Chemical Solution Deposition of Functional Oxide Thin Films

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Editors

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Preface

Chemical solution deposition (CSD) has emerged as a mature technique for the fabrication of functional oxide thin films due to a number of advantages. While the development of sol–gel type CSD processes for optical coatings of glass dates from the mid-twentieth century, the first chemical solution-deposited complex electronic oxide thin films were prepared only as recently as the 1980s. Since the initial studies, a wide variety of perovskite-related and other compounds on various types of substrates have been prepared as thin films with CSD techniques. Substantial progress in the understanding of the processes has been made which enables the fabrication of device quality films by CSD methods nowadays. Various symposia of the Materials Research Society on solution-based materials fabrication, workshops, and conferences have been held and a number of more or less comprehensive review articles and book chapters have been published on this topic. The whole diversification, however, is barely represented in the above-mentioned reviews and a comprehensive textbook on the CSD technology has not been available up to now.

The aim of the book is to comprise the experience of the last 25 years on CSD of mainly electroceramic thin films, with some extensions, as well as CSD-related application areas into a text and reference book. The content is written on a level that should be comprehensible for Material Science students in their third year. So, all the basic chemistry and physics knowledge for typical Material Science curricula should be present.

With the unexpected death of Prof. Fred Lange, author of Chap. 16, and Prof. Marija Kosec, coeditor and coauthor of several book chapters, during the work on this monograph, the community unfortunately lost two outstanding researcher personalities. While Lange was a pioneer in growing epitaxial films by CSD methods, Kosec's CSD-related work was dedicated to the understanding of complicated reactions during solution synthesis and how to control these reactions with regard to ferroelectric thin film preparation. She was always enthusiastically promoting the field of CSD processing in the materials science community. In this sense she was also an avid supporter of the European Union's program for Cooperation in Science and Technology (COST).

The editors would like to thank their 54 authors for their excellent contributions, for a wonderful communication over many years, for their willingness to adopt our ideas for modifications, and for their perseverance. Moreover the editors would like to thank Dagmar Leisten and Thomas Pössinger from IWE II, RWTH Aachen University, for their huge effort and expertly drawing, retracing, optimizing, and generation of most of the artwork of this book. They did an excellent job in creating printable figures from nonoptimal submissions and did their best to get the figures to a more uniform style. One of the editors, (TS), would also like to thank his wife and his children for their patience and understanding during the work on this book project.

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General Introduction

Chemical solution based preparation of inorganic solid state materials by sol–gel processing dates back to the mid of the nineteenth century, where Ebelmen discovered that silicon alkoxides react slowly with humidity (hydrolysis) to yield hydrated silica (gel) [1–3]. Almost 100 years later, first works to use sol–gel processes for modification of optical glasses was focused on SiO_2 layers [4] followed by further single oxide coatings, such as TiO_2, ZrO_2, Al_2O_3 etc., as well as multilayer coatings [5–7]. Since the 1950s optical coatings on large planes of glass have been produced in this way on an industrial scale [8, 9].

In the 1970s, optically transparent electrically conducting films were developed by the Philips research laboratory Aachen for heat-reflecting filters [10, 11]. In the 1980s, the pioneering works of Fukushima and coworkers [12] on metallo-organic decomposition (MOD) and of the Payne's group [13, 14] on sol–gel processing of lead zirconate titanate (PZT) thin films have been the first steps into ternary and quaternary perovskites, demonstrating that complex electronic oxide thin films can be fabricated by chemical solution deposition (CSD) reaching desired properties similar to the corresponding bulk materials. Together with the excellent works of Klee [15–18], Sayer [19, 20], Kosec [21–24], Sporn [25], Milne [26, 27], Schwartz [28, 29], and others on wet chemical synthesis of materials [30], these studies gave the impetus for a rapid international growth of this field with investigations in the world on functional oxide thin film devices. This is reflected in a number of review articles and single book chapters [31–47]. The main drivers for the research progress were ferroelectric thin film materials for applications in different kinds of memory devices, in particular ferroelectric nonvolatile memories—FERAM, as well as piezoelectric sensors and actuators, pyroelectric detectors of infrared radiation, and integrated high-permittivity (high-k) capacitors. Thus most of the reviews focus on these materials. Meanwhile the CSD method was also successfully applied in other fields of functional oxides such as conducting thin films, i.e., electron conducting, ion conducting, and superconducting films, for applications in displays, solid oxide fuels cells, and coated conductors.

The present book summarizes the developments of the last 25–30 years in the field of CSD. It covers all relevant aspects starting from the precursor chemistry via the processing aspects up to examples for applications. A generalized flow chart of the CSD procedure, the main body of which is subdivided into parts according to the different processing steps, is shown in Fig. 1.

