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PhD THESIS ABSTRACT

SUPERCONDUCTING THIN FILMS OBTAINED BY CHEMICAL SOLUTION DEPOSITION

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Abstract of the thesis

The subject of this PhD thesis is part of a research domain of great present interest in Materials Science. This domain contains the elaboration and study of superconducting oxide films with a critical temperature higher that the boiling temperature of liquid nitrogen. These films are suitable for various applications: superconducting cables, levitation trains, medical equipment, SQUID-type magnetometers, electronic domain, etc.

One of the most research superconductor materials is the ceramic oxide $YBa_2Cu_3O_{7-x}$, generally named YBCO. This oxide has a triple perovskite-type structure and it is the first superconductor with a critical temperature higher that the boiling temperature of liquid nitrogen (77K). The YBCO films can be obtained both by physical, and chemical methods.

The chemical solution deposition method (CSD) of superconductive thin films have gain a special interest due to its advantages: molecular level homogeneity for metal ions, very good stoichiometric control, no necessity for vacuum therefore no need for complicated equipment, low costs with respect to the physical deposition methods and the applicability to industrial scale.

One of the most used CSD method is the metal-organic decomposition of trifluoroacetates (TFA – MOD). Using this method superconductive YBCO films with very good superconductive properties (T_C = 92K, $J_C \sim 5 - 6$ MA/cm^2) were obtained. The main disadvantage is the release, during the thermal decomposition of the precursor solution, of a strong, very corrosive and toxic acid – hydrofluoric acid. The release of this acid has major implications on the environment.

This PhD thesis was conceived in the Superconductivity, Spintronic and Surfaces Science Centre within the Technical University of Cluj-Napoca. A part of this thesis was performed during a five months research stage at the Materials Science Institute of Barcelona.

The PhD thesis is structured as follows. Before the first chapter there is a general introduction that underlines the context and the objectives of the thesis. The main objective of this thesis is the synthesis of $YBa_2Cu_3O_{7-x}$ thin films from fluorine-free precursor solutions.

In the first chapter of this thesis is presented an elaborately bibliographic study regarding the state of the art in the high temperature superconductive materials research domain.

The second chapter lay before the reader the experimental techniques implicated in the elaboration of this thesis. Thus, it is described the rheological characterization of the

precursor solutions, the thermal analyses, the mass spectrometry, the infrared spectroscopy, the structural characterizations performed using the X-ray diffraction, the morphological characterization performed using optical microscopy, atomic force microscopy and scanning electron microscopy, and electric and magnetic characterizations performed using SQUID devices.

In the third chapter are presented the results obtained regarding the synthesis of YBCO thin films prepared from fluorine-free precursor solutions and deposited on (001)$SrTiO_3$ and (001)$LaAlO_3$ single crystalline substrates. Two strategies have been chosen that implicates two types of precursor solutions: one precursor solution with reduce content of fluorine and the second type of precursor solution with no fluorine content (fluorine-free precursor solutions). For each strategy chosen aspects of precursor solution preparation, thermal treatment optimization and the structural, morphological, electric and magnetic characterization have been addressed. The key parameters optimization for the synthesis of superconductive YBCO thin films are necessary in order to obtained epitaxial YBCO thin films on oriented single crystalline substrates. Thus, we have succeeded to optimize the morphology and the crystalline orientation degree with the crystallographic *c* axe perpendicular to the substrate plan of the superconductive YBCO thin films. The structural properties have been confronted with the electrical properties which identify the critical temperature of the transition between the normal state of the material and his superconductive state. For the YBCO films deposited from the precursor solution with a reduce content of fluorine the electrical measurements reveal that these films exhibits good superconductive properties showing a critical temperature around 91K. The YBCO films deposited from the fluorine-free precursor solutions exhibit a thickness of 160 nm and 380 nm depending if the solution were treated or not whit trietanolamine (TEA). The magnetic characterization of this films show a transition critical temperature of 90.4K and 91.3K for the films deposited from the fluorine-free precursor solution without TEA and for the films deposited from the precursor solution treated with TEA, respectively. The corresponding critical current densities are 1.6 MA/cm^2 and 2.60 MA/cm^2.

The fourth chapter presents the results regarding the synthesis of superconductive YBCO thin films deposited on (001)STO single crystalline substrates from aqueous precursor solution. In order to optimize the parameters for the thermal decomposition and elucidate the thermal decomposition mechanisms of the individual precursors and of the precursor solution we have performed thermal analyses, mass spectrometry, IR spectroscopy and X-ray diffraction on the precursors powders. Taking in account the results obtained for the precursors powders we have deposited precursor films which were thermally treated at different temperatures. Furthermore the films were structurally, morphologically and electrically characterized. The thicknesses of the final films are controlled by molar concentration of the precursor solution. The correlated analyses that the films deposited from more diluted precursor solution are thinner that the films deposited from more concentrated precursor solutions. The thinner films don't present good superconductive properties, having a critical temperature lower than 80K. On the other hand, the thicker films exhibits a transition to the superconductive state at a critical temperature around 88.7K.

After all four chapters a special section is presented containing the general conclusions and the original contributions. Thus, we have proved the possibility of obtaining superconductive YBCO films starting from precursor solution with a reduce content of fluorine, fluorine-free precursor solutions and aqueous precursor solutions. The YBCO films were structurally, morphologically, electrically and magnetically characterized. The key parameters of the synthesis process were optimized correlating the thermal analyses, mass spectrometry, IR spectroscopy and X-ray diffraction.

We underline the original contributions as follows: the use of a new preparation method for the fluorine-free and aqueous precursor solutions; the elucidation of the thermal decomposition mechanism for each individual precursor and for the precursor powder; we have obtained single crystals by concentrating the yttrium precursor solution, accepted and indexed in the Crystallographic Cambridge Data Base as a new compound; optimization of the single-step thermal treatment for the films deposited from precursor solutions with a reduce content of fluorine, and the parameters optimization of the thermal treatment for the films obtained from fluorine-free and aqueous precursor solutions.