Development and application of a green-chemistry solution deposition technique for buffer layer coating on cube-textured metal substrates in view of further deposition of rare-earth based superconductors

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Development and application of a green-chemistry solution deposition technique for buffer layer coating on cube-textured metal substrates in view of further deposition of rare-earth based superconductors

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Preface

This thesis is submitted in partial fulfilment of the requirements for obtaining the Ph.D. degree at the Technical University of Denmark.

The work described in the thesis was conducted at the Materials Research Division, Risø National Laboratory for Sustainable Energy, from 2010~2011, and at the Department of Energy Conversion and Storage, Risø Campus from 2011~2013, under the supervision of Dr. Jean-Claude Grivel.

The thesis describes the development of new green-chemistry solution deposition techniques for SrTiO$_3$ buffer-layer coatings on metal substrates in view of further deposition of YBCO superconductors.

I hereby declare that this thesis represents my own research work, apart from the sources quoted. The material of this thesis has not been previously included in a thesis, dissertation or report submitted to any other institution.

The financial support from the Danish Agency for Science, Technology and Innovation (Project No. 09-065234) is sincerely acknowledged.

Roskilde, October 2013

P. G. Asanka Pramod Pallewatta
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Bibliography
Academic Dissertation

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List of Publications / Conferences

Publications

1. Pallewatta P.G.A.P., Zhao Y., Grivel J.C. “Development of Strontium Titanate Thin films on Technical Substrates for Superconducting Coated Conductors”—Proceedings of ICEC 24-ICMC 2012, edited by K. Funaki, A. Nishimura, Y. Kamioka, T. Haruyama and H. Kumakura © Copyright by Cryogenics and Superconductivity Society of Japan 978-83-7493-589-0, 2012

2. Asanka Pramod Pallewatta, Yue Zhao, Tian Hui, Jean-Claude Grivel “Strontium Titanate Buffer Layers on Cu-33%Ni Substrates using a Novel Solution Chemistry”—The 8th Pacific Rim International Congress on Advanced Materials and Processing, Edited by: Fernand Marquis, TMS (The Minerals, Metals & Materials Society), 2013

Co-authored publications

1. Y. Zhao, J.C. Grivel, A.B. Abrahamsen, P.G.A.P. Pallewatta, D. He, J. Bednarčík, M.v. Zimmermann, “In-situ synchrotron x-ray study of the crystallization behavior of Ce$_{0.9}$La$_{0.1}$O$_{2-x}$ thin films deposited on NiW alloy substrates by chemical solution method”, Materials Letters 65 (2011) 2669~2672


3. J.-C. Grivel, Y. Zhao, A.C. Wulff, P.G.A.P. Pallewatta, J. Bednarčík, M.v. Zimmermann, In situ X-ray diffraction study of the formation of Fe(Se,Te) from various precursors, Physics Procedia 36 (2012) 600~605


Conferences


2. The 8th Pacific Rim International Congress on Advanced Materials and Processing, Waikoloa, Hawaii, USA. (2013)
List of abbreviations

AC       Alternative Current
a.u.     Arbitrary Units
AFM     Atomic Force Microscopy
BSCCO  \((\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}\)
BSE     Backscattered Electrons
DSC     Differential Scanning Calorimetry
DTA     Differential Thermal Analysis
EBSD   Electron Back Scatter Diffraction
FEG     Field Emission Gun
HTSC    High Temperature Super Conductor
PLD     Pulsed Laser Deposition
RABiTS Rolling Assisted Biaxially Textured Substrates
Ref.    Reference
RTA     Rapid Thermal Annealing
SE      Secondary Electrons
SEM     Scanning Electron Microscopy
SIMS    Secondary Ion Mass Spectroscopy
STO     \(\text{SrTiO}_3\)
SXPD    Synchrotron X Ray Powder Diffraction
TFA     Trifluoroacetic acid
TG      Thermogravimetry
TOF     Time Of Flight
XRD     X Ray Diffraction
YBCO   \(\text{YBa}_2\text{Cu}_3\text{O}_{7-5}\)
YSZ  Yttria-Stabilized Zirconia
1M2P    1-Methoxy-2-propanol
Overview

Chapter–1 (Background) is a comprehensive introduction for this research work, emphasizing the potential importance of the SrTiO₃ buffer layer applications in the field of superconductor engineering.

Chapter–2 (Motivation) gives a clear introduction about the importance of our challenging work on developing novel solution synthesis for SrTiO₃ mono-layers on Cu/Ni substrates.

Chapter–3 (Experimental) gives a detailed introduction about all the scientific methodology that has been exploited for SrTiO₃ thin film fabrication throughout this work.

Chapter–4 (Characterization Procedures) gives a detailed introduction on all the techniques that have been utilized for characterization in this work.

The following 3 chapters are focusing on the results from 3 phases of our scientific work. Each chapter includes a detailed discussion of the experimental results.

Chapter–5 (SrTiO₃ by novel solution synthesis) includes our development of a novel solution synthesis for SrTiO₃, and also describing the chemical aspects of the solution synthesis.

Chapter–6 (SrTiO₃ films with substrate dependency) focused on the distinct nature of the SrTiO₃ films fabricated on 7 different technical substrates, using the novel solution synthesis described in the previous chapter.

Chapter–7 (Further optimizations of SrTiO₃ buffer thin film fabrication) presents our work on optimizing SrTiO₃ mono-layers on Cu-33at.%Ni substrates as a promising buffer layer. This includes a comprehensive characterization of our optimized SrTiO₃ mono-layers.

Chapter–8 (Summary) presents a concise summary of our whole work.

Chapter–9 (Conclusions and Outlook) presents a concise summary of the main conclusions in our work, and some thoughts for future work.
Abstract — English

Development and application of a green-chemistry solution deposition technique for buffer layer coating on cube-textured metal substrates in view of further deposition of rare-earth based superconductors

Superconductor based energy production has been thoroughly researched by many scientists all over the world, due to the advantage of zero electric resistance that will contribute to the energy saving capabilities. Recently successful developments have been reported in coated conductor architectures which consist of YBCO superconducting coatings on cube-textured Ni based alloy tapes. Before the epitaxial deposition this superconducting layer, a buffer layer is applied on the metal substrate as a diffusion barrier which is also required to transfer the strong texture of the underlying substrate, allowing the epitaxial growth of the superconducting layer. State-of-the-art coated conductor hetero structures are mainly based on CeO₂ based buffer stacks that consist of a sequence of several different buffer layers. Buffer layers deposited by continuous chemical deposition techniques, which are the most suitable for large scale production, use to suffer from porosity and cracks that lead to material diffusion from the metal substrate into the superconductor as well as oxidation of the metal during high-temperature processing of the buffer layer.

SrTiO₃ buffer layers have attracted interest due to its low lattice mismatch with YBCO and the possibility of using this material as a single-layer buffer. Nevertheless, generally SrTiO₃ buffer layers for YBCO are still applied as SrTiO₃ multilayers. In addition, the main chemical based fabrication routes of SrTiO₃ buffer layers involve toxic and hazardous chemicals such as 2-methoxylethanol, and trifluoroacetic acid (TFA).

