectric constant (Figure 13(b)).⁴³

Figure 12 – (a) Tetragonal ($\text{YBa}_2\text{Cu}_3\text{O}_6$) and (b) Orthorhombic ($\text{YBa}_2\text{Cu}_3\text{O}_7$) YBCO perovskite structure.

Source: Adapted from BEGON-LOURS.²

Figure 13 – Barium titanate perovskite structure. (a) unit cell with barium atom in the middle. (b) Shift of the Ti atom due to an electric field resulting in the polarization.

Source: LU.⁵⁴

There are four crystalline structures depending on the temperature: cubic, tetragonal, orthorhombic and rhombohedral. From 120-1400 °C, BTO is cubic and paraelectric. As the temperature is lowered below 120 °C (Curie temperature), the structure of the material changes from cubic to tetragonal. Now the shift off-center of the Ti atom will result in a ferroelectric

behavior (spontaneous polarization). Below 0°C, it presents an orthorhombic (0 to -80°C) and rhombohedral (below -80°C) structure where BTO has the polar axis parallel to a face diagonal and a polar axis along a body diagonal, respectively.

The lattice parameters for the tetragonal structure (i.e. room temperature) is around 4.036 Å for the elongated axis (c) and 3.992 Å for the 2 others axis (a and b). It has been reported on literature a ferroelectric remanent polarization for the single crystal barium titanate of 26 $\mu\text{C}/\text{cm}^2$ and a coercive field of 1-2 kV/cm. In the case of epitaxial thin films, the remanent polarization can go up to 70 $\mu\text{C}/\text{cm}^2$ by an increase of tetragonality (c/a) and the coercive field also increase with values in the range of 25-300 kV/cm.⁵⁵

3 EXPERIMENTAL TECHNIQUES

In this chapter we introduce the basics of pulsed laser deposition (PLD), which was the method used to grow the samples of this work, followed by an overview of the experimental techniques behind the characterization of the films.

3.1 Pulsed laser deposition

Laser ablation growth techniques were very important for the advances in the study of oxide materials. However, pulsed laser deposition did not attract much attention from the scientific community until 1986, with the discovery of the first high- T_C superconductor $\text{Ba}_x\text{La}_{5-x}\text{Cu}_5\text{O}_{5(3-y)}$.⁵⁶ In fact, the discovery of superconductivity above the boiling temperature of liquid nitrogen by $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ in 1987 encouraged researchers to make great efforts to grow thin films of this perovskite material. The first YBCO thin film by PLD was manufactured shortly after its discovery.⁵⁷ There are many advantages that justifies this interests in PLD, for example, the control of the atmosphere of the growth chamber, the deposition rate from a monolayer to several nanometers per second and the characteristic of preserving complex stoichiometries. Others advantages over conventional growth systems are that it is easy to replace and to use multiple targets, excellent for prototyping complex devices and to explore a wide range of phase space. However, the PLD system remained mainly at laboratory research and its industrial applications are mostly in the future due to some major problems: small-scale depositions, non-uniform thickness, deposition of macroscopic globules of molten material and empirical optimization for novel materials. Nowadays, large area PLD and uniform thickness growth have been achieved. There are also some elaborate techniques that extinguish these particulates, such as off-axis deposition. Finally, some simulation tools would also be needed to help find optimum growth parameters for new materials.⁵⁸⁻⁶¹

The PLD growth process can be described as follow: the system consists of a vacuum chamber, a target and a substrate holder that can be rotated during the deposition, an infrared laser to heat the substrate for several hundred degrees Celsius, gas inlet to control the atmosphere/pressure of the chamber and several optics to focus the laser with the right energy density. The substrate temperature is usually measured by a pyrometer. The growth process is the following: A pulsed laser (few nanoseconds) with controlled frequency and high power, impinge on a target of sintered materials. This interaction will produce an ejected plume from the target where the vapor is collected on the substrate which is not far away from the target.⁶² This process is illustrated in Figure 14.

Regarding the quality of the film, it is not easy to control and obtain a very high-quality thin film. The composition of the plume depends on several parameters that need to be explored and determined the best condition for your situation, for example: temperature of the substrate

during the deposition, stoichiometry and roughness of the target, oxygen pressure, fluence and energy of the laser, distance between target/substrate and heat treatment after the deposition. Another possible problem is that from one deposition to the other, the laser energies may increase, the optics of the laser path blacken, the target composition may change locally and so on.

Figure 14 – Schematic of the pulsed laser deposition chamber. A pulsed laser will hit a target inside a controlled atmosphere chamber resulting in a plume that will condense on the substrate as a thin film. In this case, the heater responsible to control the substrate temperature is composed of an infrared laser.

Source: Adapted from BEGON-LOURS.²

The parameters used to grow the sample contribute to the different existing growth modes. Some of them are:

- Step-flow growth - Every substrate has a specific miscut from the preparation process. These miscuts will contribute to a surface with atomic steps where the material may diffuse to the step edge during the deposition before it forms surface islands. The step-flow growth may occurs in high miscut substrates or high-temperature deposition.⁶³
- Layer-by-Layer growth - Islands may nucleate at the surface during deposition until eventually, the islands begin to merge with each other, known as coalescence. After the coalescence, there will be many pits where the subsequent deposited material will diffuse to it to complete the layer.

- 3D Growth - This growth process is similar to the layer-by-layer growth, but after an island is formed more materials will be deposited on top of it preventing the coalescence. The surface roughness increase as more material is deposited.

In this work, all the samples were grown by pulsed laser deposition (PLD) with COMPEX-Pro™Excimer Laser device (Krypton Fluoride, KrF),⁶⁴ available at the U11-PGM beamline of LNLS, CNPEM.

3.2 Characterization Techniques

In the following we give a brief description of the techniques used to characterize the films grown during this work.

3.2.1 X-ray diffraction

In the energy range of the X-rays, the electromagnetic wave interacts mostly with the electronic clouds of the atoms and it is used to characterize the structure of the materials. The X-rays wavelength varies from 0.01 to 10 nm, similar size of an atom (around 0.1 nm) thus it is a good tool to study crystallized materials as they will provide information on the structure of the lattice of the thin films. Some examples of information that can be extracted from thin films using x-rays diffraction/reflectivity⁶⁵: crystalline structure such as symmetries of the atoms in the unit cell, unit cell size, size/shape of the nanocrystalline domains, identification of crystalline phases (e.g. parasitic phases⁶⁶) and quantitatively determination of their weights fractions and thickness and roughness of thin films by interference at low angle.

Usually, an XRD experiment is composed of three major components (illustrate at Figure 15): X-ray tube, sample and detector. The **X-rays** are generated by bombarding a target material (e.g. copper) with accelerated electrons emitted from a hot filament. This will result in K_α and K_β radiation and a broad background. In the case of copper, the radiation wavelength is around $\lambda = 1.5406 \text{ \AA}$. There are some restrictions on the sample to ensure a high-quality measurement when using a typical diffractometer, for example, the thickness and roughness of the thin film. Lastly, there are several types of **detector** for different applications. For example, the solid-state X-ray detection using hybrid pixel sensors designed at CERN (European Organization for Nuclear Research) for high-resolution powder diffraction, ultra-fast reciprocal space mapping, etc.⁶⁷

The phenomenon of diffraction is described by the Bragg law (Equation 3.1). X-rays diffracted by different crystal planes in the specular direction will travel different paths. If the difference in the path between the diffracted X-rays is equal to integers of the incident beam wavelength, it will interfere with each other constructively giving a peak in the diffractogram.

Figure 15 – Schematic of an XRD experiment for a fixed X-ray tube in the Bragg-Brentano geometry.
Source: Adapted from JAVIER.⁶⁸

Basically, the peaks in the diffractogram may be interpreted as the periodicity of the crystalline planes in the material. The Bragg's law is expressed below:

$$n\lambda = 2d\sin\theta, \quad (3.1)$$

where λ is the wavelength of the radiation, θ is the incidence angle and d is the lattice distance that separates the atomic planes in a crystal.

The strain and homogeneity of the crystal highly affect the position and the width of the peak. For example, a film strained by its substrate will shift the peak to lower or higher angles depending on the strain. For the case of compressive (tensile) strain, the unit cell of the film decreases (increases) so the peak is shifted to higher (lower) angles.²

In this work the configuration $\theta - 2\theta$ or Bragg-Brentano scan was used. The X-ray source was immobile so the sample rotated an angle θ and the detector moved an angle 2θ to maintain a difference of angle of 2θ between the incident x-ray beam and the detector. Typically it goes from 10 to 110°. During a XRD measurement in this configuration, it will have the (001) diffraction peaks of the substrate, if it is oriented along the 001 direction. In the case of measuring the diffraction peaks (001) of the film, it means that it grew in a textured way along the out-of-plane axis. Hence, using the Bragg law (Equation 3.1), it will be possible to determine the out-of-plane lattice parameter c . Figure 16 shows an example of XRD measurement of a thin film STO/YBCO (60nm).

In the ω -scan or rocking-curve, the diffraction condition is satisfied, 2θ is fixed and the ω is varied around θ . The width of the peak gives information on the quality of the epitaxy.

Figure 16 – XRD measurement ($\theta - 2\theta$) of a thin film YBCO//STO. YBCO and STO peaks (001) are accordingly indexed and the STO- K_β peaks are labeled as *.

Source: By the author.

3.2.1.1 X-ray reflectivity

X-Ray Reflectivity or XRR is used to measure the thickness of single or multilayered thin films from a few to hundreds of nanometers (depending on the roughness and electronic densities⁶⁹). The radiation reflects in different interfaces on the material and they interfere with each other giving an oscillatory behavior. The XRR measurements are done at very low incidence angle at $\theta - 2\theta$ -scan and the intensity decay quickly with the increasing of the angle (usually it goes until the intensity reaches the background level, around 10°). Figure 17 shows an example of XRR measurements for different thickness extracted from Miho Yasaka.⁶⁹ The thickness is proportional to the oscillations due to the interference between the reflections from the surface of the Au film and the interface between Au and the Si substrate.

There are a few methods to extract the thickness of such curve.⁷⁰ It is described two of them here: the thickness (t) is related to the maximum or minimum of an interference fringe (i) by the modified Bragg Equation 3.2:

$$\sin^2\theta_i = \theta_c^2 + \frac{(n_i + \Delta n)^2 \lambda^2}{4t^2}, \quad (3.2)$$

where θ_c is the critical angle, n_i is an integer and Δn is either 0 or $\frac{1}{2}$ for a minimum or maximum, respectively.

The thickness is acquired by fitting a line in a graph $\sin^2\theta$ as function of $(n + \Delta n)^2$

where the slope is equal to $\frac{\lambda^2}{4t^2}$. In other words, the thickness is equal to $\frac{\lambda}{2\sqrt{\text{slope}}}$ from the graph described before. The thickness may also be determined by a frequency analysis using the Fourier transform of the data where the graph of it will have a peak in the position of the thickness measured (details can be found at Divya Aggarwal dissertation where he explains it using the Origin software⁷¹). Lastly, the thickness may be determined using a software⁷² to fit the data and extract some parameters such as roughness and thickness.

Figure 17 – XRR measurement of Au thin film on Si substrate of thickness 5 and 20 nm.
Source: YASAKA.⁶⁹

X-Ray Reflectivity and X-Ray Diffraction measurements were done with PANalytical X'Pert Pro diffractometer with Cu K $_{\alpha}$ radiation.⁷³

3.2.2 Scanning probe microscopy

Since 1980, the Scanning Probe Microscopy or SPM techniques are used for a variety of applications with nanometers resolution, for example, to probe the topography of the sample, conducting, ferroelectric or magnetic properties, etc. It is a generic name for all techniques that involves a scanning of a nanometer tip on the surface of a sample to study nanoscale physical properties.

All SPM techniques have the same principle of operation: A nanometer-tip is placed in contact or very close to the sample which results in a highly localized interaction. A piezoelectric scanner below the sample moves it horizontally to describe a scanning pattern. During the scan, it is measured the variation in the interaction between tip and sample using a control mechanism and through a feedback system, it is changed the distance between tip-sample. The whole system

communicates with the computer that moves the scanner, acquires and convert the data resulting in the image of the sample. There is also a mechanism precise enough to move the tip and approach it to the surface of the sample.⁷⁴

3.2.2.1 Atomic force microscope

In the Atomic Force Microscope (AFM), a nanometer radius tip scan the sample in order to get the topography. The principle behind this technique is shown in Figure 18: The tip is carried by the cantilever (probe) where reflects a laser to a photodiode. When the tip approaches the surface of the sample, there are forces of interaction between them that will make the cantilever to deflect. That deflection is detected by the photodiode and converted by the computer to the topography image. The method used to get the topography is to keep constant the height of the cantilever in respect of the sample. When the tip is deflected, the laser at the photodiode is displaced and a feedback loop drives the vertical piezoelectric actuator in order to maintain the deflection constant.

Figure 18 – Schematic of an Atomic Force Microscope imaging process.

Source: BEGON-LOURS.²

There are two kinds of interactions between tip and sample depending on the distance between them. In contact mode (close range), there is a repulsive force and in order to maintain the contact with the surface, it is applied a small force on the tip. In non-contact mode, the tip is attracted by long-range Van de Waals. There is also a mid-term operation, the intermittent mode where the interaction oscillates between repulsive and attractive. In this case, it is determined the resonant frequency of the tip/cantilever system and the tip oscillates at this frequency to tap the surface of the sample periodically. The amplitude RMS (setpoint) of the oscillation is determined

by the user and the vertical piezoelectric keeps moving during the scan to maintain this setpoint constant.

The Atomic Microscope Force measurements were done with Nanosurf FlexAFM.⁷⁵

3.2.3 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy or XPS is heavily used for defining the elemental composition of the surface (within a few nanometers) of a solid. This powerful technique can retrieve the following information: Identify and quantify the elemental composition of the surface of a material, indicates the chemical bonding states, etc. Therefore it is mostly used for studying the chemistry of the samples.^{13,76}

Basically, XPS is based on the measurement of the kinetic energy of the electron ejected (photoelectron) from the absorption of a photon with sufficient energy. The kinetic energy of this outgoing electron is described by Equation 3.3 and since the frequency is known, it is possible to determine the binding energy of the corresponding measured electron. This binding energy is an element and environment specific.

$$E_K = hv - \phi - E_B \quad (3.3)$$

where E_K is the kinetic energy, h is the Planck constant, v is the frequency of the photon, ϕ is the work function and E_B is the binding energy.