These "*Parts*" plus "*Analytical Methods*" represent the organization scheme of the book which will be shortly summarized below.

Film fabrication by CSD typically begins with the solution synthesis in the chemistry lab (Part I). The main precursors are salts, carboxylates, or other metallo-organic compounds such as metal alkoxides and metal β-diketonates, which can often be purchased commercially or synthesized in-house by common chemical synthesis strategies.

By simple dissolution or refluxing them at elevated temperatures in appropriate solvents, sometimes with intermediate distillation steps, and mixing in the correct stoichiometric ratio, precursor solutions are obtained, which usually contain the desired thin film stoichiometry. Often additives such as chemical stabilizers are included during synthesis to adjust the properties of the final coating solution. Under certain circumstances compositional corrections with respect to the exact metal oxide stoichiometry are required. These comprise:

- Losses due to the volatility of a component (e.g., PbO)
- Losses due to component diffusion into the substrate (e.g., Bi loss from strontium bismuth tantalate—SBT)
- Intentional off-stoichiometry for desired generation of secondary phases or native point defects

Next, the coating solution is deposited by a number of methods (Part III). Spin- and dip coating in various modifications are the by far most frequently applied techniques. Aerosol deposition (often denoted as spray coating) and, more recently, ink-jet printing are more sophisticated methods allowing for a more conformal coating or structured coating with reduced material consumption. Subsequently, the (wet) as-deposited film is dried, pyrolyzed,[1] crystallized, and (optionally) post-annealed for further densification or microstructure manipulation (Part IV). Often, individual processing steps such as gel formation and organic removal cannot be separated as implied in Fig. 1. The conversion of the wet, as-deposited film into the desired crystalline film is induced through controlled thermal processes in the temperature range from ~200 to 800 °C, which have to be adjusted to the character

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[1] The term "pyrolysis" is normally defined as the conversion of solid organic materials into gases and liquids by indirect heat under exclusion of air, or oxygen, respectively. The material within the reaction chamber is heated to temperatures between 400 and 800 °C. The pyrolysis process is sometimes referred to as thermolysis. This is merely a preference in the choice of terminology. Although the process reaction volatizes and decomposes solid organic materials by "heat," the Greek translation of "pyro" is "fire," whereas "thermo" is more correctly, "heat." Thus—thermolysis. Hence in case of the CSD technology, the term pyrolysis is predominantly used to describe the decomposition of the organic matrix in air or oxygen [34].