Therefore, in our research the main focus was on the development of SrTiO₃ single buffer layers based on environmentally safe chemicals, to reach the engineering requirements for continuous coating of long substrate tapes. A new precursor solution for SrTiO₃ buffer layers has been successfully developed with the reagents of strontium acetate, acetic acid, titanium isopropoxide, 1-methoxy-2-propanol and 2,4-pentanedione. Using this precursor with dip-coating, high cube-textured SrTiO₃ mono-coatings on Cu-33at.%Ni tapes were reproducibly
obtained using single step annealings at 950°C in N₂-5%H₂ ambient flow. These layers were found to have a pore-free, crack-free and smooth morphology with an excellent biaxially textured surface. The simple annealing process combined with a relatively high film thickness per single coating is expected to be very advantageous in reel-to-reel applications. The thickness of these SrTiO₃ monolayers was large enough to stop the nickel and copper diffusion from the Cu/Ni substrate. Hence, the developed high quality buffer layers are expected to be acting as efficient diffusion barriers and also as a texture template for the subsequent growth of biaxially textured YBCO nanostructure.
Abstract — Danish

Udvikling af miljøvenlig metode der kan anvendes til fremstilling af tynde beskyttelseslag (bufferlag) på begge sider af tekstrurerede metal substrater, med henblik på efterfølgende deponering af sjældne jordarts-baserede superledere


Derfor var det primære fokus i vores forskning at udvikle SrTiO₃ enkelt-bufferlag baseret på miljøvenlige, ufarlige kemikalier for at opnå de ingeniørmæssige krav til kontinuer deponering på lange substratfilm. En ny reaktantopløsning til SrTiO₃ bufferlag er succesfuldt blevet udviklet med indhold af strontiumacetat + eddikesyre + titanium isopropanol + 1-methoxy-2-propanol + 2,4-pentanedione. Ved at bruge denne reaktantopløsning til dyppe-belægning, blev reproducerbare mono-belægninger af høj-struktureret SrTiO₃ på Cu-33at.%Ni film opnået. Der
立方体方位を示す結晶面を有する金属基板上で精製される希土類系超伝導体への応用として、緩衝層の成膜のための環境に優しい化学的固溶体溶着法の開発

超伝導体は、電気抵抗値がゼロになることから、主に発電機への応用が注目されている。従来の銅製のコイルを超伝導性のコイルに置き換えることによって、発電効率を大きく向上することができる。サステナブルエネルギーのために重要で、超伝導体の応用が非常に期待されている。発電機内のコイルのために実用的に応用するためには、数百メートルを超える長さを有し、低コストでパフォーマンスの優れた超伝導体の効率的な精製が要求される。近年優れた結晶方位性を示すニッケル系合金基板上の Y-Ba-Cu-O 系超伝導酸化物（YBCO）に関する有意義な研究が次々と報告されている。優れたエピタキシャル成長を得るには、これらの超伝導膜の被覆の前に、基板から超伝導層への金属の拡散を防ぎ、二軸組織化された金属基板の結晶面関係も引継がれる緩衝層の導入が必要となる。

高温超伝導性薄膜ストリップ導体は主に酸化セリウムの緩衝層を含む複数層の緩衝層からなる導体である。ここから、大量生産向けに望ましい化学溶液法で報告されている緩衝層の大半はひびが入った有孔性の緩衝層になっており、基板からの金属の拡散や、緩衝層の成長に使われる高温加熱過程で酸化してしまうなどの問題がある。

一方、結晶定数の類似性からチタン酸ストロンチウム (SrTiO₃) 系緩衝層が注目されている。しかしながら、従来の SrTiO₃系緩衝層の大半は複数層型の緩衝層であり、使用される溶液にも 2-メトキシエタノールやトリフルオロ酢酸などと非常に有毒で有害な溶剤が使用される。

高温超伝導性薄膜ストリップ導体に関するそれらの問題点を解決する目的で、本研究の重点は、大量生産向けの浸漬被覆装置へ応用可能で、環境への負担が少ない化学溶液からなる単層型緩衝層の開発に置かれた。ここで本研究は、酢酸、酢酸ストロンチウム、チタン酸テトロイソプロピル、及び 1-メトキシ-2-プロパノール、及び 2-メトキシ-2-プロパノール、及び 2,4-ペンタンジオンの化学合成を開発することに成功した。開発された溶液溶液を基に、33%ニッケル含む銅ニッケル合金配向基板上、YBCO に望ましい立方体配向性を有する SrTiO₃薄膜が成長した。5%水素含む窒素水素の混合ガス雑気中 950℃で結晶化を図り、良好な結晶配向性ならびに、ひびが含まれない非孔性のある表面が得られた。この方法は再現性の観点からも、実用的に優れた緩衝層として期待できる。単純な加熱過程の下に得られたこれらの単層型緩衝層は膜圧が 200nm を超える上で、基板からの金属拡散を防ぐことが可能であることが、飛行時間型二次イオン質量分析法による実験により確認できた。これからのことから、本研究で開発された
緩衝層は、引き継ぎ被覆される YBCO 超伝導性薄膜の、有効な保護層としても、基板からの結晶方位を引継ぐ緩衝層としても、優れた応用性があることが考えられる。
Abstract — Sinhalese

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SrTiO₃ යම ගේ වශයෙන්, මෙන් විද්‍යාජාත්මක හා මෙහෙයින්ට අක්ෂයක් අතර, SrTiO₃ අනතුරුව විශේෂ ක්‍රමතාවක් අතීතයේ සිදු හැක. 20 කාලයේ SrTiO₃ මෙහෙයින්ට ග්‍රාමික විද්‍යා අධිරාජ නිළිය පැතිර විනාශයේ අදහස්සක් විශේෂ අධිරාජ නිළිය ආශ්‍රයේ, 2- ක්‍රමතාවක් සහිතයේ මෙහෙයින්ට 2015වේ දෙසැම්බර් අතීතයේ 33% දැක්වුණු සැමාර්ග. 2015වේ දෙසැම්බර් ආසන්න ගතියමකි. මෙහෙයින්ට 5% දැක්වුණු දැක්වුණු ආසන්න පිටත අදහස්ෂන්ට 950°C නමුත් මෙහෙයින්ට දැක්වුණු දැක්වුණු දැක්වුණු 200nm දැක්වුණු දැක්වුණු දැක්වුණු SrTiO₃ ආසන්න දැක්වුණු දැක්වුණු දැක්වුණු පිටත ආසන්න දැක්වුණු දැක්වුණු 200nm දැක්වුණු දැක්වුණු දැක්වුණු SrTiO₃ ආසන්න දැක්වුණු දැක්වුණු දැක්වුණු දැක්වුණු දැක්වුණු SrTiO₃ ආසන්න දැක්වුණු දැක්වුණු දැක්වුණු දැක්වුණු SrTiO₃ ආසන්න දැක්වුණු දැක්වුණු දැක්වුණු 200nm දැක්වුණු දැක්වුණු දැක්වුණු දැක්වුණු SrTiO₃ ආසන්න දැක්වුණු දැක්වුණු දැක්වුණු දැක්වුණු SrTiO₃ ආසන්න දැක්වුණු දැක්වුණු දැක්වුණු දැක්වුණු SrTiO₃ ආසන්න දැක්වුණු දැක්වුණු දැක්වුණු.
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Chapter — 1
Background

The need of green electricity has been emphasized during the last few decades, mainly curbing the demand for nuclear energy and fossil fuels. In this trend, an unprecedented interest in renewable energy, particularly solar and wind energy, which provide electricity without giving rise to any carbon footprints. The United Nations recently launched its ‘Sustainable Energy for All’ initiative, which calls for a global target of doubling the share of renewable energy by 2030 [001]. Most significant shifts in renewables policy occurred in Japan (after the Fukushima nuclear disaster in 2011), where support has been sharply increased to promote additional renewables capacity and generation to compensate for lower nuclear power output. At the same time, exponentially growing energy consumption has been a typical aspect of this technologically advancing dynamic world, as clearly seen over the last centuries. In order to cater these increasing energy demands, present sustainable energy sources such as wind power, require up-scaling in the means of core technologies.

![Offshore wind farm “Supergrid” in the North Sea](image)

With the discovery of High-Temperature Superconductors (HTS) in 1986, a great deal of efforts has gone into HTS materials development, initiating to use for rotating machines. The greatest efforts in rotating machines has been in the area of ship propulsion motors mainly supported
Chapter 1 — Background

by US Navy, where HTS technology can be 2.5~5 times lighter and more compact than the conventional technology. Another significant development is the recognition that compact, lightweight HTS generators can enable 10 MW-class generators for offshore wind turbines. Programs towards this goal have been launched by Converteam (UK), AMSC (American Superconductor) in collaboration with TECO-Westinghouse (Canada), and by the DTU (Technical University of Denmark) in collaboration with Risø National Laboratory (Denmark). [002]

Fig. 1–2: A superconducting coil unit used for wind power turbines

HTS technology is expected to enable generators with one third the weight and one half the losses of conventional machines. These technologies would enable a significant reduction in the size and weight of 10 MW-class generators for direct-drive wind turbine systems and reduce the cost of clean energy relative to conventional copper and permanent-magnet-based generators and gearboxes. [003,004] With compact and light-weight 10 MW-class HTS generators, installation and low maintenance operation of high power wind turbine systems becomes practical and enable cost-effective access to wind resources.