The kinetic energy is measured using a spherical capacitor energy analyzer. Electrons in the central trajectory have the nominal pass energy. For a fixed capacitor potential, particles with higher kinetic energy travel a longer path (focused further outside) while particles with lower kinetic energy travel a shorter path (focused further inside).

The X-ray Photoelectron Spectroscopy measurements were done using two similar types of equipment: A chamber with TX400 X-ray source⁷⁷ and a Hemispherical energy analyzer series (PHOIBOS - SPECS)⁷⁸; K-Alpha X-ray Photoelectron Spectrometer (XPS) System (Thermo Fisher Scientific).⁷⁹

3.2.4 Low temperature electronic transport chamber

During my final project of the bachelor degree, we commissioned the homemade electronic transport chamber where it became available for ferroelectric and superconductivity measurements in our group.⁸⁰ Therefore, this work also used it to study the electronic transport properties of our thin films samples. Figure 19 shows the chamber drawing (left) and the current state at the laboratory (right). It works with pressure around 10^{-5} mTorr at room temperature, controllable temperatures from 10 to 300 K using the ARS-10HW compressor⁸¹ and a closed

cycle cryocoolers (dry cryostats)⁸² and 10 cables that give access to electrical contacts in the sample.

Figure 19 – (a) Schematic of the low temperature electronic transport chamber and (b) the current state at the laboratory.

Source: By the author.

It is used silver paint to fix and to improve the thermal conduction of the sample with the cryostat. It is used a very thin gold wire ($< 50\mu m$ diameter) for the electric contact between the sample and the chamber. Since the wires does not have insulation, it is necessary to be careful with short circuits between each other. For all the measurements it was used a LabVIEW program to control the devices and to do the analysis of the data.

For the superconductivity measurement, it was used the Lakeshore 331 to control the temperature with setpoint ramping, Agilent 34420A (nanovoltmeter) to measure the voltage with high precision and Keithley 6430 (sub-femtoamp) to apply and measure the current. The configuration used is the four-point probe method: during a voltage measurement between two electrodes using the two point-probe, it will also included the resistance of the contact. The 4-point probe consists in measuring the voltage of two inner contacts while applying a current between two outer contacts. This way the resistance measured will be entirely the sample resistance without the contact resistances.⁸³

For the ferroelectric hysteresis measurement, it was also used the Lakeshore331 to control the temperature, Agilent 34420A to measure the voltage, Keithley 6430 to measure the current, Agilent 33220A (function/arbitrary waveform generator) to apply an arbitrary waveform to measure the ferroelectric hysteresis using the PUND (Positive Up Negative Down) method (Figure 20): five voltage pulses are applied to the sample. The first negative pulse pre-polarizes the

sample to a negative state. The P pulse polarizes the sample to a positive state and consequently, it has the ferroelectric and non-ferroelectric contributions. The U pulse stays at the positive polarization state but now it only has the non-ferroelectric contributions. In this way, the current subtraction between the pulses $P - U$, in principle, allow us to obtain only the ferroelectric contribution. The same idea applies to the pulses N and D. The final hysteresis is obtained by merging the current $I_P - I_U$ for positive voltages and $I_N - I_D$ for negative voltages.⁸⁴ Experimentally, we measured the current and voltage obtained through the PUND curve and, in the end, it is expected the I-V curve shown in Figure 21 for ferroelectric materials. The ferroelectric hysteresis is obtained by integrating the current.

Figure 20 – Illustration of the PUND method for ferroelectric hysteresis. The current is measured during the pulses P-U-N-D.
Source: Adapted from FINA et al.⁸⁴

Figure 21 – Ferroelectric hysteresis and its respective I-V curve. Experimentally, it is expected this kind of behaviour in the ferroelectric materials.
Source: Adapted from NIRANJAN et al.⁸⁵

4 SUPERCONDUCTOR THIN FILMS ON STRONTIUM TITANATE SUBSTRATES

There is a wide range of applications for low and high-temperature superconductor materials. The former superconductor enabled the study of high energy physics research (accelerators), Maglev (magnetic levitation) transportation, superconducting quantum interference devices (SQUIDs) and medical devices such as magnetic resonance imaging. High temperature superconductors (HTS) are more recent and they have applications in energy transmission, generators, motors, transformers, cable in the Navy, military microwave filter systems, HTS SQUIDs and generation of high magnetic fields (world record of 32 Tesla DC magnet). Among all those applications, the last two use $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO) as the HTS superconductor.^{86–92}

Yttrium-barium-copper-oxygen or YBCO is a type II high-temperature superconductor (HTS), highly anisotropic with a critical temperature of around 93 K. For the purpose of using it as a field-effect device, it is necessary to grow high-quality ultra thin films with high- T_C and smooth surface superconducting film.

In this chapter we present the optimized parameters to grow YBCO thin films by PLD to obtain high-quality samples and subsequently design field-effect devices with ferroelectric gates. Initially we describe how the substrates were prepared to grow all our samples. Then we introduce the parameters used to grow the thin films by pulsed laser deposition (PLD), followed by the characterization of the samples.

4.1 Preparation of SrTiO_3 substrates

We used commercially available SrTiO_3 (MaTecK GmbH) with (001) orientation. Prior the growth, it is usually done a surface treatment of the substrate to leave a termination of Ti-O_2 plane that improves the quality and reproducibility of the sample favoring the step flow growth mode (smoother surface).⁹³ The surface treatment of the substrate is described below:

- **Ultrasonic cleaning:** 30 minutes DI-water $\Rightarrow$ 10 minutes acetone $\Rightarrow$ 10 minutes isopropyl alcohol;
- **Acid:** hold the substrate for 30 seconds in aqua regia ($\text{HNO}_3 + 3\text{HCl}$) $\Rightarrow$ rinse well in water $\Rightarrow$ acetone $\Rightarrow$ isopropyl alcohol;
- **Heat treatment:** The substrates are annealed in air at 900°C for 15 minutes with a rate of $10^\circ/\text{min}$;

Figure 22 shows a typical AFM topography and its line profile of our substrates. The height of the atomic steps are about 4 Å, and correspond to one SrTiO_3 lattice parameter. One

Figure 22 – (a) Typical AFM topography after heat treatment of our STO substrates and (b) line profile with atomic steps of height $\approx 4 \text{ \AA}$.

Source: By the author.

can notice long range terraces, with approximately 40nm in width. Such conditions indicate a TiO_2 termination, which are the best for YBCO growth.

4.2 Pulsed laser deposition growth

To grow an epitaxial thin film is important to consider the lattice mismatch between the film and the substrate. There are many reports of *c*-axis oriented YBCO thin films on SrTiO_3 (STO), despite the lattice mismatch between them: STO cubic structure has a lattice parameter of 0.3905 nm and YBCO orthorhombic structure $a = 0.382 \text{ nm}$ and $b = 0.388 \text{ nm}$.⁹⁴

The PLD parameters have a high influence on the quality of the film. They are: growth temperature and pressure, target to substrate distance, energy and fluence of the laser, frequency and number of shots, heat treatment and controlled chamber-atmosphere. Even if there are several reports on YBCO grow by PLD, each system is quite unique and needs optimization for each target material. Thus, we started from a set of parameters found in the literature, but it was essential to study some of them one by one. The expected final result for this project is a superconducting film with high- T_C and sharp transition, smooth surface, few unit cells thick and good crystalline quality. These characteristics will be evaluated by means of electric transport measurements, atomic force microscope and X-ray diffraction.

Table 1 describes these PLD parameters for the superconductor samples grew during this project. They will be divided into three groups, characterized by the changed parameter in the series: growth temperature, deposition rate and oxygen pressure during the heat treatment (known as annealing). The growth temperature is usually one of the most critical parameters in film deposition.⁹⁵ Therefore, the first three samples (group 1) we studied the growth temperature from 680 to 780 °C with steps of 50 °C. Next, the growth temperature was fixed at 780 °C and the frequency of the shots (similar to deposition rate) was studied from 1 to 10 Hz (group 2). For the last group we increased the oxygen pressure of the annealing after the deposition to 1 bar (group 3). Some parameters were fixed for all the samples mentioned above: oxygen pressure

Table 1 – Summarize of the parameters used to grow our films.

YBCO_#	Growth Temp [°C]	Preablation shots	Frequency [Hz]	Growth Shots	Pressure [mBar]
680C	680	6000	3	10000	100
780C	780	6000	3	10000	100
730C	730	6000	3	10000	100
6Hz	780	3000	6	4000	100
3Hz	780	3000	3	4000	100
1Hz	780	3000	1	4000	100
10Hz	780	3000	10	4000	100
1Bar	780	3000	6	2000	1000

Source: By the author.

0.125 mbar, distance target-substrate around 44 mm, laser energy of 250 mJ, fluence of $1.2 \frac{J}{cm^2}$ and annealing temperature of 600 °C.

4.3 Group 1: growth temperature

In this section we will analyze three samples with different growth temperatures ranging from 680 to 780 °C. First, we will discuss the measurement of X-ray diffraction to understand how the growth temperature influences on the crystalline structure of the sample. Second, by means of atomic force microscope we determined their roughness. Finally, the transport measurements results are reported to study the superconducting properties of the samples. All samples in this group are around 150 nm thick.

4.3.1 Structural properties

X-ray diffraction (XRD) measurements were performed using Cu K_α radiation in the Bragg-Brentano geometry. Figure 30 shows the XRD patterns of the three samples: YBCO thin films grown by PLD with growth temperature from 680 to 780 °C. The YBCO_780C (red) only showed (00 l) diffraction peaks indicating that it is c -axis oriented on the STO substrate. However, YBCO_680C and YBCO_730C (blue and dark yellow, respectively) contains (00 l) and (h 00) diffraction peaks indicating that there are c -axis and a -axis oriented grains. This mixed orientation has already been reported by Chang-Hoon Kim et al., arguing that films more than 150nm thick start to nucleate a -axis orientation.^{96,97} Nevertheless, increasing the temperature to 780 °C, the thin film became c -axis oriented, suppressing the (h 00) diffraction peaks. The thermal conditions are very important for the orientation of the film as reported by J. F. Hamet et al. YBCO grown with lower temperature tends to be a -axis oriented and higher temperature c -axis oriented.[?]

Figure 23 – X-ray diffractograms ($\theta - 2\theta$) for samples YBCO_680C (blue), YBCO_730C (dark yellow) and YBCO_780C (red). YBCO and STO peaks are indexed accordingly, $\text{STO-}K_\beta$ peaks are labeled as *.

Source: By the author.

4.3.2 Topography

The surface roughness was evaluated using atomic force microscopy (AFM) in the intermittent mode for all samples within a region of $10 \times 10 \mu\text{m}^2$. Some of the results were extracted from Figure 27 using the free software Gwyddion.⁷ The equation 4.1 demonstrates how the root-mean-square (RMS) roughness is calculated:

$$S_q = \sqrt{\frac{1}{N} \sum_{x=1}^N (z - \bar{z})^2}, \quad (4.1)$$

where S_q is the standard deviation of the height values within a given area, N is the number of points, z is the height and $\bar{z}$ is the average of the z values of the analyzed area.

The surface roughness of the thin films obtained here are all around 30nm, a quite high value which increases the difficulty to measure precisely the thickness by X-ray reflectivity (XRR) measurements. However, it is necessary to keep in mind that the sample contains some large grains that greatly contributes with the RMS roughness calculation. Nevertheless, the high value of roughness can also be explained by the absence of a buffer layer between the substrate

Figure 24 – AFM image of $10 \times 10 \mu m$: (a) YBCO_680C, (b) YBCO_730C and (c) YBCO_780C. The surface roughness for each image: (a) 30.6 nm , (b) 31.6 nm and (c) 32.8 nm . Height from 0 to 280 nm as shown in color ruler.

Source: By the author.

and the high-temperature superconductor or a multilayer structure that would improve the surface smoothness and the electrical properties of the YBCO.

Figure 24 shows AFM images $10 \times 10 \mu m^2$ for the three samples. The temperature and the presence of mixed grains of a -axis and c -axis orientation did not greatly affected the surface roughness, it remained around 30 nm . However, the YBCO_730C which is the sample with higher intensity diffraction peak for a -axis, contains larger grains in smaller amounts than YBCO_680C and YBCO_780C over the same area.

4.3.3 Superconductivity

As explained in Subsection 3.2.4, the resistance vs temperature curve was obtained from 10 to 300 K, using a low-temperature electronic transport chamber. All samples were measured by the four-point probe method, except YBCO_780C where it was used the two-point probe. The contact pads are composed of 4 squares of around $0.5 \times 0.5 \text{ mm}^2$ of Ti (20 nm)/Au (100 nm) which are deposited by electron beam at the LNNano, CNPEM (refer to Figure 25, left).

Figure 25 (right) shows the resistivity measurements for the three samples of the YBCO thin films. The inset is the slope of each curve to extract the critical temperature (peak). It is important to note that the critical temperature found here is slightly lower than expected because of the surface quality of the film since its morphology greatly affects the superconducting properties. Also, the a -axis orientation inhibits the transport of the superconducting current resulting in a lower critical temperature.^{96,98} Nevertheless, YBCO_680C is superconductor with a critical temperature of 83 K. YBCO_780C seems to be superconductor with a critical temperature of 87 K but there is a remaining resistance because it was measured using two probe geometry. Lastly, YBCO_730C has a transition at 78 K, but the resistance in this state is still around 100Ω indicating a metal behavior instead of superconducting. This remaining resistance may be explained by the topography where larger grains (see Fig27(b)) can be responsible for an

Figure 25 – Left: Scheme of a Au/Ti/YBCO/STO used to measure resistivity in four probe geometry of the YBCO thin film. Right: Resistivity-Temperature (RT) measurements of YBCO_680C, YBCO_780C and YBCO_730C.