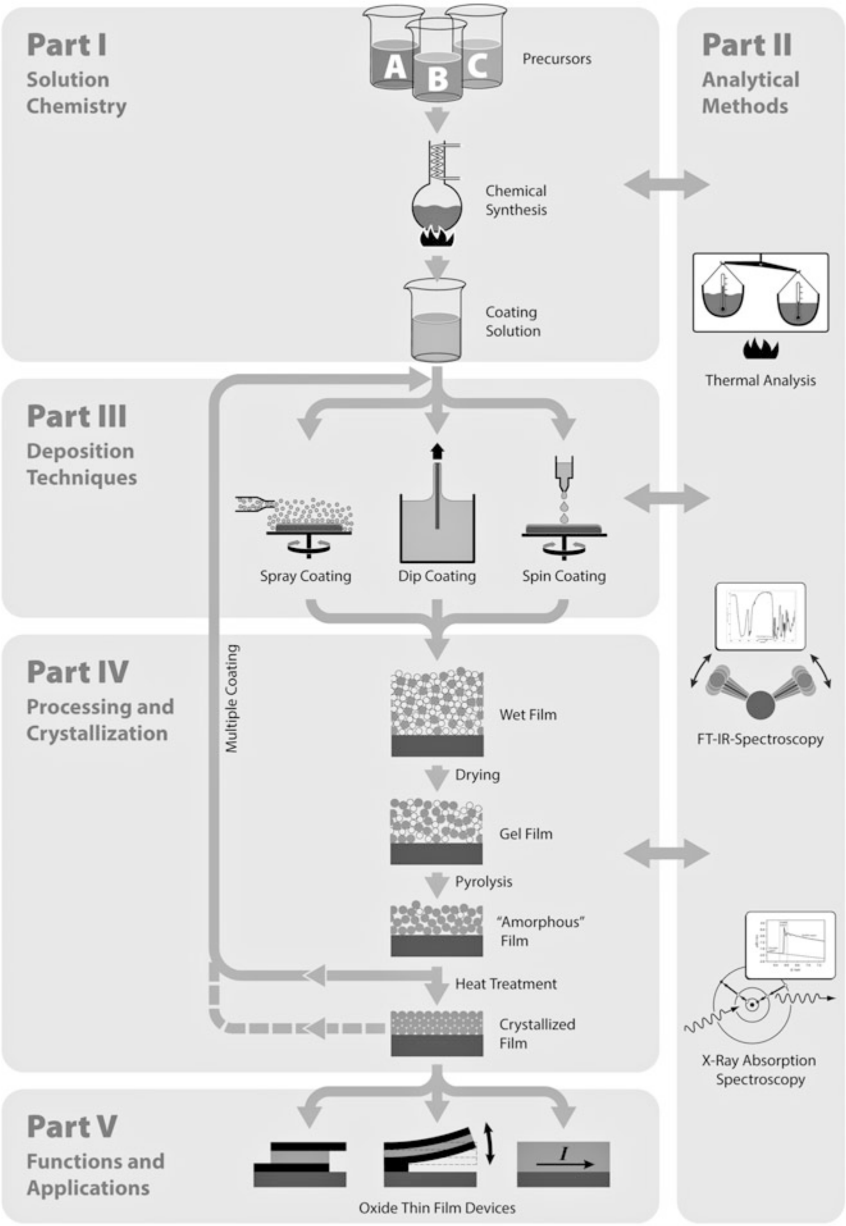

Fig. 1 Flow chart of a typical CSD process. It shows schematically the different processing steps starting with solution synthesis, followed by deposition and crystallization, and ending with functional oxide thin film devices. Frequently applied analytical methods are shown on the *right*

of the nucleation and growth behavior of the material under study. Typically hot plates in combination with a conventional furnace or a rapid thermal annealing (RTA) oven are employed for this transformation process. In specific cases, such as temperature-sensitive substrates, the use of lasers for the annealing may be indicated [48]. Depending on the specific CSD route and film deposition method, numerous variations in thermal processing conditions are utilized. For example, if the desired film thickness is not obtained in the first coating cycle, the deposition and thermal process sequence are repeated to prepare thicker films. When the desired film thickness is obtained, a final thermal treatment at a still higher temperature may be employed to initiate crystallization, to improve microstructure, or to increase film density.

As indicated by the double arrows in Fig. 1, the process can be monitored at various stages by a number of analytical methods (Part II). X-ray diffraction (XRD) and electron microscopy (scanning—SEM[2] and transmission—TEM), well established and often available in material science labs, are the standard methods to characterize phase and morphology of pyrolyzed and crystallized films. To study the solution chemistry and phase evolution, thermal analysis and Fourier transform infrared spectroscopy (FTIR) are the most frequently applied methods. Moreover X-ray absorption spectroscopy, although more sophisticated, is often employed since it yields structural information from the precursors independent of the physical state, i.e., also from solutions and amorphous solids.

Finally oxide thin film devices, such as capacitors, piezoelectric actuators, or conductors for various fields of applications can be fabricated from the crystallized films (Part V).

In order to implement the CSD method for a thin film material system, a number of general prerequisites for the precursor solutions, the substrates, and processing itself have to be fulfilled in order to yield the desired results:

(a) Sufficient solubility of all educts in the solvent, i.e., formation of a stable 1-pot coating solution
(b) Acceptable long-term stability of the precursor solution—reasonable minimum times are about 1 month
(c) Selection of precursor systems that leaves solely the cations and oxygen present upon pyrolysis and crystallization
(d) Adjusted solution rheology, i.e., modification of the solutions depending on the applied coating technique to avoid failures such as striations in spin coating, or sticking, and uncontrolled purging, respectively, of the precursor ink in the nozzles of an inkjet printer
(e) Adequate wettability of the substrate.
(f) Homogeneity, ideally at an “*atomic*” level, should be retained during the whole process, i.e., macroscopic phase separation of precursor components in the solution, during drying or pyrolysis must not occur

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[2] Sometimes the term FESEM is used instead of SEM to indicate that the microscope works with a field emission cathode.

(g) Crack and compositional nonuniformity formation during thermal processing have to be avoided
(h) Marginal interdiffusion of film and substrate constituents
(i) Minimal degradation of substrate properties during film processing.

If these requirements are fulfilled and if processing conditions are optimized, the CSD technique represents a rapid and cost-effective method of synthesizing high quality functional oxide thin films.

Organization of the Book

According to Fig. 1 the book is subdivided into the following five parts, which are further subdivided into individual chapters:

- Part I—Solution Chemistry
- Part II—Analytical Methods
- Part III—Deposition Techniques
- Part IV—Processing and Crystallization
- Part V—Functions and Applications

Each "*Part*" starts with a short survey on the corresponding content. A complementary "*Appendix*" chapter containing practical recipes for CSD processing concludes the book.

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