---

1 Racetrack coil based on a winding of 5 mm wide high temperature superconducting tape. Electrical contact is provided by copper block at the two ends of the winding and thin copper wires are soldered onto the tape, whereby 4 point voltage measurements can be performed on selected sections of the tape. The inner and outer frame is made of 316 stainless steel and provides mechanical support for the coil. A circuit board is mounted on the left hand side of the steel frame for connection of voltage probe wires. The square hole of 150 mm × 60 mm in the middle can be fitted around an iron core of a test machine under construction at DTU. [004]
1.1 – Introduction to Superconductors

In general, the electrical resistivity of a metallic conductor decreases gradually as temperature is lowered. In ordinary conductors, such as copper or silver, this decrease is limited by impurities and other defects. Even near absolute zero, a real sample of a normal conductor shows some resistance. In a superconductor, the resistance drops abruptly to zero when the material is cooled below its critical temperature. Superconductors have virtually no resistance to electric current, offering the possibility of new electric power equipment with improved energy efficiency compared to today's devices. Superconductivity is a phenomenon that occurs below a critical transition temperature \( T_c \) below which the material is superconducting and above which it is normal or non-superconducting. In the superconducting state, the material has no electrical resistance, where the electricity is conducted without any losses.

Superconductivity was first discovered in Mercury below 4.2K in the year 1911 by a Dutch physicist, Heike Kamerlingh Onnes. [005] For a material to be considered as a superconductor, it has to exhibit two distinctive properties:

1.1.1 – Zero resistivity \( (r=0 \text{ for } T<T_c) \)

When a superconductor is cooled below \( T_c \), the cloud of individual electrons that characterizes the normal state transforms itself into a quantum fluid of highly correlated pairs of electrons. Below \( T_c \) a conduction electron of a given momentum and spin gets weakly coupled with electron of exactly the opposite momentum and spin. These pairs are called Cooper Pairs and they all move in a single coherent motion. Once this collective, highly coordinated, state of coherent 'super-electrons' (Cooper pairs) is set into motion, its flow is continued without any dissipation. [006] There is no scattering of ‘individual’ pairs of the coherent fluid, and therefore no resistivity. However, if a current higher than the critical current density \( J_c \) is passed, superconductivity disappears. [007, 008]
Chapter 1 — Background

1.1.2 — Perfect diamagnetism (B=0)

The magnetic inductance becomes zero inside the superconductor when the material is cooled below \( T_c \) and the external magnetic field is below \( H_c \) (critical magnetic field) the magnetic flux is expelled from the interior of the superconductor. This effect is called the Meissner effect. \[009\]

1.1.3 — Types of Superconductors

Superconductors are classified into two types based on their \( T_c \) and magnetic properties:

1.1.3.1 — Type I Superconductors

They require extremely low temperatures for them to be superconducting. Also, type I superconductors repel the magnetic field until their critical magnetic field \( (H_c) \) is reached. Above \( H_c \), the material goes back to the normal state. The type I superconductors have been of limited practical usefulness because their critical magnetic fields and critical temperatures are low. Well known Type I superconductors are listed in Table 1–1.

1.1.3.2 — Type II Superconductors

Type II superconductors have much higher critical magnetic fields and higher critical temperatures than type I superconductors. They usually exist in a vortex state with normal cores surrounded by superconducting region hence allowing some magnetic field penetration. They can carry much higher current densities while remaining in the superconducting state. Due to the above advantages Type II have greater practical applications. Table 1–2 lists some of the Type II superconductors.

1.1.4 — Yttrium Barium Copper Oxide High Temperature Superconductors (YBCO HTSC)

Superconducting transition \( (T_c) \) of 93 K was observed by Wu et al in \( \text{YBa}_2\text{Cu}_3\text{O}_{7-\delta} \) which was the first ceramic material to show superconductivity above the boiling temperature (77K) of liquid nitrogen. \[010\] This moved the critical temperatures of superconducting materials from the range of liquid helium temperatures to those of liquid nitrogen temperatures. The reduction in cooling requirements promised to greatly reduce the cost of superconducting technology and widen its range of applications. The YBCO structure is described as an oxygen-depleted layered
pervoskite crystal. The so called 1-2-3 superconductors form as layers of Cu and O atoms
sandwiched between layers containing the other elements in the compound. The Cu / O layers
are made of planes of atoms and by the chains of alternating Cu and O atoms. These atom
layers are important for the electrical properties of 1-2-3. Nevertheless, there are three metallic
elements in the compound. The lattice is composed of so-called perovskite layers (ACuO₃)
where A is a rare-earth or alkaline-earth element (ex: Y or Ba in YBCO). The term 7-δ in the
chemical formula implies a slight deficiency of oxygen. If δ =0, the lattice is in the orthorhombic
phase whereas in the case of δ =0.5, the material has a tetragonal structure. Only the
orthorhombic configuration is superconducting but it is stable only at temperatures below
500°C. [011~013] Physical parameters of YBCO are summarized in table 1–3. [014]
Table 1–1: Superconducting Transition Temperatures for Type I Elements

<table>
<thead>
<tr>
<th>Element</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>1.750</td>
</tr>
<tr>
<td>Indium</td>
<td>3.408</td>
</tr>
<tr>
<td>Lead</td>
<td>7.196</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>Mb</td>
</tr>
<tr>
<td>Osmium</td>
<td>0.660</td>
</tr>
<tr>
<td>Rhenium</td>
<td>1.697</td>
</tr>
<tr>
<td>Tantalum</td>
<td>4.470</td>
</tr>
<tr>
<td>Thallium</td>
<td>2.380</td>
</tr>
<tr>
<td>Tin</td>
<td>3.722</td>
</tr>
<tr>
<td>Tungsten</td>
<td>W</td>
</tr>
<tr>
<td>Zinc</td>
<td>0.850</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.517</td>
</tr>
<tr>
<td>Iridium</td>
<td>0.113</td>
</tr>
<tr>
<td>Mercury</td>
<td>4.154</td>
</tr>
<tr>
<td>Niobium</td>
<td>9.250</td>
</tr>
<tr>
<td>Protactinium</td>
<td>Pa</td>
</tr>
<tr>
<td>Ruthenium</td>
<td>0.490</td>
</tr>
<tr>
<td>Technetium</td>
<td>Tc</td>
</tr>
<tr>
<td>Thorium</td>
<td>1.380</td>
</tr>
<tr>
<td>Titanium</td>
<td>0.400</td>
</tr>
<tr>
<td>Vanadium</td>
<td>V</td>
</tr>
<tr>
<td>Zirconium</td>
<td>Zr</td>
</tr>
</tbody>
</table>

Table 1–2: Superconducting Transition Temperatures for Type II Superconductors

<table>
<thead>
<tr>
<th>Material</th>
<th>$T_c$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_3$Ga</td>
<td>14.5</td>
</tr>
<tr>
<td>$V_3$Si</td>
<td>17</td>
</tr>
<tr>
<td>Nb$_3$Sn</td>
<td>18</td>
</tr>
<tr>
<td>Nb$_3$Ge</td>
<td>24</td>
</tr>
<tr>
<td>YBa$_2$Cu$<em>3$O$</em>{7-\delta}$</td>
<td>93</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Ca$_2$O$_x$</td>
<td>85</td>
</tr>
<tr>
<td>Bi$_2$Sr$_2$Ca$_3$O$_x$</td>
<td>110</td>
</tr>
<tr>
<td>Tl$_2$Ba$_2$Ca$_2$Cu$<em>3$O$</em>{10}$</td>
<td>125</td>
</tr>
<tr>
<td>HgBa$_2$Ca$_2$Cu$_3$O$_9$</td>
<td>164</td>
</tr>
</tbody>
</table>
YBCO High Temperature Superconductors