Source: By the author.

incorrect oxygenation and also by the mixed orientation (*a*-axis and *c*-axis) as measured in the XRD.⁹⁹

To summarize, the sample YBCO_780 presented only *c*-axis oriented grains meanwhile YBCO_680 and YBCO_730 also presented *a*-axis oriented grain. The *a*-axis grains are known to inhibit superconducting current transport, as seen in the superconductivity measurements of sample 730C, which have a higher amount of these grains as measured by XRD. Regarding the AFM measurements, the calculated RMS roughness remained the same for the three samples but there were larger grains in smaller amounts for the 730 sample. Therefore, we fixed the temperature at 780 °C for the next sample groups because we would like *c*-axis oriented films and higher as possible superconducting transitions such as the 780C sample.

4.4 Group 2: frequency of the deposition laser

In this section, we will analyze four samples grew with different frequencies of the deposition laser: 1, 3, 6 and 10 Hz. These frequencies can be used to calculate the following deposition rate: 0.14, 0.42, 0.85 and 1.43 Å/s, respectively. The growth temperature was fixed at 780 °C.

4.4.1 Structural properties

First, the structural properties of the samples were studied by XRD. Figure 30 shows the XRD measurements for this group of samples where it presented the (00*l*) diffraction peaks

Figure 26 – X-ray diffractograms ($\theta - 2\theta$) for samples YBCO_1Hz (orange), YBCO_3Hz (black), YBCO_6Hz (purple) and YBCO_10Hz (green). YBCO and STO peaks are indexed accordingly, STO- K_β peaks are labeled as * and the peak around 10° (labeled as # in the figure) is assigned to multiple diffraction peaks of the substrate.
Source: By the author.

indicating a *c*-axis oriented growth on STO. The YBCO_1Hz (orange) also present a very low-intensity peak around 47° for the (200) diffraction peak. Despite this very low-intensity diffraction peak, all the four samples from 1 to 10 Hz presented a very similar structure according to the XRD measurement.

4.4.2 Topography

Figure 27 shows the topography of the studied samples using the AFM. The surface roughness decreased 15 nm compared with samples of group 1, which is expected for thinner samples, except for the YBCO_1Hz where it maintained equal to the thicker samples (YBCO_680C-780C). The slower deposition rate favored a similar 3D growth mode increasing the surface roughness. Figure 27(e) (inset) shows a small region ($1.5 \times 1.5 \mu m$) of the YBCO_10Hz and apparently there was a formation of stripe-like structure, further studies are required to understand the growth mechanism and its consequences.

Figure 27 – AFM image of $10 \times 10 \mu\text{m}$: (a) YBCO_1Hz, (b) YBCO_3Hz, (c) YBCO_6Hz and (d) YBCO_10Hz. Inset (e) AFM image $1.5 \times 1.5 \mu\text{m}$ of YBCO_10Hz. The surface roughness for each image: (a) 34.4 nm , (b) 17.1 nm , (c) 14.1 nm and (d) 16.1 . Height from 0 to 195 nm as shown in color ruler.

Source: By the author.

4.4.3 Chemical surface analysis

The surface analysis was done using X-Ray Photoelectron Spectroscopy (XPS) and analyzed using the CasaXPS software.¹⁰⁰ First, a survey scan is measured from 0 to 1300 eV to determine all elements presents in the surface of the sample, including possible contaminants. Afterward, a higher resolution scan for specific elements such as yttrium (Y), barium (Ba), cooper (Cu) and oxygen (O). It is important to note that superconducting cuprates easily reacts with air, so it is expected the formation of oxides, carbonates and hydrates or hydroxides.¹⁰¹

Figure 28 (a) shows a typical survey scan for our samples. The only contaminant element found during a meticulous analysis of this measurement was carbon, what is expected from the exposure of the sample to the air.¹⁰² Other elements were also found as expected: yttrium, barium, copper and oxygen (YBCO) as described in the same figure. Table 2 shows the atomic concentration for each sample extracted from the survey scan using the CasaXPS software. All samples were grown by PLD using the parameters described in Table 1 did not present the expected surface stoichiometry (1:2:3). As the measurements of XPS were made months after

Table 2 – Atomic concentration in all samples extracted from CasaXPS software.

% Atomic concentration of	YBCO_680C	YBCO_730C	YBCO_6Hz	YBCO_3Hz	YBCO_1Hz	YBCO_10Hz	YBCO_1Bar
Y	38.48	35.35	41.03	42.94	46.35	36.76	41.09
Ba	37.05	39.79	41.75	39.24	30.11	38.11	41.49
Cu	24.46	24.86	17.22	17.83	23.54	25.14	17.43

Source: By the author.

the growth of the samples, it is possible that the oxidation of the surface has compromised the stoichiometry calculation, as reported by A. Gauzzi et al where samples with higher oxidation state did not have a good agreement between measured and expected stoichiometric values.¹⁰³

Figure 28 (b)-(e) shows the high resolution scans for the samples YBCO_1-10Hz and YBCO_1Bar (sample from group 3: 6 Hz and 1 Bar annealing pressure) after the charge compensation using the C 1s peak at 284.5. Analyzing the results of the five samples, we have two types of spectra. One that presented two peaks on the barium spectrum and another one that also have the two peaks, but the second one has lower intensity. In other words, the samples presented very similar XPS measurements.

In more details, two peaks were measured in the oxygen spectrum with BE around 531.2 and 528.3 eV. Both are expected for the YBCO material, i.e. a signature of the superconducting cuprate. The two main peaks from the barium measurement are well separated (around 15 eV) because of the spin-orbit splitting. The barium main peak around 779.7 eV and the smaller intensity peak around 777.4 eV are also signature of YBCO lattice. The yttrium is not well separated as expected from spin-orbit splitting because of the multiple chemical states that are present in the sample. Nevertheless, the peak around 155.8 eV is associated with Y_2O_3 and the peaks around 157.6 eV and 153.3 eV are assigned to the YBCO material. The copper 2p spectra are composed of 2 peaks separated by spin-orbit splitting and 2 satellites. By studying the satellites of copper it is possible to evaluate its valence: The CuO spectrum has satellites with higher intensities of valences Cu^{+2} at BE around 943 eV. Cu_2O with Cu^{+1} valence has satellites with very weak intensities shifted to BE around 945 eV and a narrow $Cu_{2p_{3/2}}$ peak.^{101,103,104}

Particularly to our films, the YBCO_6Hz and YBCO_1Bar also presented the 777.4 eV peak in the barium spectrum, however, its intensity is lower compared to the other samples. This peak, as mentioned above, is a signature of the YBCO lattice and it is shown in Figure 28 (c). The yttrium, oxygen and copper presented similar trends for all the five samples compared.

4.4.4 Superconductivity

Figure 29 shows the resistivity measurements for the four samples. It is notable a small decrease in the critical temperature compared with the first group and that can be explained by

Figure 28 – XPS measurement: (a) Typical survey scan of our YBCO sample to detect any impurities at the surface. The peaks are labeled with the corresponding elements. Higher resolution for each element: (b) yttrium 3d, (c) barium 3d, (d) copper 2p and (e) oxygen 1s.
Source: By the author.

the decrease of the thickness of the samples (from 143 to 57 nm) since it is already reported similar results.¹⁰⁵ The YBCO_3Hz and YBCO_1Hz presented different types of contributions for the superconducting transition. In the case of the former, the two contributions (two peaks in the first derivative) have different critical temperatures as shown in the inset of the figure and this can be explained with a non-homogeneous distribution of oxygen inside the sample, creating zones with different critical temperature. In the case of the YBCO_1Hz, it seems that most of the contributions are non-superconducting resulting in a linear increase of resistance after the superconducting transition. Hence, it is observed that lower frequencies deposition indicates an suppression of the superconducting properties and higher frequencies deposition makes the SC transitions sharper, i.e. increases the oxygen homogeneity of the sample.^{99,106}

Figure 29 – Resistivity-Temperature measurements: YBCO_1Hz, YBCO_3Hz, YBCO_6Hz and YBCO_10 Hz. Inset is the slope for each sample to get the critical temperature. All samples grown at 780 °C.

Source: By the author.

In conclusion, low frequencies of the deposition laser contributes to higher roughness and worst superconducting property. Meanwhile, higher frequencies have resulted in sharper superconducting transitions and lower surface roughness. Chemical surface analysis by XPS indicates only carbon contamination, but the measured values differ from expected stoichiometry which is justified by surface oxidation.

4.5 Group 3: high pressure

This group is composed of only one sample in which the annealing pressure has been adjusted to 1 bar and the number of shots to 2000 (thickness reduced by half). The growth temperature and frequency of shot were fixed at 780 °C and 6 Hz, respectively. The thickness reduction was necessary to perform X-ray reflectivity measurements to determine the thickness of the samples. Meanwhile, the growth temperature was maintained at 780 °C, similar to the previous group, and the frequency of the laser was set at 6 Hz because it had satisfactory superconducting properties.

4.5.1 Structural properties

The YBCO_1Bar also presented c-axis oriented thin film. Figure 30 shows its XRD measurement and this diffractogram is very similar to the one measured of the sample YBCO_6Hz.

Figure 30 – X-ray diffractograms ($\theta - 2\theta$) for samples YBCO_1Bar (grey). YBCO and STO peaks are indexed accordingly, STO- K_β peaks are labeled as * and the peak around 10° (labeled as # in the figure) is assigned to multiple diffraction peaks of the substrate.

Source: By the author.

X-ray reflectivity (XRR) measurements determined the thickness of this sample. It was used the methods described in Subsection 3.2.1.1. However, the high interface roughness of

Figure 31 – X-ray reflectivity measurement and thickness analysis. (a) Linear fit and (b) Fourier transform to extract the thickness from (c) XRR data (measured and simulated).

Source: By the author.

the samples makes XRR measurements difficult because it introduces an exponential decay to the signal measured. It is recommended that the roughness should be less than tens of nanometers.^{107,108} Therefore, due to limitations of thickness and roughness, the XRR measurement is only acquired for the thinner sample and then the thickness is extrapolated for the other samples.

Figure 31 shows the different methods used for sample YBCO_1Bar to extract the thickness. Figure 31.(a) is a linear sine-square fit of the angle as a function of the squared index for each minimum of the interference fringes. The thickness is calculated using the equation (proportional to the slope of the fit) as described in the figure. Another method is to calculate the Fourier transform of the data and plotting with a horizontal axis in the scale of the lattice vector

Table 3 – Thickness determined by XRR of the YBCO thin films where YBCO_680C, YBCO_6Hz and YBCO_1Bar have 10000, 4000 and 2000 deposition laser shots, respectively.

-	YBCO_680C	YBCO_6Hz	YBCO_1Bar
Thickness [nm]	143.05	57.22	28.61

Source: By the author.

Figure 32 – AFM image of $10 \times 10 \mu m$ of YBCO_1Bar sample. The extracted surface roughness was 13.6 nm . Height from 0 to 255 nm as shown in color ruler.

Source: By the author.

q_z . The thickness value can be estimated by the peak position in the resulting graph. Figure 31.(c) shows the data measured and the simulation using the software XOP 2.4 from The European Synchrotron (ESRF).¹⁰⁹ All methods gave close thickness values: $28.6 \pm 0.2 \text{ nm}$. The result was extrapolated to the other samples as shown in Table 3.

4.5.2 Topography

Figure 32 demonstrates the topography of YBCO_1Bar sample. The calculated roughness is about 13.6 nm and it looks very similar to the YBCO_6Hz sample. It is important to note that despite being a thinner sample, the roughness practically did not changed.

4.5.3 Superconductivity

Lastly, the sample with higher oxygen pressure during the annealing (YBCO_1Bar) did not have superconducting properties (Figure 33). It is reported in the literature that higher oxygen

Figure 33 – Resistivity-Temperature (RT) measurement: YBCO_1Bar (6 Hz, 1 bar annealing). Inset is the slope to extract the critical temperature.
Source: By the author.

pressure would likely promote *a*-axis outgrowth that could suppress the superconductivity but in the XRD measurements, the film only presented *c*-axis orientation.⁹⁶ Therefore, this suppression can be explained in the way that the high pressure of oxygen during the heat treatment promoted the material to the overdoped regime where it does not have superconducting properties.

4.6 Partial conclusions

Increasing the growth temperature indicated an improvement in the quality of epitaxy by suppressing the *a*-axis oriented grains. In other words, the sample with 780 °C showed only *c*-axis oriented crystalline structure. In addition, it was observed that increasing the frequency of the deposition laser resulted in superconducting transition sharper. Meanwhile, the higher annealing pressure suppressed the superconducting transition despite of the sample is *c*-axis oriented.

In summary, Table 4 displays both roughness and critical temperature values for all studied samples. Different growth temperatures (680 – 780 °C) did not have major changes in surface roughness. Thinner samples reduced surface roughness, except the 1 Hz sample and

Table 4 – Summarize of the parameters used to grow our films. Roughness (σ_{rms}) of the YBCO films determined by AFM images of $10 \times 10 \mu m$ using the free software Gwyddion. The critical temperature (T_C) of the measured samples extracted from the peak found in the first derivative of the RT curve.

YBCO_#	Growth Temp. [°C]	Frequency [Hz]	Growth Shots	Pressure [mBar]	Roughness [nm]	Critical Temp. [C]
680C	680	3	10000	100	30	83
730C	730	3	10000	100	32	78
780C	780	3	10000	100	31	87
1Hz	780	1	4000	100	34	83
3Hz	780	3	4000	100	17	74
6Hz	780	6	4000	100	14	76
10Hz	780	10	4000	100	16	78
1Bar	780	6	2000	1000	14	-

Source: By the author.

the one with higher oxygen pressure during annealing. Meanwhile, the critical temperature of the superconducting transition as exposed on the mentioned table was extracted by using the first derivative of the resistance-temperature curve. The sample with a -axis oriented grains had a lower critical temperature (680 and 730 °C). The YBCO_780C has the highest temperature transition, but it is important to consider that its superconducting transition was extracted from a 2-probe measurement method, different from the 4-probe method used in the other samples. The decrease of the T_C for the other samples (1-10 Hz) can be attributed to the changed of thickness from 143 to 57 nm.