### Table 1–3: Physical parameters of YBCO

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition Temperature</td>
<td>Tc=92 K</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>$3.2 \times 10^{-2}$ Wcm$^{-1}$K$^{-1}$ (at 300K)</td>
</tr>
<tr>
<td>Specific Heat Capacity</td>
<td>0.39 J/g K</td>
</tr>
<tr>
<td>Thermal expansion Coefficients</td>
<td>$\alpha_a=11\times 10^{-6}$K$^{-1}$ $\alpha_c=25\times 10^{-6}$K$^{-1}$</td>
</tr>
</tbody>
</table>

---

**Fig. 1–3**: Crystal structure of YBCO

#### 1.2 – Importance of a buffer layer

**1.2.1 – YBCO thin film applications**

The discovery of the Cuprate HTC (HTSC) in 1986 marked the beginning of a new era not only in the theoretical value in solid state physics in general, but also in the aspect of potential applications in industry. Soon after the discovery, the quests for the practical applications lead to the investigation on the current carrying capacity of this new material at the boiling point of liquid nitrogen of 77K. The first experiment on the sintered polycrystalline bulk YBCO samples was rather disappointing, because the large angle grain boundaries severely limited supercurrent flow especially in a magnetic field. With the knowledge that textured cuprate films can carry high current density, the second generation (2G) HTSC materials become promising in practical applications. The quick success on small single crystal substrates introduced the idea of depositing HTSC film on a flexible inexpensive metal tape substrate with a proper texture along the length. The cost consideration highlights the use of a metal tape together which can be scale up for commercial applications. Researchers have been able to
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fabricate YBCO wire by starting with a strip of textured nickel or other inexpensive metals. The strip is coated with a layer of isolating material i.e. a buffer layer, and then a thin layer of YBCO is added. Recent YBCO films having a critical current density in the ranges of 1~10 million amperes per square centimeter have also been reported. [015~016]

The surface resistance of HTS thin films such as 2G YBCO is orders of magnitude lower than that of normal metals in the microwave frequency region. [017,018] This makes these materials excellent candidates for device applications. But YBCO is still in developmental stages and is slowly ramping up for commercial applications. So far, only BSCCO ((Bi,Pb)2Sr2Ca2Cu3O10) first-generation (1G) wires were the commercial product and are manufactured for sale in large quantities. Nevertheless, many research work on 2G wires / tapes have been in development worldwide since the mid-1990s mainly due to the following advantages over the BSSCO. [019]

1. YBCO tapes have greater critical current and critical current density than BSCCO tapes.
2. Due to greatly thinner superconducting layer in YBCO compared to BSCCO, the AC losses are lower in YBCO tape than in a BSCCO tape.
3. The price of an YBCO tape could become 5 fold less than a BSCCO tape because an YBCO tape uses less costly components (such as silver) than a BSCCO tape. [020]

Important commercial applications include power transmission cables, fault current limiters, transformers, generators and motors. In military applications, high temperature superconducting generator and magnet programs for airborne applications have been initiated due to their significantly lighter weight and more compact nature. [021,022] Another advantage of YBCO wire is their intrinsic behavior in the presence of a strong magnetic field. Enhancements in flux pinning of at least a factor of two have been demonstrated for Metal Organic Chemical Vapor Deposition (MOCVD) and Metal Organic Deposition (MOD) deposited YBCO films. Considering all this, HTSC power cables manufactured with YBCO tapes are promising compared with conventional BSCCO HTS cables.
Importance of a buffer layer

1.2.2 – Architecture of YBCO Superconductor tapes

Most key techniques in developing a thin film focus on three parts: substrate (as the support), buffer layers (as a base for texture and for preventing interdiffusion), and superconductor layer (current carrier). The coated conductor process starts with a long and flexible tape-shaped metallic substrate, typically 50~100 μm thick. The substrate is coated with a multifunctional oxide buffer layer, typically less than 1 μm thick, usually consisting of multiple layers and providing a textured template surface for epitaxial deposition of the 1~4 μm thick YBCO HTS layer. A passivating Ag layer of a few μm, a thicker metallic stabilization layer and possibly insulation complete the conductor. Preparation of a such substrate with a buffer layer over it, is an integral part of any film deposition process, which provide the underlying foundation for the superconducting film. Then it is also important that the film formation will have to be meet with following 3 conditions.

① Film/substrate lattice matching
To carry high critical current density \(J_c\), superconducting thin film must be well textured to minimize weak links at high-angle grain boundaries in the film. [023] Controlled crystallographic orientation of the film with respect to the underlying layers is required for the epitaxial growth of high \(T_c\) films. Typically, the in-plane lattice spacing of the oxide film should closely match that of the substrate or exhibit a reasonably close near-coincidence site lattice match, such as by rotating 45° with respect to the principle axes. For compounds with cubic or tetragonal crystal structure, oxide substrates with a square-planar surface orientation, such as the (001) face of a cubic oxide crystal, are ideal for c-axis oriented films.

② Thermal expansion matching
Thermal expansion match between HTSC films, substrates and intermediate buffer layers is essential to provide adequate film adhesion and to avoid film cracking during thermal cycling.
Chapter 1 — Background

③ Chemical compatibility

Of course, any chemical reaction between the substrate and film will likely inhibit good epitaxy, and may prevent the formation of the desired phase. The substrate material should also be stable against thermal cycling with no significant phase transitions. For all the specific film growth methods, the underlying substrate must be nonreactive in the oxygen rich ambient environment which is required for YBCO growth and processing. The most commonly used substrate/buffer layer manufacturing techniques that showed best results are two types: Ion Beam Assisted Deposition (IBAD) and Rolling Assisted Biaxially Textured Substrates (trademarked RABiTS™ by Oak Ridge National Laboratory). [024]

1.2.3 – Substrates for YBCO Superconducting tapes

When selecting a substrate material, the above prerequisites should be satisfied, also with additional preferences such as high-temperature stability, dielectric and magnetic properties, suitable mechanical properties (e.g., ductility and strength), size availability (length, width, and thickness) as well as cost effectiveness for a large-scale production. Surface quality of substrates such as roughness, cleanliness, and grain boundary grooving also play a significant role for the buffer and the YBCO growth. Metallic substrates with non-magnetic or minimum magnetic hysteresis loss are preferred for the application of superconductor wire in alternative magnetic field. Metallic substrates have obvious advantages in making long and flexible tapes. Among the metallic materials, Ni and Ni-based alloys have very good stability and oxidation resistance at an elevated temperature. High quality biaxial textures have been demonstrated on these materials through the RABiTS technique with cubic percentage even higher than 99%. Different categories of Ni base alloys, such as Ni-Cr and Ni-W, have been developed in the consideration of mechanical and magnetic properties. Cu-based tapes also have been proposed as substrates for coated conductors. [025] Such tapes could also have the potential advantage over Ni of being inexpensive and non-magnetic. Compared to Ni and Ni alloys, Cu and Cu alloys have the lower cost, a sharp cube texture developed easily and higher thermal conductivity, no chemical reactivity with YBCO,
**Importance of a buffer layer**

and no ferromagnetic contribution to hysteretic AC losses in many power applications. But the primary disadvantage is that Cu is much more susceptible to oxidation. [026,027]

1.2.4 – Buffer layers for YBCO Superconducting tapes

Buffer layers function as a texture template and a reaction barrier between the YBCO and the substrates. In the RABiTS route, the texture is formed on a metallic substrate, hence the buffer layer acts more as a barrier, preventing diffusion of metal atoms up into the superconductor, as well as prevents oxygen diffusing down through to the substrate to cause oxidation of the metal. In order to be an effective barrier, it is important that the buffer layer is free of cracks, which are usually caused by stress induced through differential thermal contractions. Thus, a buffer material having a closely matched thermal expansion coefficient with the substrate and superconductor is desired. The basic requirements for a buffer layer are to be biaxially textured with suitable lattice parameters and non-reactive with a HTSC layer.

Various buffer layer materials have been investigated for their suitability as candidates for YBCO superconducting tapes. Potential materials range from simple oxides (MO, MO₂, M₂O₃; M: metal or rare-earth) to more complex compound oxides exhibiting the perovskite (ABO₃) or pyrochlore (A₂B₂O₇) structure. The direct deposition on Ni-based cube-textured substrates requires a hydrogen containing gas atmosphere during annealing to avoid the uncontrolled oxidation of the Ni tape.

In 1996, Goyal et al. [028] demonstrated for the first time a high current density (0.9MA/cm²) YBCO film deposited by laser ablation on Ni RABiTS substrates with CeO₂ and YSZ buffer layers. The strong biaxial texture of the metal (in-plane 6°~7° FWHM) is conferred to the superconductor by deposition of intermediate oxide layers, which serve both as a chemical and as a structural buffer. Since then CeO₂ has been widely used as a buffer layer in various single crystalline and metallic substrates. In 1997, Paranthaman et al. [029] and He et al. [030] firstly showed that an epitaxial CeO₂ layer cracked extensively when its thickness exceeds 50 nm. Nevertheless, problems associated with CeO₂ cracking may be overcome by depositing a layer of YSZ on top. [031] Thus Ni/CeO₂/YSZ/YBCO became a standard architecture in early-coated conductor studies.[032] Since YSZ does not have good lattice match with YBCO, a second CeO₂
Chapter 1 — Background

layer, the cap layer, is added on top of the YSZ. There are some other multilayer compositions reported such as Ni/LaNiO$_3$/SrRuO$_3$/YBCO [033], Ni-W/La$_2$Zr$_2$O$_7$/CeO$_2$/YBCO [034], Ni-W/Y$_2$O$_3$/La$_2$Zr$_2$O$_7$/CeO$_2$/YBCO [035].

1.3 – SrTiO$_3$ as a promising buffer layer

These multilayer buffer compositions cause significant complexity in the fabrication process which is attributed to the manufacturing cost of the superconducting tape [077]. Simply because, a cost is incurred for every layer, in the means of material-cost (for chemicals, gases, etc.), and overhead-cost (for electricity, construction, etc.). In addition, during the fabrication process for multi-layers, multiple steps including vacuum and/or heat treatment processes would inevitably slow down the overall production speed. Therefore a single buffer layer is highly desired to replace the multi-layer architecture, which will definitely reduce the number of processing steps and simplify manufacturing. Several single buffer layer materials for YBCO superconductors have been studies such as Yttria-Stabilized Zirconia (YSZ), Y$_2$O$_3$ [036], LaMnO$_3$ [037], La$_{0.7}$Sr$_{0.3}$MnO$_3$ [038], La$_2$Zr$_2$O$_7$ [039], NdGaO$_3$ [040], and SrTiO$_3$ [041–083]. Here, SrTiO$_3$ is also one of the most popular crystal substrates that have been achieved with high quality YBCO films.

Fig. 1–4: Schematic view of a single-buffer layer architecture
SrTiO₃ as a promising buffer layer

1.3.1 – Advantages of SrTiO₃ buffer layers

Table 1–4 shows some properties of the materials used as templates for YBCO superconducting thin films. The suitability of SrTiO₃ as a buffer layer is emphasized by the combination of following features.

① Single buffer layer capability
Considering the buffer layers for YBCO that has been investigated during past years, only few cases can be highlighted as single buffer layers, such as yttria-stabilized zirconia (YSZ), Y₂O₃, LaMnO₃, La₀.₇Sr₀.₃MnO₃, La₂Zr₂O₇, and SrTiO₃. Single buffer layer capability would be a cost efficient advantage, reducing the number of processing steps and simplifying the whole manufacturing process.

② Low lattice mismatch with YBCO
SrTiO₃’s low lattice mismatch of 1.43 % is highly desirable for minimizing the chances of lattice defects in a fine YBCO hetero-epitaxial growth on SrTiO₃.

③ Close thermal expansion with metallic substrates such as Ni, Cu/Ni alloys
Coefficient of thermal expansion $\alpha$ of SrTiO₃ ($\alpha \approx 10.4 \times 10^{-6}/^\circ$C) is closer to the $\alpha$ of metallic substrates such as Ni, Cu/Ni ($\alpha \approx 12.2\sim13.4 \times 10^{-6}/^\circ$C) [124], providing adequate film adhesion and to avoid film cracking during thermal cycling. In one of most popular buffer layer materials CeO₂, it is known that cracks are appearing in CeO₂ when thicker than 100 nm [124], limiting the applicability of single buffer layers thicker than 100 nm.

④ Direct compatibility with BaF₂ based YBCO deposition techniques
BaF₂ based YBCO deposition is a very effective method applied in the field of coated conductors. For this process, O₂ with H₂O vapour introduction is used for the annealing ambient environment at the elevated temperatures of $\approx 740^\circ$C [094]. Sensitivity to the water vapour would be an issue, disturbing the epitaxial growth of YBCO on the buffer layer. In the case of SrTiO₃ applying in BaF₂ process [066], it is reported that oxygen
diffusion is low, and also doesn’t react with the H₂O vapours. In other hand, some popular buffer layer materials such as MgO reacts with H₂O vapour, which precludes its use as a substrate for films grown by methods that require the presence of H₂O [048].

1.3.2 – Properties of SrTiO₃

A SrTiO₃ single crystal provides a good lattice match to most materials with Perovskite structure. It is an excellent substrate for epitaxial growth of HTS and many oxide thin films. SrTiO₃ single crystal has also been used widely for special optical windows and as high quality sputtering target [126].

As illustrated in figure 1–5, SrTiO₃ undergoes an extensively studied phase transition T_tr ≈ 105 K. At room temperature (T > 300 K), [095] the crystal structure is cubic with the lattice parameter a=3.905 Å. At temperatures lower than 105 K, SrTiO₃ exists as a less symmetric tetragonal phase, induced by mechanical stress. This tetragonal distortion is due to the rotation of the oxygen translator in the xy-plane. [096] The schematic view of the SrTiO₃ cubic perovskite structure is shown in figure 1–6.
SrTiO$_3$ as a promising buffer layer

Table 1–4: Template materials used for YBCO deposition

<table>
<thead>
<tr>
<th>Material</th>
<th>Crystal structure</th>
<th>Lattice constant (nm)</th>
<th>Plane Space d (nm)</th>
<th>Misfit to YBCO (%)</th>
<th>Dielectric Constant $\varepsilon$</th>
<th>$\alpha$ (10$^{-6}$/°C)$^2$</th>
<th>Melting point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBCO Yba$_2$Cu$<em>3$O$</em>{6.88}$</td>
<td>orthorhombic</td>
<td>a=0.3817 b=0.3883 c=1.1633</td>
<td>(a+b)/2=0.385</td>
<td>0</td>
<td>7.9</td>
<td>1150</td>
<td></td>
</tr>
<tr>
<td>Zr$<em>{0.8}$Y$</em>{0.2}$O$_{1.9}$</td>
<td>cubic</td>
<td>a=0.5147</td>
<td>0.3640</td>
<td>-5.45</td>
<td>27</td>
<td>10.3</td>
<td>2680</td>
</tr>
<tr>
<td>CeO$_2$[^3]</td>
<td>cubic</td>
<td>a=0.5411</td>
<td>0.3826</td>
<td>-0.62</td>
<td>15</td>
<td>9.9</td>
<td>2600</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>cubic perovskite</td>
<td>a=0.3905</td>
<td>0.3905</td>
<td>+1.43</td>
<td>300</td>
<td>10.4</td>
<td>2080</td>
</tr>
<tr>
<td>LaAlO$_3$</td>
<td>cubic perovskite</td>
<td>a=0.3792</td>
<td>0.3792</td>
<td>-1.51</td>
<td>25</td>
<td>9.2</td>
<td>2100</td>
</tr>
<tr>
<td>LSAT (LaAlO$<em>3$)$</em>{0.3}$ (Sr$_2$AlTaO$<em>6$)$</em>{0.7}$</td>
<td>cubic perovskite</td>
<td>a=0.3868</td>
<td>0.3868</td>
<td>+0.47</td>
<td>22</td>
<td>10.9</td>
<td>1840</td>
</tr>
<tr>
<td>LaMnO$_3$</td>
<td>cubic perovskite</td>
<td>a=0.3880</td>
<td>0.3880</td>
<td>+0.78</td>
<td>11.2</td>
<td>1880</td>
<td></td>
</tr>
<tr>
<td>La$_2$Zr$_2$O$_7$</td>
<td>cubic pyrochlore</td>
<td>a=1.0786</td>
<td>0.3813</td>
<td>+7.36</td>
<td>20</td>
<td>9.1</td>
<td>2200</td>
</tr>
<tr>
<td>BaZrO$_3$</td>
<td>cubic perovskite</td>
<td>a=0.4193</td>
<td>0.4193</td>
<td>+8.91</td>
<td>20.9</td>
<td>2600</td>
<td></td>
</tr>
<tr>
<td>Y$_2$O$_3$</td>
<td>cubic perovskite</td>
<td>a=1.0550</td>
<td>0.3723</td>
<td>-3.30</td>
<td>13</td>
<td>8.5</td>
<td>2410</td>
</tr>
<tr>
<td>MgO</td>
<td>cubic</td>
<td>a=0.4216</td>
<td>0.4216</td>
<td>+9.35</td>
<td>9.8</td>
<td>8.0</td>
<td>1990</td>
</tr>
<tr>
<td>NdGaO$_3$</td>
<td>orthorhombic perovskite</td>
<td>a=0.5430 b=0.5500 c=0.7700</td>
<td>0.3840 0.3890 0.3840 0.3890</td>
<td>-0.26 + 1.04</td>
<td>25</td>
<td>7.8</td>
<td>1600</td>
</tr>
<tr>
<td>NiO</td>
<td>cubic</td>
<td>a=0.4177</td>
<td>0.4177</td>
<td>+8.49</td>
<td>10</td>
<td>1990</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>cubic</td>
<td>a=0.3520</td>
<td>0.3520</td>
<td>+9.54</td>
<td>13.4</td>
<td>1455</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>cubic</td>
<td>a=0.3610</td>
<td>0.3610</td>
<td>+6.78</td>
<td>16.5</td>
<td>1085</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>cubic</td>
<td>a=0.5430</td>
<td>+0.27</td>
<td>11</td>
<td>3.12</td>
<td>1410</td>
<td></td>
</tr>
<tr>
<td>SiO$_2$ / Quartz</td>
<td></td>
<td>a=0.5150 c=1.3860</td>
<td>3.8</td>
<td>0.59</td>
<td>1720</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al$_2$O$_3$ / Sapphire</td>
<td>hexagonal</td>
<td>a=0.4758 c=1.2990</td>
<td>-11.5</td>
<td>8.31</td>
<td>2040</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