5 FERROELECTRIC THIN FILMS

Particularly today there is a need for miniaturization of devices to increase, for instance, the information storage density. With that in mind, it is expected to push fabrication and characterization methods to the nanoscale level. In this chapter, we will introduce a technique to measure ferroelectric hysteresis using the tip of an atomic force microscopy with the PUND method. Briefly, the objective of this chapter can be divided into two parts:

- Growth and characterization of superconductor-ferroelectric heterostructures, with emphasis in obtain good crystalline, morphological and transport properties. Such information can be used in future works to implement a field-effect superconductor device;
- Implement ferroelectric characterization at the nanoscale, using an atomic force microscope (AFM).

In this way, it will be presented the first superconductor/ferroelectric heterostructure sample grew by PLD, followed by its characterization.

5.1 Growth - PLD

Initially, it was used the superconductor $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ primarily as bottom electrode, barium titanate BaTiO_3 as ferroelectric material and Ti/Au as top electrode (refer to Figure 34). The growth parameters are described in Table 5. It is important to note that all previous knowledge acquired from the superconductor studies were implemented here which means that we used the same substrate treatment and growth parameters of the best quality film discussed at Section 4. It is important to note that the growth of both materials was done sequentially and *in-situ*, i.e. the growth of BTO started after the YBCO annealing without exposing the sample to the atmosphere.

Figure 34 – Schematic of the studied sample: STO/YBCO/BTO/Ti/Au where Ti and Au are represented by dark gray and orange, respectively.

Source: By the author.

The growth parameters are described in Table 5. We kept the deposition conditions of the YBCO_6Hz which has a growth temperature of around 780°C and a laser pulse frequency of 6 Hz. This sample presented single-phase *c*-axis oriented growth verified by X-ray diffraction and superconductivity transition.

Since we are going to use a nanometer-scale radius tip of the atomic force microscope to measure the ferroelectric hysteresis, the gold top electrodes are very important to detect the polarization charges otherwise it would be a very low signal-to-noise ratio. However, it seems that the most important factor in ferroelectric materials to detect these polarization charges comes with the size of the switched area.¹¹⁰ The top electrode was deposited by sputtering after the sample characterization.

Table 5 – Summarize of important parameters used to grow our films.

-	Growth conditions						
	Growth Temp [$^{\circ}\text{C}$]	Annealing Temp [$^{\circ}\text{C}$]	Annealing Time [min]	Frequency [Hz]	Growth Shots	Growth Pressure [mBar]	Fluence [$\frac{\text{J}}{\text{cm}^2}$]
YBCO	775	600	60	6	4000	0.125	1.2
BTO	740	650	30	3	10000	0.103	1.3

Source: By the author.

5.2 Structural properties

Particularly for this sample, the X-ray diffractogram was obtained using a monochromated X-ray beam with a cobalt target ($\lambda = 1.79\text{\AA}$). Figure 35 shows the XRD pattern for the studied sample where it clearly demonstrated a *c*-axis oriented film was grown on STO substrate since it shows only the (00*l*) peaks. Since the sample is composed of two different materials, the Bragg-Brentano scan will probe the peaks (00*l*) of both thin film materials. Hence, Figure 35 shows the peaks for YBCO and BTO indicating high crystalline quality growth.

5.3 Topography

Figure 36 refers to the atomic force microscopy measurement of the discussed sample. Not surprisingly, the sample presented a high surface roughness. From the AFM measurements discussed in the last chapter, it is expected a high roughness from the BTO because the YBCO at the bottom presented roughness around 14nm . Two possible solutions need to be investigated: either by an introduction of a buffer layer between the SC and the substrate or using a different substrate with a closer lattice parameter. Nevertheless, the sample YBCO/BTO has a roughness around 26nm extracted from the figure below using the software Gwyddion.

Figure 35 – (a) X-ray diffractogram ($\theta - 2\theta$) using cobalt X-rays tube ($\lambda = 1.79\text{\AA}$) the heterostructure YBCO/BTO. All peaks from YBCO, BTO and STO are indexed accordingly.

Source: By the author.

5.4 Hysteresis measurement

Nowadays in our scientific group, there are two systems capable of measuring the ferroelectric hysteresis of thin films:

- The low-temperature electronic transport chamber discussed at Chapter 3.2.4 where it is possible to measure ferroelectric hysteresis in vacuum controlling the temperature from 20 to 300K.
- Measuring the hysteresis using the same electronic components as the other system but implementing it together with the atomic force microscope at room temperature.

The first one requires a more complex sample preparation such as indium bonding with very thin golden wires. This way the gold electrodes may be accessed by external cables while the sample is in a vacuum environment with total control over temperature. Regarding the studied sample described in this chapter, we measured first the resistance as a function of the temperature to check the quality of the bottom electrode (YBCO). Figure 37 left shows the RT of the bottom

Figure 36 – AFM topography of $5 \times 5 \mu\text{m}$ of YBCO/BTO sample on STO substrate. Roughness (σ_{rms}) around 25.6 nm calculated by Gwyddion.
Source: By the author.

Figure 37 – Eletronic transport measurements of the STO/YBCO/BTO sample. Left: resistance as function of temperature measurement of the bottom electrode (YBCO) showing the superconductivity transition. Right: I-V measurement of the ferroelectric BTO with leak current features.
Source: By the author.

electrode where the YBCO presented a superconductor transition at around 78K and a low resistance which is suitable for a bottom electrode. At the right of the figure, it is presented the current as a function of the voltage using the PUND curve (see chapter 3.2.4) of the BTO thin film. This result indicates only the leakage current component, suppressing any ferroelectric evidence. Since the switching current is proportional to the frequency, increasing the frequency could reinforce the ferroelectric characteristics of the sample mitigating the presented loss but that would require additional instruments which will be described later.⁸⁴

As described above, the second method uses the electronic components of the low-temperature electronic transport chamber together with the atomic force microscope at room temperature. The schematic is described in Figure 38. First, It is applied a PUND-like curve with controlled frequency and voltage using an arbitrary waveform generator at the tip of the microscope. Second, the AFM is set in contact mode and then it is measured by the current of the bottom electrode to the ground using a current amplifier. The current as a function of the applied voltage (I-V) is shown using the LabVIEW program that controls the cited components.

Figure 39 shows the first test of I-V curve measurement on a silicon substrate with a gold film on top. It was used a voltage sweep from -10 to $20V$ of the Keithley 6430 instrument. It was observed an asymmetric curve from -9 to 4 mA due to the formation of Schottky barriers of different heights.¹¹¹

Finally, it was measured a test sample of $\text{DyScO}_3/\text{SrRuO}_3/\text{BiFeO}_3/\text{SrRuO}_3$ to probe the ferroelectric properties of the bismuth ferrite (BFO) at the nanoscale level. This sample was grown via PLD and patterned by photolithography, followed by ion milling process at the Ramesh Lab - University of California, Berkeley by Everton Bonturim. Figure 40 left shows the optical microscope image where the circles are the SRO electrodes of $16\mu\text{m}$ of diameter. The right side of the figure shows the I-V measurement on top of the SRO electrode. Unfortunately, it presented the same characteristics as the BTO measurement described before (Figure 37).

As already mentioned, the ferroelectric component is proportional to frequency of the input waveform. By increasing the frequency, one could intensify the ferroelectric characteristics high enough to disregard the leakage current. With that in mind, we used the same waveform with higher frequencies and measured the current using a low noise current preamplifier Stanford SR570. Using a standard oscilloscope, we could observe the I-V curve in real-time using the X-Y channel.

Figure 41 shows the I-V measurements for different values of frequencies. For low

Figure 38 – Schematic of the ferroelectric hysteresis measurement using PUND and atomic force microscopy.

Source: Adapted from OWOONG KWON et al.¹¹⁰

Figure 39 – Current-voltage curve of a silicon substrate with a gold thin film as electrode.
Source: By the author.

Figure 40 – Left: optical microscope image of the surface of the DSO / SRO(20nm) / BFO(100nm) / SRO(20nm) thin film. The circles shown here are the top electrode made of SRO of 16μm. Right: I-V curve measurement on one of the SRO electrodes to probe the ferroelectric properties of the BFO film.
Source: By the author.

frequencies (e.g. 1 – 5 kHz), the leakage current component predominates the ferroelectric component. And for higher frequencies (10 and 20 kHz), the ferroelectric contribution increases and the curve indicate a transition to the positive and negative expected peaks for ferroelectric materials. Nevertheless, the curve of 20 kHz still have some important unanswered questions such as the oscillation noise and the saturation of the hysteresis curve.

Figure 41 – Current versus voltage loop for different frequencies from 1 to 20 kHz. This measurement uses the PUND waveform before the compensation (i.e. subtraction of peaks) for the 1 to 10 kHz. For the 20 kHz curve, it is calculated the PUND compensation and it is shown the ferroelectric hysteresis in red.

Source: By the author.

5.5 Partial conclusions

The sample superconductor-ferroelectric heterostructure grown by PLD presented a *c*-axis oriented grains by x-ray diffraction and a surface roughness similar to the thicker YBCO samples from last chapter (YBCO_6Hz). The macroscopic ferroelectric hysteresis measurement in low frequency indicated a leakage current behavior, meanwhile, the nanoscale ferroelectric hysteresis measurement with higher frequencies of a test sample indicated a transition from leakage current (low frequencies) to ferroelectric behavior (higher frequencies).

6 CONCLUSIONS

In this master's thesis, we studied the influence of pulsed laser deposition growth parameters in the fabrication of superconductor thin film. We also grew heterostructure involving superconductor and ferroelectric thin films in order to give the first steps towards the designing of a field effect device. Finally, we commissioned a method of measuring ferroelectric hysteresis at a nanoscale level using an atomic force microscope.

First, we studied mainly two growth parameters: growth temperature and frequency of the laser (growth rate). The temperature varied from 680 to 780°C and the frequency varied from 1 to 10Hz. The former parameter variation changed drastically the structure of the material by introducing *a*-axis oriented grains for low temperatures, meanwhile, for 780°C, the thin film became *c*-axis oriented independently of the variation of the laser frequency. Regarding the atomic force microscope measurements, we observed that for low frequency (1 Hz) the surface roughness is higher than other samples with the same thickness. Nevertheless, the XPS measurements made possible to extract the surface stoichiometry and although it did not present the stoichiometry expected (Y123), they all have the satellites in the Cu2p scan that represents the Cu⁺² valence which is very important for superconductivity. Lastly, we could observe an improvement in the superconductivity transition by the resistivity curve with the increase of the frequency of the laser or growth rate where the films with 6 and 10Hz have a critical temperature of 76 and 78K, respectively.

Finally, we grew a heterostructure involving a superconductor and a ferroelectric thin film. The sample clearly showed results of *c*-axis oriented grains grown on strontium titanate substrate by results of x-ray diffraction measurements. However, the surface roughness still maintained high values such as 25nm which may be solved by introducing a buffer layer for the YBCO thin film. Unfortunately, the hysteresis measurements in the electronic transport chamber showed mainly results of leakage current, suppressing any ferroelectric evidences. Afterward, the same instruments were used together with the atomic force microscope to measure I-V curves at the nanoscale level. First the I-V curve of a silicon substrate with a gold thin film was measured and we could observe the asymmetric behavior as expected from a metal semiconductor junction. Lastly, we measured the ferroelectric hysteresis for different frequencies of a material with small electrodes of several micrometers which results also in a leakage current-like curve for low frequencies. However, for higher frequencies, the ferroelectric component increased and we could observe the appearance of the positive and negative peaks from the switching current.

7 PERSPECTIVES

There are some important points that need to be studied for the completeness of this work:

- Rocking-curve and phi-scan measurements to check the quality of the epitaxy and to confirm the (h00) peaks.
- Growth studies involving other parameters for the high-temperature and the ferroelectric thin films such as oxygen pressure during deposition, thickness, distance target-substrate and fluence of the deposition laser.
- Addition of a buffer layer (e.g. cerium oxide) between the substrate and the superconductor to improve its roughness and electrical properties.
- Piezoresponse force microscopy measurements together with the ferroelectric characterization in order to clarify the switched area region and to validate the obtained ferroelectric information of the samples.
- X-ray photoelectron spectroscopy in-situ measurements of new superconductor samples and measurement of the used target to determine the real stoichiometry.

REFERENCES

- 1 AHN, J.-M. T. C. H.; MANNHART, J. Electric field effect in correlated oxide systems. **The Science of Nature**, v. 424, p. 1015–1018, 2003.
- 2 BEGON-LOURS, L. **Ferroelectric field-effects in high-*tc* superconducting devices**. 2017. 192 p. Ph. D. Thesis (Philosophy) – Faculté de Physique, Université Pierre et Marie Curie, Paris. 2017. Available from: <<https://tel.archives-ouvertes.fr/tel-01568185>>. Accessible at: 23 Jan. 2018.
- 3 SHERRILL, C. D. **Introduction to electron correlation**. 2009. Available from: <<http://vergil.chemistry.gatech.edu/courses/chem6485/pdf/intro-e-correlation.pdf>>. Accessible at: 23 Jan. 2018.
- 4 PEREZ-MUÑOZ, A. M. et al. In operando evidence of deoxygenation in ionic liquid gating of YBa₂Cu₃O_{7-x}. **Proceedings of the National Academy of Sciences**, v. 114, n. 2, p. 215–220, Dec. 2016. doi: 10.1073/pnas.1613006114.
- 5 LU, N. et al. A review for compact model of graphene field-effect transistors. **Chinese Physics B**, v. 26, n. 3, p. 036804, 2017.
- 6 GOLDMAN, A. M.; MARKOVIĆ, N. Superconductor-insulator transitions in the two-dimensional limit. **Physics Today**, v. 51, n. 11, p. 39-44, Nov. 1998. doi: 10.1063/1.882069.
- 7 ZHOU, Y.; RAMANATHAN, S. **Correlated electron materials and field effect transistors for logic: a review**. 2013. Available from: <<https://arxiv.org/ftp/arxiv/papers/1212/1212.2684.pdf>>. Accessible at: 23 Jan. 2017.
- 8 SUPERCONDUCTING quantum computing. 2018. Available from: <https://en.wikipedia.org/wiki/Superconducting_quantum_computing>. Accessible at: 02 Nov. 2018.
- 9 SAKAI, S.; TAKAHASHI, M. Recent progress of ferroelectric-gate field-effect transistors and applications to nonvolatile logic and FeNAND flash memory. **Materials**, v. 3, n. 11, p. 4950–4964, 2010. Available from: <<http://www.mdpi.com/1996-1944/3/11/4950>>. Accessible at: 05 Nov. 2018.
- 10 DELFT, D. van; KES, P. The discovery of superconductivity. **Physics Today**, v. 63, n. 9, p. 38–43, 2010. doi: 10.1063/1.3490499.
- 11 MEISSNER, W.; OCHSENFELD, R. Ein neuer effekt bei eintritt der supraleitfähigkeit. **Naturwissenschaften**, v. 21, p. 787–788, Nov. 1933.
- 12 ONNES, H. K. The resistance of pure mercury at helium temperatures. **Communications Physics Laboratory University Leiden**, v. 12, 1911.
- 13 CHINTAMANENI, V. K. **Fabrication of oxide superconducting thin films using colloid of nanoparticles as precursor**. 2006. 104 p. (Masters thesis) - Department of Mechanical and Materials Engineering, Wright State University, Dayton, 2006.

-
- 14 SHENG, J. et al. Recovery time of high temperature superconducting tapes exposed in liquid nitrogen. **Physica C: superconductivity and its applications**, v. 527, Suppl. C, p. 50-54, 2016.
- 15 MAEDA, H.; TANAKA, Y.; FUKUTOMI, M.; ASANO, T. A new high- T_c oxide superconductor without a rare earth element. **Japanese Journal of Applied Physics**, v. 27, n. 2A, p. L209, 1988.
- 16 SHENG, Z. Z.; HERMANN, A. M. Bulk superconductivity at 120 K in the $TlCa/BaCuO$ system. **Nature**, v. 332, p. 138–139, 1988. doi.org/10.1038/332138a0.
- 17 SCHILLING, A. et al. Superconductivity above 130 K in the $Hg-Ba-Ca-Cu-O$ system. **Nature**, v. 363, p. 56–58, 1993. doi.org/10.1038/363056a0.
- 18 HIKAMI, S.; HIRAI, T.; KAGOSHIMA, S. High transition temperature superconductor: Y-ba-cu oxide. **Japanese Journal of Applied Physics**, v. 26, n. 4A, p. L314, 1987.
- 19 PENG, F. et al. Hydrogen clathrate structures in rare earth hydrides at high pressures: possible route to room-temperature superconductivity. **Physical Review Letters**, v. 119, n. 10, p. 107001, Sept. 2017. doi/10.1103/PhysRevLett.119.107001.
- 20 TINKHAM, M. **Introduction to superconductivity**. 2nd ed. 1996. Available from: <<http://www.physics.fudan.edu.cn/tps/people/jzhao/BookPaper/Introduction%20to%20superconductivity.pdf>>. Accessible at: 12 Dec. 2017.
- 21 HOWE, B. A. **Crystal structure and superconductivity of $YBa_2Cu_3O_{7-x}$** . 2014. 68 p. (Masters thesis) — Minnesota State University, Minnesota, 2014.
- 22 JACOBS, T. **Unraveling the cuprate superconductor phase diagram**: Intrinsic tunneling spectroscopy and electrical doping. 2016. 78 p. Ph. D. Thesis (Philosophy) – Department of Physics, Stockholm University, Sweden. 2009. Available from: <<https://www.diva-portal.org/smash/get/diva2:920919/FULLTEXT01.pdf>>. Accessible at: 09 Jan. 2019.
- 23 HIGH-TEMPERATURE superconductivity. 2018. Available from: <https://en.wikipedia.org/wiki/High-temperature_superconductivity>. Accessible at: 02 Nov. 2018.
- 24 VALASEK, J. Piezo-electric and allied phenomena in Rochelle salt. **Physical Review**, v. 17, p. 475–481, Apr. 1921. doi/10.1103/PhysRev.17.475.
- 25 BUSCH, G.; SCHERER, P. A new seignette-electric substance. **The Science of Nature**, v. 23, n. 43, p. 737–738, Oct. 1935.
- 26 PEASE, R. S.; BACON, G. E. Ferroelectric structure of potassium dihydrogen phosphate. **Nature**, v. 173, p. 443–444, Mar. 1954. doi: 10.1038/173443b0.
- 27 CROSS, L. E.; NEWNHAM, R. E. **History of ferroelectrics**. Available from: <http://ieee-uffc.org/wp-content/uploads/2016/11/cross_newnham.pdf>. Accessible at: 02 Nov. 2018.
- 28 MARTIN, L. W.; RAPPE, A. M. Thin film ferroelectric materials and their applications. **Nature Reviews Materials**, v. 2, 2016. doi.org/10.1038/natrevmats.2016.87.

- 29 LIRA-CANTU, M. **The future of semiconductor oxides in next-generation solar cells.** Amsterdam: Elsevier, 2017.
- 30 XIAO, B. **Growth, characterization and applications of multifunctional ferroelectric thin films.** 2009. 137 p. Ph. D. Thesis (Philosophy) – Faculté de Physique, Virginia Commonwealth University, Virginia. 2009. Available from: <<https://scholarscompass.vcu.edu/cgi/viewcontent.cgi?article=2935context=etd>>. Accessible at: 23 Oct. 2018.
- 31 DEVONSHIRE, A. F. XCVI Theory of barium titanate. **Philosophical Magazine**, v. 40, p. 1040–1063, Jul. 1949. doi: 10.1080/14786444908561372.
- 32 LÜKER, A. **A short history of ferroelectricity.** 2018. Available from: <http://groups.ist.utl.pt/rschwarz.daemon/rschwarzgroup_files/Ferroelectrics_files/A%20Short%20History%20of%20Ferroelectricity.pdf>. Accessible at: 02 Nov. 2018.
- 33 FANNING, D. M. **Structure property relations in ferroelectric materials.** 2000. 158 p. Ph. D. Thesis (Philosophy) – Department of Physics, University of Illinois, Urbana-Champaign, 2000 Available from: <http://www.ucl.ac.uk/ucapikr/theses/Fanning_thesis.pdf>. Accessible at: 23 Oct. 2018.
- 34 DAMJANOVIC, D. Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics. **Reports on Progress in Physics**, v. 61, n. 9, p. 1267, 1998.
- 35 PIETRO, F. et al. **Ferroelectric crystals for photonic applications:** including nanoscale fabrication and characterization techniques. Berlin: Springer-Verlag, 2014. doi: 10.1007/978-3-642-41086-4.
- 36 LIU, Y.; WANG, S.; CHEN, Z.; XIAO, L. Applications of ferroelectrics in photovoltaic devices. **Science China Materials**, v. 59, n. 10, p. 851–866, Oct 2016. doi.org/10.1007/s40843-016-5102-0.
- 37 SHIN, H. et al. Large nonlinear optical response of polycrystalline $\text{Bi}_{0.25}\text{La}_{0.75}\text{Ti}_3\text{O}_{12}$ ferroelectric thin films on quartz substrates. **Optics Letters**, v. 32, n. 16, p. 2453–2455, Aug 2007.
- 38 LIN, Y. et al. Enhancing grain boundary ionic conductivity in mixed ionic–electronic conductors. **Nature Communications**, v. 6, n. 6824, 2015. doi: 10.1038/ncomms7824.
- 39 DUNN, S.; STOCK, M. Artificial photosynthesis use of a ferroelectric photocatalyst. **MRS Proceedings**, v. 1446, p. mrss12–1446–u02–07, 2012.
- 40 CHOI, T. et al. Switchable ferroelectric diode and photovoltaic effect in BiFeO_3 . **Science**, v. 324, n. 5923, p. 63–66, 2009.
- 41 CHANTHBOUALA V. G. et al. Ferroelectric memristor. **Nature Materials**, v. 11, p. 860–864, 2012.
- 42 ISHIWARA, H. Ferroelectric random access memories. **Journal of Nanoscience and Nanotechnology**, v. 12, n. 5923, p. 7619–7627, 2012.
- 43 OSMAN, K. I. **Synthesis and characterization of BaTiO_3 ferroelectric material.** 2011. 176 p. Ph. D. Thesis (Philosophy) – Faculty of Engineering, Cairo University, Egypt. 2011. Available from: <http://www.iaea.org/inis/collection/NCLCollectionStore/_Public/44/079/44079115.pdf> Accessible at: 23 Oct. 2018.

- 44 DUMONT, A. **Synthesis, characterization and application of barium titanate particles in light emitting devices**. 2016. 110 p. Ph. D. Thesis (Philosophy) – York University, Canada. 2014. Available from: <https://yorkspace.library.yorku.ca/xmlui/bitstream/handle/10315/32333/Dumont_Antoine_2016_Masters.pdf?sequence=2&isAllowed=y>. Accessible at: 23 Oct. 2018.
- 45 SHAW, J. M.; SEIDLER, P. F. Organic guest editors electronics: introduction. **IBM Journal of Research and Development**, v. 45, n. 1, 2001.
- 46 GLOVER, R. E.; SHERRILL, D. M. Changes in superconducting critical temperature produced by electrostatic charging. **Physics Review Letters**, v. 5, n. 6, p. 248–250, 1960.
- 47 SAKAI, S. Theoretical study of electric-field effects in high- T_c oxide superconductors using an ultrathin-metal-insulator superlattice model. **Physics Review B**, v. 47, n. 14, p. 9042–9047, 1993.
- 48 AHN, C. H. et al. Electrostatic modulation of superconductivity in ultrathin $\text{GdBa}_2\text{Cu}_3\text{O}_{7-x}$ films. **Science**, v. 284, n. 5417, p. 1152–1155, May. 1999. doi: 10.1126/science.284.5417.1152.
- 49 XIANG, L. et al. Electrostatic control of the evolution from a superconducting phase to an insulating phase in ultrathin $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films. **Physical Review Letters**, v. 107, n. 2, p. 27001, July 2011. doi: 10.1103/PhysRevLett.107.027001.
- 50 TILLEY, R. J. D. The ABX_3 Perovskite Structure. In: _____ **Perovskites: structure-property relationship perovskites**. Chichester: John Wiley & Sons, 2016. p. 1-41, doi: 10.1002/9781118935651.ch1.
- 51 KHARE, N. **Handbook of high-temperature superconductor electronics**. New York: Marcel Dekker, 2003.
- 52 BREIT, V. et al. Evidence for chain superconductivity in near-stoichiometric $\text{YBa}_2\text{Cu}_3\text{O}_x$ single crystals. **Physical Review B**, v. 52, n. 22, p. 15727-15730, Dec. 1995. doi: 10.1103/PhysRevB.52.R15727.
- 53 WU, M. K. et al. Superconductivity at 93 K in a new mixed-phase Y-Ba-Cu-O compound system at ambient pressure. **Physical Review Letters**, v. 58, n. 9, p. 908-910, Mar. 1987. doi: 10.1103/PhysRevLett.58.908.
- 54 LU, H. Enhancement of ferroelectrics: strain-engineered ferroelectric thin films. **Berkeley Scientific Journal**, v. 20, n. 1, Jan. 2015. Available from: <<https://escholarship.org/content/qt7ns02212/qt7ns02212.pdf?nosplash=eb599d3d3155ead533371255c8ea192>>. Accessible at: 23 Jan. 2018.
- 55 EVERHARDT, A. **Novel phases in ferroelectric BaTiO_3 thin films**: enhanced piezoelectricity and low hysteresis. 2017. 104 p. Ph. D. Thesis (Philosophy) – University of Groningen, Netherlands. 2011. Available from: <[https://www.rug.nl/research/portal/publications/novel-phases-in-ferroelectric-batio3-thin-films\(2a096d45-fbe9-4e91-9cb0-96005224db78\).html](https://www.rug.nl/research/portal/publications/novel-phases-in-ferroelectric-batio3-thin-films(2a096d45-fbe9-4e91-9cb0-96005224db78).html)> Accessible at: 23 Oct. 2018.
- 56 BEDNORZ, J. G. Possible high- T_c superconductivity in the BaLaCuO system. **Zeitschrift für Physik B - condensed matter**, v. 64, n. 2, p. 189–193, June 1986. doi: 10.1007/BF01303701.

- 57 DIJKKAMP, D. et al. Preparation of Y-Ba-Cu oxide superconductor thin films using pulsed laser evaporation from high- T_C bulk material. **Applied Physics Letters**, v. 51, n. 8, p. 619–621, 1987. Available from: <<https://doi.org/10.1063/1.98366>>. Accessible at: 10 Oct. 2018.
- 58 BLANK, D.; DEKKERS, J.; RIJNDERS, A. Pulsed laser deposition in Twente: from research tool towards industrial deposition. **Journal of physics D: applied physics**, v. 47, n. 3, p. 034006, 2014.
- 59 OXFORD INSTRUMENTS. **Pulsed laser deposition**. 2018. Available from: <<https://www.oxinst.com/learning/view/article/pulsed-laser-deposition>>. Accessible at: 02 Nov. 2018.
- 60 BOFFA, V. et al. High-quality ybco thin films grown by off-axis pld geometry. **IEEE Transactions on Applied Superconductivity**, v. 7, p. 1189–1192, 1997. doi: 10.1109/77.620711.
- 61 GREER, J. A. History and current status of commercial pulsed laser deposition equipment. **Journal of Physics D: applied physics**, v. 47, n. 3, p. 034005, 2014. Available from: <<http://iopscience.iop.org/article/10.1088/0022-3727/47/3/034005>>. Accessible at: 10 Oct. 2018.
- 62 SOONMIN, H. A brief review of the growth of pulsed laser deposited thin films. **British Journal of Applied Science and Technology**, v. 14, n. 6, Mar 2016. Available from: <<http://www.sciencedomain.org/abstract/13537>>. Accessible at: 25 Oct. 2018.
- 63 LIPPMAN, M. et al. OHASHI, S.; KOINUMA, H. Growth mode mapping of SrTiO₃ epitaxy. **Applied Physics Letters**, v. 76, n. 17, p. 2439–2441, 2000. Available from: <<https://doi.org/10.1063/1.126369>>. Accessible at: 25 Oct. 2018.
- 64 COHERENT INC. **COMPex the excimer laser** – market leading UV-technology. 2018. Available from: <<https://www.coherent.com/lasers/laser/excimer-lasers-and-applications/compex>>. Accessible at: 02 Nov. 2018.
- 65 GIANNINI, C. et al. X-ray diffraction: a powerful technique for the multiple-length-scale structural analysis of nanomaterials. **Crystals**, v. 6, n. 8, 2016. Available from: <<http://www.mdpi.com/2073-4352/6/8/87>>. Accessible at: 20 Nov. 2018.
- 66 MORI, T. J. A.; MOULS, C. L.; MORGADO, F. F.; SCHIO, P.; CEZAR, J. C. Parasitic phases at the origin of magnetic moment in BiFeO₃ thin films grown by low deposition rate RF sputtering. **Journal of Applied Physics**, v. 122, n. 12, p. 124102, 2017. Available from: <<https://doi.org/10.1063/1.5003764>>. Accessible at: 20 Nov. 2018.
- 67 MALVERN PANALYTICAL. 2018. Available from: <<https://medipix.web.cern.ch/licensees/malvern-panalytical>>. Accessible at: 02 Nov. 2018.
- 68 CASTILLO, J. T. **Spin-dependent transport in oxide multiferroic tunnel junctions**. 2014. 171 p. Ph. D. Thesis (Philosophy) – Facultad de Ciencias Físicas, Universidad Complutense de Madrid, Spain. 2014. Available from: <<http://webs.ucm.es/info/gfmc/files/thesis/TesisJTornos.pdf>>. Accessible at: 23 Oct. 2018.
- 69 YASAKA, M. X-ray thin-film measurement techniques: V. x-ray reflectivity measurement. **The Rigaku Journal**, v. 26, n. 2, 2010. Available from: <<https://pdfs.semanticscholar.org/d0ef/7d336a63e9b02e3d24f6086908f8f55873ed.pdf>>. Accessible at: 15 Nov. 2018.