[^2] $\alpha$: coefficient of thermal expansion
[^3] CeO$_2$: structurally compatible to YBCO with its unit cell (0.541 nm) equal to the diagonal length of the a-b lattice plane of the YBCO cell.
Fig. 1–6: Schematic illustration of a SrTiO$_3$ unit cell

Grey atoms: Sr; Yellow atom: Ti; Red atoms: O

The Ti atom sits in the centre of the cube, which corners are formed by the Sr atoms. We can describe the positions of all atoms in a SrTiO$_3$ crystal by the general formula 1–1, described by the primitive vectors as defined in formula 1–2, where the primitive vectors for a simple cubic lattice are given by formula 1–3.

\[ R = R_b + \delta_i \cdot R_b \]  
\[ R_b = n_1 a_1 + n_2 a_2 + n_3 a_3 \]  
\[ a_1 = \begin{pmatrix} a \\ 0 \\ 0 \end{pmatrix}, \quad a_1 = \begin{pmatrix} 0 \\ a \\ 0 \end{pmatrix}, \quad a_1 = \begin{pmatrix} 0 \\ 0 \\ a \end{pmatrix} \]  

And, the positions of the Ti atom, Sr atom, and the 3 O atoms per SrTiO$_3$ cell are given by formulas 1–4, 1–5 and 1–6 respectively, where the lattice parameter $a = 3.905$ Å.

\[ \delta_{Ti} : 0 \quad 0 \quad 0 \]  
\[ \delta_{Sr} : \frac{a}{2} \quad \frac{a}{2} \quad \frac{a}{2} \]
SrTiO$_3$ as a promising buffer layer

\[ \delta_0 : \frac{a}{2} \ 0 \ \frac{a}{2} ; \ 0 \ \frac{a}{2} \ 0 ; \ 0 \ 0 \ \frac{a}{2} \]

The O atoms are bound to the Ti atom by strong covalent bonding: the oxygen $p_x$ and $p_y$ orbitals overlap in the $xy$-plane with the $d_{x^2-y^2}$ orbitals of the Ti atom. In the $z$-direction, the covalent bonding is accomplished by the overlap between the $p_z$ orbital of O and the $d_{3z^2-r^2}$ orbital of Ti. Conversely, the bonding involving the Sr atom is ionic, since the Sr atom is easy to transl and will donate enough electrons to satisfy all covalent bonds. The bonding is thus partly covalent (O–Ti) and ionic (Sr with the TiO$_6$ octahedra) [097].

Although successful results were documented on SrTiO$_3$ grown on various templates as summarized in table 1–4, when we consider the work reported on metal alloy substrates, many of them had utilized multi-coatings [051, 057, 060, 064, 067, 072, 078, 084, 086].

1.3.3 – Deposition techniques for SrTiO$_3$ buffer layers

In general, the most popular film-deposition methods can be mainly classified into 2 categories as ‘Physical methods’ and ‘Chemical methods’, and then sub-classified as shown in figure 1–6. For SrTiO$_3$ thin films, many among these methods have been employed for depositing thin films.
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1.4 – Introduction to Chemical Solution Deposition (CSD)

The chemical solution deposition (CSD) method is expected to be a very efficient method for coating long tapes, especially because of its simple applicability to reel-to-reel dip-coating processes. When considering the film fabrication methods such as Pulsed Laser Deposition (PLD) [077, 097], sputtering [096], and Chemical Vapour Deposition (CVD) [056] the use of high vacuums make the complication of the whole fabrication infra-structure, also attributing high costs. Therefore, the applicability through non-vacuum techniques such as chemical solution deposition (CSD) broadens the large-scale industrial possibilities in a positive way, where many work on SrTiO₃ have successfully performed using CSD based fabrication. [052, 053, 057, 059, 060, 062~064, 067, 069~072, 074~076, 078, 079, 081, 082, 084, 086, 087, 091]
1.4.1 – Dip coating method

Starting from the wet chemical precursor, the coatings can be easily obtained by different deposition techniques such as spin coating, dip coating, and spray coating. Among these 3 coating techniques, dip coating is expected to be the most appropriate technique applicable for thin films fabrications on long tapes, mainly due to the following advantages.

① No waste of the precursor material
② Simultaneous coating of the both sides of the long tape
③ Ease of applicability for reel-to-reel thin film fabrication on long tapes

Dip coating methods can be mainly classified into two different processing techniques:

① Lifting processes in which the parts to be coated are withdrawn from the solution and simultaneously covered with a liquid film.
② Lowering processes, in which the parts to be coated remain at rest and the liquid level is lowered.

The lifting process is the more economical for large/long substrates and it is also universally applicable. The lifting operation must be completely smooth and shockless and has to be so slow that the liquid film adhering to the substrate surface is left in a flow zone which is very short. The adherent liquid film partly flows down the substrate and solidifies after solvent evaporation, hydrolysis and condensation. Its thickness distribution in the vertical direction is dependent only on evaporation of the solvent and becomes stationary during the lifting, so that the solid film finally takes up a constant thickness along the lifting direction [098]. With regular operation at quiet liquid surface, film formation is also very uniform along the horizontal dipping line. The uniformity of the deposited film can be controlled by watching the interference fringes of the system which are formed during evaporation of the solvent and volatile reaction products. During lifting, the fringes should run as horizontally as possible and, at constant lifting speed, remain always at about the same distance above the surface of the coating solution.
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As well as having dependence on lifting speed, the thickness $D$ of the coating is mainly a function of the concentration of the solution and of the angle of inclination of the coated surface with the surface of the solution. At constant temperature and humidity, the approximate relation between film thickness and lifting speed for vertical movement is given in equation 1–7 [099].

$$D \approx k \sqrt[3/2]{v}$$  \hspace{1cm} 1–7

Here the constant of proportionality $k$ contains all the other properties affecting the layer thickness such as viscosity, surface tension and vapour pressure of the solution. The investigations of Schröder [100] also showed that a non-linear relation may exist between the film thickness $d$ and the concentration $c$ of the coating solution. This non-linearity comes from an increase in the viscosity of the solution with increasing concentration.

In dip-coating, it is very important that supporting parts (required to hold the substrates), should not be immersed because of the danger that solution residues could rinse in strips over the uniformly coated surface. On a narrow-brimmed area at the lower end of the substrate withdrawn from the coating solution, a strong increase in film thickness occurs caused by adhering liquid residues. The length of this useless zone depends on the shape of the edge, lifting speed and viscosity of the solution and is normally between 2 and 10 mm.
1.4.2 – Solution chemistry

The fundamental step in this process is the hydrolysis of suitable metal organic compounds whose hydrolysis reaction products are then converted into the final oxide coatings. For the production of homogeneous coatings with specific properties from liquid films, the solutions used must possess special physical and chemical characteristics. To obtain such proper characteristics, according to Schröder [100], the four following requirements must be fulfilled.

1. The initial compounds must have an adequate solubility and the solution formed may only have a minor tendency towards crystallization during solvent evaporation. These requirements are generally met by those compounds which either already dissolve in a colloidal or polymeric state or reach such a state by reaction with the solvent, or which remain after solvent evaporation as a gel-like non crystalline residue.

2. To obtain good wetting of the substrate, the contact angles formed with the solution have to be sufficiently small. Wettability can be improved in some cases by the addition of wetting agents to the solution. The wettability of the substrate is decreased by insufficient cleanliness.

3. The solution must have an adequate durability (without getting any precipitations) and the processing conditions must be maintained constant. Durability is sometimes difficult to realize with solutions of colloidal or polymeric character, but by using stabilizers it could be improved.

4. To obtain reproducible solid and homogeneous oxide films, drying and heating must be carried out carefully. During this process the solidification of the film structure should occur without the appearance of cracks or haze and at the same time high bonding strength to the substrate must develop.
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CSD processing of metal alkoxides to yield ceramics is typically divided into the following stages.
1. Solution synthesis
2. Gelation
3. Conversion to an amorphous oxide
4. Crystallization

CSD processing involves a transition from a fluid state, or ‘sol’ to a viscoelastic solid state, or ‘gel’. Therefore this method is also well-known as Sol-Gel method. Gels may be produced by two distinct processes: (i) gelation of colloidal sols, or (ii) polymerization of metal alkoxide solutions. In colloidal processing, the term ‘sol’ refers to the dispersion in solution of colloids, or fine solid particles with dimensions in the range of 10~1000Å. Gelation in these systems occurs when the solvent layers associated with the particles begin to interact, either through loss of part of the liquid phase or addition of electrolyte species. The result of this interaction is the loss of translational motion of the particles, and the formation of a rigid network or ‘gel’ structure, wherein the remaining liquid phase is entrapped. The colloidal sol-gel route thus involves the preparation of a gel from an initial suspension of colloidal particles, and historically, has been the most widely studied gelation route for the preparation of silica gels. Three types of precursor species lead to the formation of colloidal gels: colloidal sols; inorganic salts; and metal alkoxides (where intermediate species must first form). [101, 102]

Gel formation in polymeric systems proceeds by different mechanisms. Polymeric oxide gels are almost exclusively prepared from metal alkoxide solutions. Metal alkoxide compounds have the general formula: M(OR)n where M is a metal ion; R is an alkyl group; and n is the valence of the metal.

Normally the alkoxide is dissolved in its parent alcohol and hydrolyzed by the addition of water. In the case of more electronegative metals or metalloids, the alkoxide is dissolved in acid or base catalyst. In aqueous or organic solvents, the precursors are hydrolyzed and condensed to form inorganic polymers composed of M–O–M bonds. For inorganic precursors (salts), hydrolysis proceeds by the removal of a proton from an aqua ion to form a hydroxo (–OH) or oxo (=O) ligand. Condensation reactions involving hydroxo ligands result in the formation of
bridging hydroxyl (M−μ(OH)−M) or oxo (M−O−M) bonds. [098] The condensation reaction which occurs between hydrolyzed metal alkoxide species, not only results in the formation of metal-oxygen-metal bonds, but as condensation proceeds and becomes more extensive, a three dimensional oxide network is formed. When the dimensions of the network become macroscopic with respect to the sample size, ‘gelation’ is observed. [099, 101~103]

The hydrolysis and condensation reactions leading to formation of polymeric gels are given in following reactions in figures 1–7, 1–8, and 1–9.

\[
\begin{align*}
R\text{O}_\text{M} & \quad + \quad H\text{O}H \\
\text{RO} & \quad \text{OR} \\
\text{RO} & \quad \text{OR}
\end{align*}
\]

Fig. 1–7 : Partial hydrolysis

\[
\begin{align*}
R\text{O}_\text{M} & \quad + \quad H\text{O} \text{M} \text{OR} \\
\text{RO} & \quad \text{OR} \\
\text{RO} & \quad \text{OR}
\end{align*}
\]

Fig. 1–8 : Dealcoholation Condensation

\[
\begin{align*}
R\text{O}_\text{M} & \quad + \quad H\text{O} \text{M} \text{OR} \\
\text{RO} & \quad \text{OR} \\
\text{RO} & \quad \text{OR}
\end{align*}
\]

Fig. 1–9 : Dehydration Condensation

Condensation leading to polymerization and network formation may occur through either (i) dehydration or (ii) dealcoholation. Control over the hydrolysis conditions, \textit{i.e.}, the ratio of water to metal alkoxide, additive concentration and type, and alkoxide concentration, governs not only the extent of hydrolysis, but also the polymeric structure resulting from the condensation
Chapter 1 — Background

reactions. Interestingly, structural differences introduced in wet gels through control of the hydrolysis conditions are observed in dried gels and also fired ceramic microstructures.

For both inorganic and metal-organic precursors, the structure of the evolving oligomers or polymers (composed of $\text{M}–\text{O}–\text{M}$ or $\text{M}–\mu\text{(OH)}$–$\text{M}$ bonds) depends on the extent of hydrolysis and the preferred coordination number or functionality of the metal. For an example in $\text{Mg}^{2+}$ it is reported that functional and versatile ligands such as $\left[\text{OCH(CHOCH}_2\text{OCH}_3\right]$ allow the magnesium atoms to attain high coordination numbers in clusters. [098]

In the case of inorganic precursors, the extent of hydrolysis is generally controlled by the $\text{Ph}$, while the effective functionality may be controlled through complexation with mono- or multidentate anionic species [099]. Modification of the alkoxide with chelating or bridging multidentate ligands is generally used to reduce both the effective functionality and the overall extent of condensation.
Chapter 2 — Motivation

Chapter — 2
Motivation

2.1 — SrTiO$_3$ by novel solution synthesis

Impressive developments have been realized on CSD based SrTiO$_3$ thin films during the past two decades. For practical application on reel-to-reel industrial thin film fabrication with green chemistry, the following facts have to be taken into account very seriously.

2.1.1 — Maximum lifetime/stability of the precursor solution

In CSD based SrTiO$_3$ thin film fabrication, a short lifetime of the precursor solution results in the need of changing the precursor solution frequently, inducing additional costs, and also producing more chemical waste over time. 2,4-pentanedione based precursor solutions are meant to have longer lifetimes, due to their chemical susceptibility to hydrolysis, than in the case of butoxy ligands, and the inhibited accessibility to reactive alkoxide species [049]. However, different combinations with other reagents may affect their lifetime. In reported work on CSD based SrTiO$_3$ thin films, precursor solutions with lifetimes of several days [051], 1 week [078], several weeks [043], 1 month [052], and several months [041] were described. These ‘physical’ lifetimes were determined based on the time between synthesis and precipitation. After a precipitation, the cationic stoichiometry between Sr and Ti in the solution would be changed, because of the material loss that contributes the precipitation reaction. Hence, even the dip-coating is attempted only using the solution part of the precipitated solution, the resulting film would contain a different cationic/organic composition compared to the fresh solution. Therefore, when we consider the precursor solution’s ‘practical’ lifetime based on the final film properties, the ‘practical’ lifetime is generally equal or shorter than its ‘physical’ lifetime. In our research, the precursor’s ‘practical’ lifetime was considered prioritizing the resulting surface texture of the final films, based on the orientation factors of $\theta$–$2\theta$ scans.
2.1.2 – Maximum safety with the ingredient chemicals

In previously reported SrTiO₃ thin film fabrication performed with CSD methods, some ingredient chemicals present potential toxic hazard. The harmful properties of the most popular chemicals used in the reported scientific literature regarding CSD based SrTiO₃ thin films, can be summarized as table 2–1. Strontium acetate that has been used as the strontium source for the precursor solution could be considered as ingredient with minimum toxic hazard.