- 70 BROWER, D. T.; REVAY, R. E.; HUANG, T. C. A study of x-ray reflectivity data analysis methods for thin film thickness determination. **Powder Diffraction**, v. 11, n. 2, p. 114–116, 1996.
- 71 AGGARWAL, D. **Frequency analysis of X-Ray reflectivity data by FFT**. 2016. 49 p. (Masters thesis) — Amity Institute of Applied Sciences, Amity University, Uttar Pradesh, 2016.
- 72 STOEV, K. N.; SAKURAI, K. Review on grazing incidence x-ray spectrometry and reflectometry. **Spectrochimica Acta Part B: atomic spectroscopy**, v. 54, n. 1, p. 41 – 82, 1999. Available from: <<http://www.sciencedirect.com/science/article/pii/S0584854798001608>>. Accessible at: 15 Nov. 2018.
- 73 MALVERN PANALYTICAL TECHNOLOGIES. **X’Pert Powder**. 2017. Available from: <<http://www.panalytical.com/XPert3-Powder.htm>>. Accessible at: 02 Nov. 2018.
- 74 NEVES, B. R. A.; VILELA, J. M. C.; ANDRADE, M. S. Microscopia de varredura por sonda mecânica: uma introdução. **Cerâmica**, v. 44, p. 212 – 219, 1998. Available from: <http://www.scielo.br/scielo.php?pid=S0366-69131998000600002script=sci_abstracttln=pt>. Accessible at: 15 Nov. 2018.
- 75 NANOSURF. **FlexAFM**. 2017. Available from: <<https://www.nanosurf.com/en/products/flex-axiom-afm-for-materials-research>>. Accessible at: 02 Nov. 2018.
- 76 VAN DER HEIDE, P. Introductin. In: _____. **X-ray photoelectron spectroscopy**. Hoboken: John Wiley and Sons, Inc., 2011. cap. 1. p. 1-12. doi: 10.1002/9781118162897.ch1.
- 77 PSP VACUUM TECHNOLOGY. **TX400 X-ray source**. 2017. Available from: <http://www.pspvacuum.com/_x-ray_source.html>. Accessible at: 02 Nov. 2018.
- 78 SPECS SURFACE NANO ANALYSIS GmbH. **Hemispherical energy analyzer series**. 2017. Available from: <http://www.specs.de/cms/front_content.php?idart=122>. Accessible at: 02 Nov. 2018.
- 79 THERMO FISHER SCIENTIFIC. **K-Alpha X-ray photo-electron spectrometer (XPS) system**. 2018. Available from: <<https://www.thermofisher.com/order/catalog/product/IQLAADGAAFFACVMAHV>>. Accessible at: 02 Nov. 2018.
- 80 OLIVEIRA, F. F. M. **Crescimento e caracterização de filmes finos de materiais ferroelétricos**. 2015. 46 p. Trabalho de Conclusão do Curso (Tecnólogo - Sistemas de Telecomunicações) - Faculdade de Tecnologia, Universidade de Campinas, Limeira, 2015. Available from: <<https://sistemas2.ft.unicamp.br/tcc/upload/monografia/9573TGICrescimentoFilmesFinos.pdf>>. Accessible at: 10 Nov. 2018.
- 81 ADVANCED RESEARCH SYSTEMS. **ARS-10HW compressor**. 2017. Available from: <<https://www.arscryo.com/ars-10hw-compressor/>>. Accessible at: 02 Nov. 2018.
- 82 ADVANCED RESEARCH SYSTEMS. **Closed cycle cryocoolers**. 2017. Available from: <<https://www.arscryo.com/closed-cycle-cryocoolers/>>. Accessible at: 02 Nov. 2018.
- 83 MICCOLI, I. et al. The 100th anniversary of the four-point probe technique: the role of probe geometries in isotropic and anisotropic systems. **Journal of Physics: condensed matter**, v. 27, n. 22, p. 223201, 2015.

- 84 FINA, I. et al. Nonferroelectric contributions to the hysteresis cycles in manganitethin films: A comparative study of measurement techniques. **Journal of Applied Physics**, v. 109, n. 7, p. 074105, 2011. doi.org/10.1063/1.3555098>.
- 85 NIRANJAN, M. K.; KARTHIK, T.; ASTHANA, S.; PAN, J. Theoretical and experimental investigation of raman modes, ferroelectric and dielectric properties of relaxor $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3$. **Journal of Applied Physics**, v. 113, n. 12, p. 194106, 2013. Available from: <https://www.researchgate.net/publication/306200399_Theoretical_and_experimental_investigation_of_raman_modes_ferroelectric_and_dielectric_properties_of_relaxor_na12bi12tio3>. Accessible at: 09 Jan. 2018.
- 86 MUYARI, J. et al. Fabrication process of ybco thin film starting from amorphous film for microstrip line device. **Physics Procedia**, v. 27, Suppl. C, p. 280–283, 2012. doi: 10.1016/j.phpro.2012.03.465.
- 87 HOTT, R. **Application fields of high-temperature superconductors**. 2003. Available from: <<http://adsabs.harvard.edu/abs/2003cond.mat..6444H>>. Accessible at: 21 Nov. 2018.
- 88 SELVAMANICKAM, V. **Recent advances in high temperature superconductors and potential applications**. 2014. Available from: <<http://vmsstreamer1.fnal.gov/Lectures/Colloquium/presentations/141008Selvamanickam.pdf>>. Accessible at: 02 Nov. 2018.
- 89 FAGALY, R. L. Superconducting quantum interference device instruments and applications. **Review of Scientific Instruments**, v. 77, n. 10, p. 101101, 2006. doi.org/10.1063/1.2354545.
- 90 TSUKAMOTO, A. et al. Process of fabricating ybco squids for 51-channel hts mcg system. **IEEE Transactions on Applied Superconductivity**, v. 15, n. 2, p. 177–180, June 2005.
- 91 LORENZ, M. et al. High-quality y-ba-cu-o thin films by pld-ready for market applications. **IEEE Transactions on Applied Superconductivity**, v. 11, n. 1, p. 3209–3212, Mar. 2001.
- 92 THE NATIONAL HIGH MAGNETIC FIELD LABORATORY. **New world-record magnet fulfills superconducting promise**. 2017. Available from: <<https://nationalmaglab.org/news-events/news/new-world-record-magnet-fulfills-superconducting-promise>>. Accessible at: 02 Nov. 2018.
- 93 MICHELY THOMAS, K. J. **Islands, mounds and atoms**. Berlin: Springer-Verlag, 2004. (Springer series in surface sciences, v. 42).
- 94 YURTCAN, M. et al. $\text{Yb}_{2}\text{Cu}_{3}\text{O}_{7-x}$ thin film growth on different substrates by pulsed laser deposition. **Eastern Anatolian Journal of Science**, v. 3, n. 2, p. 1–7, 2017.
- 95 CHRISTEN, H. M.; ERES, G. Recent advances in pulsed laser deposition of complex oxides. **Journal of Physics: condensed matter**, v. 20, n. 26, p. 264005, 2008.
- 96 PARK, J. H.; JEONG, Y. S.; LEE, S. Y. Investigation on the relation between the thickness and the orientation of epitaxially grown ybco thin films by laser ablation. **Thin Solid Films**, v. 318, n. 1, p. 243 – 246, 1998.
- 97 GWYDDION - Free SPM data analysis software, 2017. Available from: <http://gwyddion.net/>. Accessible at: 02 Nov. 2018.

- 98 VERO, J. C. D. et al. Post deposition heat treatment effects on ceramic superconducting films produced by infrared nd:yag pulsed laserdeposition. In: CZERWINSKI, F. (Ed.). **Heat treatment**. Rijeka: IntechOpen, 2012. cap. 9. doi.org/10.5772/51291.
- 99 FAVRE, S. **Superconductores de alta temperatura crítica: fabricación y estudio de cerámicas de PrY-123**. 2015. p. Ph. D. Thesis (Philosophy) – Facultad de Ciencias, Universidad de la República, Uruguay. 2015. Available from: <<https://www.colibri.udelar.edu.uy/jspui/handle/123456789/6462?mode=full>>. Accessible at: 09 Jan. 2019.
- 100 CASAXPS: processing software for XPS, AES, SIMS and more, 2016. Available from: <<http://www.casaxps.com/>>. Accessible at: 02 Nov. 2018.
- 101 BONGERS P. F.; SCHLENKER, C.; STRITZKER, B. **High Tc superconductors**. Amsterdam: North-Holland, 1989.
- 102 STREIN, E. **Studying and eliminating adventitious carbon contamination on silicon wafers**. 2008. 45 p. (Bachelor of Science) – Department of Physics and Astronomy, Brigham Young University, Provo, Utah, 2008. Available from: <<http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.705.1855rep=rep1type=pdf>>. Accessible at: 21 Nov. 2018.
- 103 GAUZZI, A. et al. Aes, xps and sims characterization of yba2cu3o7 superconducting high tc thin films. **Vacuum**, v. 41, n. 4, p.870 – 874, 1990.
- 104 MOULDER J. F. et al. **Handbook of X-ray photoelectron spectroscopy**. Minnesota: Perkin-Elmer Corporation , 1995.
- 105 SHCHERBAKOVA, O. et al. Inhomogeneities in yba2cu3o7 thin films with reduced thickness. **Physica C: superconductivity**, v. 479, p. 102 – 105, 2012. doi.org/10.1016/j.physc.2011.12.009.
- 106 LIANG, R. et al. Preparation and characterization of homogeneous YBCO single crystals with doping level near the SC-AFM boundary. **Physica C: superconductivity**, v. 383, n. 1-2, p. 1-7, 2002.
- 107 MILJEVIC, B. **Characterization of growth and real structure of nitride based semiconductor devices by use of synchrotron radiation**. 2012. 176 p. Ph. D. Thesis (Philosophy) – University of Novi Sad, Serbia. 2014. Available from: <https://www.researchgate.net/publication/268448002_Characterization_of_Growth_and_Real_Structure_of_Nitride_Based_Semiconductor_Devices_by_Use_of_Synchrotron_Radiation>. Accessible at: 23 Oct. 2018.
- 108 BAUMBACH, T. **X-ray reflectivity by rough multilayers**. Berlin: Springer, 1999. doi: 10.1007/3-540-48696-8_8.
- 109 X-RAY ORIENTED PROGRAMS (XOP), 2016. Available from: <<http://www.esrf.eu/Instrumentation/software/data-analysis/xop2.4>>. Accessible at: 02 Nov. 2018.
- 110 OWOONG, K. et al. Direct probing of polarization charge at nanoscale level. **Advanced Materials**, v. 30, n. 1, p. 1703675. Available from: <<https://onlinelibrary.wiley.com/doi/abs/10.1002/adma.201703675>>. Accessible at: 21 Nov. 2018.

111 CHIQUITO, J. et al. Back-to-back schottky diodes: the generalization of the diode theory in analysis and extraction of electrical parameters of nanodevices. **Journal of Physics: condensed matter**, v. 24, p. 225303, 2012.

Annex

ANNEX A - PARASITIC PHASES AT THE ORIGIN OF MAGNETIC MOMENT IN BiFeO_3 THIN FILMS GROWN BY LOW DEPOSITION RATE RF SPUTTERING

Parasitic phases at the origin of magnetic moment in BiFeO_3 thin films grown by low deposition rate RF sputtering

Thiago J. A. Mori, Caroline L. Moulis, Felipe F. Morgado, Pedro Schio, and Júlio C. Cezar

Citation: *Journal of Applied Physics* **122**, 124102 (2017);

View online: <https://doi.org/10.1063/1.5003764>

View Table of Contents: <http://aip.scitation.org/toc/jap/122/12>

Published by the *American Institute of Physics*

Articles you may be interested in

[Composition-driven magnetic and structural phase transitions in \$\text{Bi}_{1-x}\text{Pr}_x\text{Fe}_{1-x}\text{Mn}_x\text{O}_3\$ multiferroics](#)
Journal of Applied Physics **122**, 124103 (2017); 10.1063/1.4993152

[Conduction mechanism in epitaxial \$\text{BiFe}_{0.95}\text{Mn}_{0.05}\text{O}_3\$ thin film](#)
Journal of Applied Physics **122**, 124101 (2017); 10.1063/1.5003248

[Enhanced magnetization in morphologically and magnetically distinct \$\text{BiFeO}_3\$ and \$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\$ composites](#)
Journal of Applied Physics **122**, 104101 (2017); 10.1063/1.5001566

[Kinetic pathway of the ferroelectric phase formation in doped \$\text{HfO}_2\$ films](#)
Journal of Applied Physics **122**, 124104 (2017); 10.1063/1.5003918

[The effects of \$\text{PbZn}_{1/3}\text{Nb}_{2/3}\text{O}_3\$ -doping on structural, thermal, optical, dielectric, and ferroelectric properties of \$\text{BaTiO}_3\$ ceramics](#)
Journal of Applied Physics **122**, 124105 (2017); 10.1063/1.5005516

[Polar ordering and structural distortion in electronic domain-wall properties of \$\text{BiFeO}_3\$](#)
Journal of Applied Physics **122**, 075103 (2017); 10.1063/1.4998456

SciLight
 Sharp, quick summaries illuminating
 the latest physics research

Sign up for **FREE!**

AIP
Publishing

Parasitic phases at the origin of magnetic moment in BiFeO₃ thin films grown by low deposition rate RF sputtering

Thiago J. A. Mori,^{1,a)} Caroline L. Mouls,^{1,2} Felipe F. Morgado,^{1,3} Pedro Schio,¹ and Júlio C. Cezar¹

¹Laboratório Nacional de Luz Síncrotron, Centro Nacional de Pesquisa em Energia e Materiais, Campinas, SP 13083-970, Brazil

²Instituto de Física Gleb Wataghin, Universidade Estadual de Campinas, Campinas, SP 13083-859, Brazil

³Instituto de Física de São Carlos, Universidade Estadual de São Paulo, São Carlos, SP 13566-590, Brazil

(Received 16 March 2017; accepted 6 September 2017; published online 22 September 2017)

A series of epitaxial BiFeO₃ thin films has been grown under high partial pressure in a pure O₂ atmosphere, which leads to a low deposition rate. The samples grown under these conditions have presented an evolution of the quality of the epitaxy as the deposition temperature increases, however, spurious β -Bi₂O₃ and supertetragonal BiFeO₃ phases are present in the films grown at higher temperatures. The presence of γ -Fe₂O₃ is reported in one growing condition, and has been attributed to the origin of hysteretic ferromagnetic behavior. A second kind of magnetism, with higher magnetic moment and anhysteretic behaviour, is attributed to the presence of mixed phases of BiFeO₃. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.5003764>]

I. INTRODUCTION

Materials which present simultaneously two or more ferroic orders are called multiferroics.¹ Among these, magnetoelectric materials possess both magnetic (ferro- and/or antiferromagnetism) and ferroelectric ordering.^{2–5} Such a magnetoelectric effect is very interesting from the point of view of fundamental physics, and could also lead to applications in spintronics and other fields.^{6–13} A magnetoelectric device would allow one, for instance, to reverse magnetization by applying an electric field instead of a magnetic field.^{14,15} However, there are very few single-phase magnetoelectric multiferroic materials due to chemical incompatibility between magnetism and ferroelectricity.¹⁶ Besides that, in order to use the magnetoelectric effect in spintronic devices, it is needed to grow thin films of magnetoelectric materials.⁹

Among the magnetoelectric multiferroic materials suitable for applications, bismuth ferrite (BiFeO₃, BFO) has attracted much attention as it is perhaps the only known single-phase perovskite exhibiting coupled antiferromagnetic and ferroelectric ordering with transition temperatures higher than 300 K, which is essential for applications.^{17–20} BFO's crystallization in the perovskite structure makes it compatible with many other functional compounds, and its large ferroelectric polarization (especially in thin films) makes it suitable for electronic devices.²¹ Aiming at possible BFO-based devices, different techniques to synthesize high-quality BFO thin films have been exploited. Much efforts have been directed toward modifying and tuning the material's magnetic and electric properties through crystallinity, strain engineering,^{22,23} ferroelectric and/or magnetic domain boundary control.^{24,25} In this context, there is a need for methods compatible with the mass-production scenario and allowing fabrication of BFO-based systems with precise control over the film's properties, without the presence of spurious phases.

Several thin film deposition techniques have been used during the past decade such as pulsed laser deposition (PLD), chemical vapour deposition (CVD), atomic layer deposition (ALD), and radiofrequency (RF) magnetron sputtering. All of them, with their special features, have allowed epitaxial BFO thin films to be grown on single crystal substrates such as SrTiO₃ (STO), NdScO₃, GdScO₃, DyScO₃, etc. Nevertheless, the growing condition which allows a pure and stoichiometric BFO phase to be obtained is always very narrow, so that very small changes in the deposition parameters can lead to major changes in the film's properties and/or to the nucleation of spurious phases. In this sense, some groups have reported on unexpected magnetic moment in epitaxial thin films. For instance, Marchand *et al.* recently observed enhanced magnetization in ALD-grown BFO films which was attributed to the formation of magnetic domain walls and breaking of the helimagnetic antiferromagnetic order due to the phase confinement within the nanocrystalline morphology.²⁶ On the other hand, PLD-grown BFO films have been reported to present magnetic moment arising from parasitic phases formed mainly by iron oxides.^{27,28}

In this work, we report on the structural and magnetic characterization of a series of epitaxial BFO thin films grown by low deposition rate RF magnetron sputtering. Initially, we present the structural and morphological characterization, performed by X-ray diffraction (XRD) and atomic force microscopy (AFM), which shows evidence of parasitic phase nucleation in some samples. In the sequence, we discuss the presence of anhysteretic or hysteretic magnetic behavior in magnetization measurements carried out by SQUID magnetometry. The origin of the magnetic moment, for each case, is attributed to different parasitic phases.

II. EXPERIMENTAL METHODS

The samples were grown in an AJA Orion sputtering system by sputtering a stoichiometric BiFeO₃ target. A pure

^{a)}Electronic mail: thiago.mori@lnls.br

O₂ flux was kept in the chamber and a plasma was sustained by an impedance matched 100 W (RF) power. The base pressure prior to the deposition was lower than 8×10^{-8} Torr, whilst the deposition pressure was 30 mTorr. It is important to notice the unusual sputtering atmosphere (usually an atmosphere of Ar + O₂ is used for the reactive sputtering of oxides) and deposition pressure (usually a total pressure between 2 and 10 mTorr is used for magnetron sputtering deposition). These unusual conditions lead to a low deposition rate of the order of 1 Å/min, allowing the films to be epitaxially grown on single crystal STO (001) substrates. Samples were deposited at four different temperatures: 400 °C, 500 °C, 600 °C and 700 °C. Their thicknesses (as determined by X-ray reflectivity) are approximately 45 nm. The samples were post-annealed at the same temperature of the deposition, at a pressure of 75 Torr of pure oxygen, before bringing them to room temperature.

The structural characterization was performed by X-ray diffraction techniques. Some measurements were carried out on a Panalytical X'Pert Pro diffractometer with Cu K_α radiation, and others at the XRD2 beamline of the Brazilian Synchrotron Light Laboratory (LNLS) with a monochromatic beam of energy 7.5 keV. Standard Bragg-Brentano ($\theta - 2\theta$) diffractograms were acquired to verify the out-of-plane crystallinity of the films and investigate parasitic phases. Rocking curves at the BFO (001) peak were collected to estimate the crystallite size through the Debye-Scherrer equation. X-ray reflectivity measurements, acquired in small incidence angles, provided information about the thicknesses of the samples. Reciprocal space maps (RSM) around the asymmetric (103) reflections of BFO and STO were measured to study the symmetry and in-plane strain. Atomic force microscopy images, taken on a Park NX10 microscope in the tapping mode, were acquired to study the local topography. The magnetic characterization was carried out on a Quantum Design MPMS[®] 3 VSM-SQUID magnetometer. The magnetization curves presented here have the diamagnetic signal of the substrate subtracted.

III. RESULTS AND DISCUSSION

X-ray diffractograms taken at the XRD2 beamline of the LNLS, with 7.5 keV photons in the Bragg-Brentano geometry ($\theta - 2\theta$), are shown in Fig. 1. The narrow STO (001) and (002) peaks are identified around $2\theta \approx 25^\circ$ and $2\theta \approx 50^\circ$, with the (001) and (002) BFO—in pseudocubic notation—just next to them (lower angle direction). The average crystallite sizes in the [001] direction were estimated from the FWHM of rocking curves collected at the BFO (001) peak position, by using the Debye-Scherrer equation. The values are about half of the nominal thicknesses, for all the samples, indicating that the epitaxial layer does not fill the entire structure. It could be forming a grainy film, or there could be nucleation of other phases instead. In fact, the diffractograms of the samples grown at higher temperatures present evidence of parasitic phases. The sample grown at 600 °C presents peaks around 34° , which can be indexed as related to the (220) and (002) planes of β -Bi₂O₃ (BO), and another one around 54° related to γ -Fe₂O₃ (FO). The peak around

FIG. 1. X-ray diffractograms ($\theta - 2\theta$) for all samples, taken with 7.5 keV monochromatic radiation. The two narrow and very low intensity peaks around 33° and 37° (labelled as * in the figure) are assigned to multiple diffraction peaks of the substrate.

42° , which is present for the samples grown at higher temperatures (600 °C and 700 °C) is due to the formation of a tetragonal phase of BFO with a giant c/a ratio. Such a super-tetragonal phase (ST-BFO), which would lead to a higher ferroelectric polarization,²⁹ is reported to be more stable than the monoclinic phase when BO is present.³⁰ The presence of these BO, FO and ST-BFO parasitic phases is accompanied by topographic features and unusual magnetic behavior that will be discussed further.

Looking at the diffractograms in Fig. 1, one can observe an evolution of the BFO (002) peak. Firstly, it is important to point out that the split of the peak suggests the presence of grains with different crystallographic properties. Starting from the lowest growing temperature, 400 °C, the peak evolves from a distorted and split peak to a single and well-defined peak—accompanied by the ST-BFO peak around 42° —for the samples grown at higher temperatures. The unit cell of the samples grown at lower temperatures is significantly distorted, the c parameters (estimated from the most intense peak) being as high as 4.112 Å and 4.144 Å for samples grown at 400 °C and 500 °C, respectively, whilst the values for samples grown at 600 °C and 700 °C are 4.070 Å and 4.072 Å, respectively.

Figure 2 presents the reciprocal space maps (RSM) near the (103) reflections of the BFO film and the STO substrate. It is worth noting the improvement of the epitaxy of the c -oriented BFO films as the BFO (103) peak (in lower Q_z) becomes narrower and more intense for films grown at higher temperatures, corroborating the analysis of the $\theta - 2\theta$ measurements. Using the vertical line close to $Q_x = 1.61 \text{ Å}^{-1}$ —drawn in all RSM of Fig. 2 as a guide for the eyes, it can be observed that only the sample grown at 700 °C presents a strong compressive strain, with the in-plane cell parameter being 3.893 Å against 3.905 Å of the other samples which all follow the substrate parameter. The strain of this sample is estimated to be around 1.69%, whilst the strain of the others is around 1.38% (considering the BFO bulk in-plane cell

FIG. 2. Reciprocal space maps around the STO/BFO (103) reflections for BFO thin films deposited at 700 °C, 600 °C, 500 °C and 400 °C (from top left to bottom right). The RSM were acquired with $\text{CuK}_{\alpha 1,2}$ radiation. The vertical line close to $Q_x = 1.61 \text{ \AA}^{-1}$ is a guide for the eyes at the Q_z position of the STO substrate peak.

parameter as $3.96 \text{ \AA}$). The strong compressive strain of the sample grown at 700 °C is related to the formation of the super-tetragonal phase, whose peak is stronger and located at a lower angle (stronger tetragonality) for the sample grown at 700 °C than that at 600 °C, and not present for the others.

It is possible to draw the following scenario from the XRD analysis: starting from the sample with the lowest epitaxy quality grown at 400 °C, the BFO quality is improved at 500 °C, but the beginning of the nucleation of a phase with higher tetragonality also takes place, which can be inferred analyzing the splitting and the shoulders on the left side of the (002) peak of this sample. The structural evolution to mixed BFO and ST-BFO phases keeps going on for sample 600 °C, and the epitaxy quality of BFO is much better (with a c/a ratio of 1.041), whilst the ST-BFO peak is clearly identified. Nevertheless, the nucleation of BO (and accompanying FO phases) is strongly favored at this temperature, which may also help with the stabilization of the ST-BFO phase. Furthermore, the sample 600 °C presents a broad peak around the region between ST-BFO and BFO peaks, suggesting that the transition from one phase to the other is not completed for this growing condition. Finally, the sample deposited at the highest temperature, 700 °C, presents an excellent quality BFO phase, with a c/a ratio of 1.047 due to the strong in-plane compressive strain caused by the coexistence of the supertetragonal phase, which is also epitaxial and well nucleated at this growing temperature.

The topography of the thin films is presented in Fig. 3. The samples grown at lower temperatures present smaller grains and low roughness, with the roughness average

FIG. 3. Atomic force microscopy topographic images of samples grown at 700 °C, 600 °C, 500 °C and 400 °C (from top left to bottom right).

evaluated over an area of $2 \times 2 \mu\text{m}^2$ being less than 0.4 nm for samples grown at 400 °C and 500 °C. On the other hand, the samples grown at higher temperatures present some square-shaped features with heights of tens of nm. These features have already been reported and attributed to the nucleation of $\beta\text{-Bi}_2\text{O}_3$ outgrowths.^{27,28,30,31} Indeed, by second harmonic Kelvin probe force microscopy (not shown), it was observed that there is a difference in the conductance between the square-shaped features and the rest of the surface, confirming that the regions are constituted by different phases (BO is much more conducting than BFO). The BO outgrowths are numerous and clearly observed on the surface of the sample grown at 600 °C, as expected due to the remarkable BO peaks that are present in the diffractogram of this sample. Although not presenting BO peaks in the diffractogram, samples grown at 500 °C and 700 °C also seem to present some degree of nucleation of bismuth oxide. This hypothesis is supported by the presence of some small square-shaped features in the topography of the sample grown at 500 °C (Fig. 3), and a few outgrowths observed in the AFM image of the sample grown at 700 °C (Fig. 3). We suggest that the BO phase nucleation is favored around 600 °C. In the case of the sample grown at 700 °C, it may appear during some stage of the growth mechanism to help the ST-BFO phase to nucleate, afterwards it is decomposed (possibly during the post-annealing) due to the volatility of Bi.

The remarkable presence of bismuth oxide on the surface of the sample grown at 600 °C suggests the formation of some iron oxide as well, so it does the peak around 54° in its diffractogram. Magnetization curves of all the samples, taken at room temperature, are shown in Fig. 4. All the samples, but the 600 °C one, present no measurable hysteretic behavior within the limits of the instrument. The small hysteretic behavior observed for other samples is due to the remanence of the magnet and has also been observed in

FIG. 4. Magnetic hysteresis loops measured at room temperature for samples grown at 400 °C, 500 °C, 600 °C and 700 °C.

paramagnetic reference samples. Besides that, zero field cooling (ZFC) and field cooling (FC) magnetization curves were also acquired (not shown here), and no vestige of superparamagnetic behavior was found for any sample. By its turn, the film deposited at 600 °C shows a significant coercive field even at room temperature. Such hysteretic ferromagnetic behavior, in accordance with the X-ray diffraction data, suggests the presence of some ferromagnetic iron oxide (likely γ -Fe₂O₃, a ferromagnetic phase with Curie temperature higher than 850 K). Considering the magnetic moment per formula unit of γ -Fe₂O₃ as $2.5 \mu_B$ and its density as 4.9 g/cm^3 , the volume of the FO parasitic phase necessary to generate the magnetic moment of the sample grown at 600 °C would be around 7% of the thin film volume. However, this volume of FO is surely overestimated, as we consider that all the magnetic moment is generated by this parasitic phase. This is not the case as other origins of magnetic moment may be present, and are not possible to be distinguished. Indeed, there is evidence of anhysteretic contribution to the magnetic moment, clearly observed in the sample grown at 700 °C, which will be discussed further.

The magnetic moment observed for the sample grown at 600 °C, together with the absence of either FO diffraction peaks or a magnetic coercive field in the structural and magnetometry analysis of the sample grown at 700 °C—which also presents a few BO outgrowths on the surface—strengthens the point that the coercivity of the sample grown at 600 °C is due to the presence of the iron oxide phase even though the total saturation magnetization may also be due to other contributions. This observation agrees with some results reported in the literature for BFO films grown by PLD.²⁷ Nevertheless, our low deposition rate films deposited by magnetron sputtering nucleate parasitic phases even for lower thicknesses than the expected according to this reference. This reference also suggests a role of the strain in stabilizing a metastable BFO phase detrimental to the stable BO one; however, the sputtered films reported here present the BO and FO parasitic phases together with strained metastable BFO. Moreover, the nucleation of iron oxide seems to not have any clear dependence on the presence of bismuth oxide.

Another kind of magnetism, being anhysteretic and presenting higher magnetic moment, is attributed to structural changes. This behavior is clearly observed for the sample grown at 700 °C (see Fig. 4), yet is probably present in the other samples as well. Indeed, there are several reports about the changes in the magnetic properties of BFO accompanying structural modifications.^{32,33} Such structural changes can arise, for instance, from doping, size confinements in nanostructures or due to the development of mixed BFO phases that can lead to the distortion of the spin cycloid structure.^{32,34–40} The latter one is clearly the case of the sample grown at 700 °C, according to its diffraction pattern, which evidences the coexistence of two well-defined distinct phases of BFO.

Starting from the lowest temperature, the sample grown at 400 °C—with lower epitaxy quality—presents a very low magnetic moment. Increasing the growing temperature, the sample grown at 500 °C shows a little higher moment, with the BFO phase quality getting improved, and some features in the XRD suggesting the very beginning of the ST-BFO phase nucleation. The structural disorder caused by the nucleating stage of the ST-BFO phase and the remarkable presence of non-magnetic BO make the magnetic moment of the sample grown at 600 °C smaller even though the presence of FO (in a very small quantity) leads to hysteretic ferromagnetic behavior. In turn, when the growing temperature is as high as 700 °C, the stabilization via strain of the ST-BFO phase is responsible for the higher magnetic moment observed in this sample. This result is consistent with data reported by other authors. For instance, in Ref. 34, the authors report on the enhancement of the rhombohedral BFO magnetization as a consequence of a piezomagnetic coupling to the adjacent tetragonal-like phase and epitaxial constraint.

It is worth mentioning that the presence of Fe²⁺ in oxygen deficient BFO films has also been reported to lead to a high magnetic moment in epitaxial thin films free of spurious phases.^{21,41} However, the high oxygen partial pressure in the chamber during the deposition of the samples reported here, as well as the post-annealing carried out at even higher pressures, is expected to preclude the reduction of the film. Nevertheless, the presence of oxygen vacancies is hard to be measured experimentally, and magnetic moment coming from the presence of Fe²⁺ in the BFO structure cannot be totally disregarded even though it is very unlikely.

IV. CONCLUSION

In summary, we have managed to grow epitaxial BFO thin films by RF magnetron sputtering in an unusual environment of high partial pressure and pure O₂. The samples presented an evolution of the quality of epitaxy with the deposition temperature. The spurious β -Bi₂O₃ phase is present in samples deposited at higher temperatures and is shown by square-shaped outgrowths on the surface. This parasitic phase is known to have higher conductance, and could be a problem to the application of BFO thin films in ferroelectric and magnetoelectric devices. The coexistence of the super-tetragonal phase of BFO is also observed in the same samples. The XRD analysis of the sample grown at 600 °C also presents evidence of γ -Fe₂O₃ nucleation. As it is the only sample to present clear hysteretic

ferromagnetic behavior, the origin of the coercive field in this film is attributed to the small nucleation of the iron oxide spurious phase. Nevertheless, the sample grown at 700 °C presents a strong anhysteretic magnetic behavior, with high saturation magnetization and no indication of spurious iron oxide phases; therefore, the origin of its magnetic moment is attributed to the coexistence of two mixed BFO phases. In mixed phase nanostructures, the BFO film nanocrystalline morphology is prominently relevant to their magnetic properties.

ACKNOWLEDGMENTS

This work was supported by FAPESP (Project No. 2012/51198-2). Some of the XRD measurements were performed at the XRD2 beamline of the LNLS/CNPEM under Project Nos. 20150162 and 20160908. The authors thank the LNNano/CNPEM for XRD/XRR, AFM and sputtering facilities, the LIEC/UFSCar for the SQUID measurements, and M. M. Soares for important discussions regarding the structural characterization. P.S. thanks FAPESP for financial support (Project No. 2012/18397-1). J.C.C. acknowledges support from CNPq (Project No. 309354/2015-3).

- ¹H. Schmid, *Ferroelectrics* **162**, 317 (1994).
- ²M. Fiebig, *J. Phys. D: Appl. Phys.* **38**, R123 (2005).
- ³N. A. Spaldin and M. Fiebig, *Science* **309**, 391 (2005).
- ⁴D. I. Khomskii, *J. Magn. Magn. Mater.* **306**, 1 (2006).
- ⁵W. Eerenstein, N. D. Mathur, and J. F. Scott, *Nature* **442**, 759 (2006).
- ⁶S. Fusil, V. Garcia, A. Barthélémy, and M. Bibes, *Annu. Rev. Mater. Res.* **44**, 91 (2014).
- ⁷S.-W. Cheong and M. Mostovoy, *Nat. Mater.* **6**, 13 (2007).
- ⁸S. Dong, J.-M. Liu, S.-W. Cheong, and Z. Ren, *Adv. Phys.* **64**, 519 (2015).
- ⁹R. Ramesh and N. A. Spaldin, *Nat. Mater.* **6**, 21 (2007).
- ¹⁰C. W. Nan, M. I. Bichurin, S. Dong, D. Viehland, and G. Srinivasan, *J. Appl. Phys.* **103**, 031101 (2008).
- ¹¹A. Rodzinski, R. Guduru, P. Liang, A. Hadjikhani, T. Stewart, E. Stimphil, C. Runowicz, R. Cote, N. Altman, R. Datar, and S. Khizroev, *Sci. Rep.* **6**, 20867 (2016).
- ¹²R. K. Kotnala, R. Gupta, and S. Chaudhary, *Appl. Phys. Lett.* **107**, 082908 (2015).
- ¹³R. Gupta, S. Chaudhary, and R. K. Kotnala, *ACS Appl. Mater. Interfaces* **7**, 8472 (2015).
- ¹⁴J. T. Heron, J. L. Bosse, Q. He, Y. Gao, M. Trassin, L. Ye, J. D. Clarkson, C. Wang, J. Liu, S. Salahuddin, D. C. Ralph, D. G. Schlom, J. Iñiguez, B. D. Huey, and R. Ramesh, *Nature* **516**, 370 (2014).
- ¹⁵T. Zhao, A. Scholl, F. Zavaliche, K. Lee, M. Barry, A. Doran, M. P. Cruz, Y. H. Chu, C. Ederer, N. A. Spaldin, R. R. Das, D. M. Kim, S. H. Baek, C. B. Eom, and R. Ramesh, *Nat. Mater.* **5**, 823 (2006).
- ¹⁶N. A. Hill, *J. Phys. Chem. B* **104**, 6694 (2000).
- ¹⁷M. Guennou, M. Viret, and J. Kreisel, *C.R. Phys.* **16**, 182 (2015).
- ¹⁸J. F. Scott, *NPG Asia Mater.* **5**, 72 (2013).
- ¹⁹G. Catalan and J. F. Scott, *Adv. Mater.* **21**, 2463 (2009).
- ²⁰D. Sando, B. Xu, L. Bellaiche, and V. Nagarajan, *Appl. Phys. Rev.* **3**, 011106 (2016).
- ²¹J. Wang, J. B. Neaton, H. Zheng, V. Nagarajan, S. B. Ogale, B. Liu, D. Viehland, V. Vaithyanathan, D. G. Schlom, U. V. Waghmare, N. A. Spaldin, K. M. Rabe, M. Wuttig, and R. Ramesh, *Science* **299**, 1719 (2003).
- ²²A. Agbelele, D. Sando, C. Toulouse, C. Paillard, R. D. Johnson, R. Rüffer, A. F. Popkov, C. Carrétéro, P. Rovillain, J.-M. Le Breton, B. Dkhil, M. Cazayous, Y. Gallais, M.-A. Méasson, A. Sacuto, P. Manuel, A. K. Zvezdin, A. Barthélémy, J. Juraszek, and M. Bibes, *Adv. Mater.* **29**, 1602327 (2017).
- ²³C.-Y. Kuo, Z. Hu, J. C. Yang, S.-C. Liao, Y. L. Huang, R. K. Vasudevan, M. B. Okatan, S. Jesse, S. V. Kalinin, L. Li, H. J. Liu, C.-H. Lai, T. W. Pi, S. Agrestini, K. Chen, P. Ohresser, A. Tanaka, L. H. Tjeng, and Y. H. Chu, *Nat. Commun.* **7**, 12712 (2016).
- ²⁴T. E. Quicke, L. T. Schelhas, R. A. Farrell, N. Petkov, V. H. Le, and S. H. Tolbert, *Nat. Commun.* **6**, 6562 (2015).
- ²⁵G. Catalan, J. Seidel, R. Ramesh, and J. F. Scott, *Rev. Mod. Phys.* **84**, 119 (2012).
- ²⁶B. Marchand, P. Jalkanen, V. Tuboltsev, M. Vehkamäki, M. Puttaswamy, M. Kemell, K. Mizohata, T. Hatanpää, A. Savin, J. Räisänen, M. Ritala, and M. Leskelä, *J. Phys. Chem. C* **120**, 7313 (2016).
- ²⁷H. Béa, M. Bibes, S. Fusil, K. Bouzehouane, E. Jacquet, K. Rode, P. Bencok, and A. Barthélémy, *Phys. Rev. B -Condens. Matter Mater. Phys.* **74**, 020101 (2006).
- ²⁸H. Béa, M. Bibes, A. Barthélémy, K. Bouzehouane, E. Jacquet, A. Khodan, J. P. Contour, S. Fusil, F. Wyczisk, A. Forget, D. Lebeugle, D. Colson, and M. Viret, *Appl. Phys. Lett.* **87**, 072508 (2005).
- ²⁹A. J. Hatt, N. A. Spaldin, and C. Ederer, *Phys. Rev. B -Condens. Matter Mater. Phys.* **81**, 054109 (2010).
- ³⁰H. Liu, P. Yang, K. Yao, K. P. Ong, P. Wu, and J. Wang, *Adv. Funct. Mater.* **22**, 937 (2012).
- ³¹H. Toupet, F. Le Marrec, J. Holc, M. Kosec, P. Vilarhino, and M. G. Karkut, *J. Magn. Magn. Mater.* **321**, 1702 (2009).
- ³²J. Wu, Z. Fan, D. Xiao, J. Zhu, and J. Wang, *Prog. Mater. Sci.* **84**, 335 (2016).
- ³³D. Kim and D. Lim, *J. Korean Phys. Soc.* **62**, 734 (2013).
- ³⁴Q. He, Y.-H. Chu, J. T. Heron, S. Y. Yang, W. I. Liang, C. Y. Kuo, H. J. Lin, P. Yu, C. W. Liang, R. J. Zeches, W. C. Kuo, J. Y. Juang, C. T. Chen, E. Arenholz, A. Scholl, and R. Ramesh, *Nat. Commun.* **2**, 225 (2011).
- ³⁵Y. Wang, J. Li, J. Chen, and Y. Deng, *J. Appl. Phys.* **113**, 103904 (2013).
- ³⁶N. T. Huong, S.-H. Lee, T. Atabaev, M. Kurisu, and N. H. Hong, *Adv. Condensed Matter Phys.* **2015**, 371802 (2015).
- ³⁷Y. Wei, X. Wang, J. Jia, and X. Wang, *Ceram. Int.* **38**, 3499 (2012).
- ³⁸K. Singh, A. Gautam, K. Sen, R. K. Kotnala, M. Kumar, P. Gautam, and M. Singh, *J. Appl. Phys.* **109**, 123911 (2011).
- ³⁹F. Yan, T. J. Zhu, M. O. Lai, and L. Lu, *Scr. Mater.* **63**, 780 (2010).
- ⁴⁰S. Pradhan and B. Roul, *Phys. B: Condens. Matter* **407**, 2527 (2012).
- ⁴¹W. Eerenstein, F. D. Morrison, J. Dho, M. G. Blamire, J. F. Scott, and N. D. Mathur, *Science* **307**, 1203 (2005).