As a key ingredient of titanium source, titanium isopropoxide could be considered as a safer chemical when compared with titanium butoxide. Trifluoroacetic acid (TFA) is used in many SrTiO₃ research works because of its applicability as a strong acidic solvent. But, besides its highly corrosive and rapidly penetrating nature, highly-toxic and corrosive fumes mainly containing hydrogen fluoride (HF) can be easily produced upon contact with moisture, causing extremely dangerous health and technical issues [108, 123]. Therefore, if TFA is used in a reel-to-reel industrial deposition process, stringent safety measures have to be applied to the whole workspace, contributing to extra costs.

Table 2–1: Most popular chemical ingredients, and their safety/hazardous indicators

Green-shaded rows shows the information of the ingredients of our novel solution synthesis (coded as Chemistry–III in following chapters)

<table>
<thead>
<tr>
<th>SrTiO₃ work</th>
<th>Chemical</th>
<th>Boiling point °C</th>
<th>CAS number</th>
<th>NFPA rating</th>
<th>Hazard class</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Health</td>
<td>Flammability</td>
</tr>
<tr>
<td>084</td>
<td>strontium isopropoxide</td>
<td>—</td>
<td>88863-33-6</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>051, 060</td>
<td>strontium acetate</td>
<td>—</td>
<td>543-94-2</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>053, 060</td>
<td>trifluoroacetic acid</td>
<td>72.4</td>
<td>76-05-1</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>051, 071</td>
<td>acetic acid</td>
<td>118</td>
<td>64-19-7</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>053, 059</td>
<td>titanium butoxide</td>
<td>314</td>
<td>5593-70-4</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>086</td>
<td>titanium 2,4-pentanedionate</td>
<td>—</td>
<td>97281-09-9</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>043, 060</td>
<td>titanium isopropoxide</td>
<td>232</td>
<td>546-68-9</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>041, 054</td>
<td>2-methoxyethanol</td>
<td>125</td>
<td>109-86-4</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>084</td>
<td>1-methoxy-2-propanol</td>
<td>119</td>
<td>107-98-2</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>047, 060</td>
<td>2,4-pentanedione</td>
<td>140</td>
<td>123-54-6</td>
<td>2</td>
<td>3</td>
</tr>
</tbody>
</table>
2.1.3 – Reproducibility

In addition to the solution synthesis mentioned in previous chapters, many recipes have been approached referring the published literature. Many recipes could not be successfully repeated, probably due to the lack of technical know-how, and limited technical information provided in those publications.

Therefore, a precursor solution has to be accomplished with a maximum ‘practical’ lifetime/stability, maximum safety, and an excellent reproducibility, in order to construct a continuous reel-to-reel fabrication process.

Thoroughly considering all these facts, many experiments were done in order to develop a green chemistry based – SrTiO₃ precursor that would be practically promising for an excellent surface texture. In the published scientific literature on CSD based SrTiO₃ thin film fabrication, the used chemical synthesises can be briefly summarized as shown in table 2–2.

Based on this table 2–2, several alternative recipes were considered. TFA, and 2-methoxyethanol based precursors were taken out of consideration because of the toxic hazard of the ingredient chemicals. Based on the work reported by Siegal [059], Ong [067] and Zhu [072], different titanium sources (Ti isopropoxide + 2,4-Pentanedione, and Ti isopropoxide + H₂O + 2,4-Pentanedione) were attempted. But, the solution preparation was not successful due to the precipitation. Even though some methanol based recipes [051, 064, 072, 078] were also attempted, all those preparations were failed due to the precipitation. Result was the same, even retried with anhydrous methanol.
### Chemical ingredients used for SrTiO₃ solution synthesis

<table>
<thead>
<tr>
<th>Chemical ingredients</th>
<th>Coating Method</th>
<th>Substrate</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr Metal + Ti isopropoxide + 2-Methoxyethanol + Triethaloamine</td>
<td>spin-c</td>
<td>SiO₂</td>
<td>041</td>
</tr>
<tr>
<td>Sr hydroxide + Acetic acid + Ti isopropoxide + 2-Methoxyethanol</td>
<td>spin-c</td>
<td>Si, glass</td>
<td>043</td>
</tr>
<tr>
<td>Sr 2-ethyl hexanoate + Ethanol + Ti isopropoxide + 2,4-Pentanedione</td>
<td>sol-gel</td>
<td>Si, SiO₂</td>
<td>047</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + Methanol</td>
<td>spin-c</td>
<td>Si, LaAlO₃</td>
<td>051</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + 2-Methoxyethanol</td>
<td>spin-c</td>
<td>Ni, LaAlO₃</td>
<td>052</td>
</tr>
<tr>
<td>Sr acetate + TFA + Ti butoxide + Methanol</td>
<td>dip-c</td>
<td>Ni</td>
<td>053</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + 2-Methoxyethanol</td>
<td>spin-c</td>
<td>Ni, LaAlO₃</td>
<td>054</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + 2,4-Pentanedione + Methanol</td>
<td>spin-c</td>
<td>Sr</td>
<td>057</td>
</tr>
<tr>
<td>Sr acetate + TFA + Ti isopropoxide + Methanol</td>
<td>spin/dip</td>
<td>Ni</td>
<td>059</td>
</tr>
<tr>
<td>Sr acetate + TFA + Ti isopropoxide + 2,4-Pentanedione + Methanol</td>
<td>spin-c</td>
<td>Ni</td>
<td>060</td>
</tr>
<tr>
<td>Sr acetate + TFA + Ti isopropoxide + 2,4-Pentanedione</td>
<td>spin/dip</td>
<td>Ni</td>
<td>067</td>
</tr>
<tr>
<td>Sr acetate + TFA + Ti isopropoxide + 2,4-Pentanedione</td>
<td>spin-c</td>
<td>Ni</td>
<td>068</td>
</tr>
<tr>
<td>Sr di-i-propoxy and Ti tetra-ipropoxy precursors</td>
<td>spin-c</td>
<td>LaAlO₃</td>
<td>070</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + 2,4-Pentanedione + Butanol</td>
<td>spin-c</td>
<td>Ni</td>
<td>071</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + Methanol</td>
<td>spin-c</td>
<td>Ni</td>
<td>072</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti isopropoxide + 2,4-Pentanedione</td>
<td>spin-c</td>
<td>Ni, Ni/W</td>
<td>073</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti isopropoxide + Methanol</td>
<td>spin-c</td>
<td>LaAlO₃</td>
<td>078</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + 2-Methoxyethanol</td>
<td>spin-c</td>
<td>LaAlO₃</td>
<td>082</td>
</tr>
<tr>
<td>Sr isopropoxide + Ti isopropoxide + Butanol + 1-Methoxy-2-propanol</td>
<td>spray</td>
<td>Ni/W</td>
<td>084</td>
</tr>
<tr>
<td>Sr acetate + Propionic acid + Ti 2,4-pentanediionate + 2-Methoxyethanol</td>
<td>spin-c</td>
<td>Ni/W</td>
<td>086</td>
</tr>
<tr>
<td>Sr acetate + Acetic acid + Ti butoxide + 2-Methoxyethanol</td>
<td>spin-c</td>
<td>Hastelloy</td>
<td>087</td>
</tr>
</tbody>
</table>
**SrTiO$_3$ by novel solution synthesis**

The main technical issue in SrTiO$_3$ precursor synthesis is believed to be the high moisture sensitivity of the titanium source. Most of the commercially available Ti alkoxides are high moisture sensitive reagents, except Ti 2,4-pentanedionate. Therefore, many attempts were done developing a precursor using this low moisture-sensitive titanium source. In addition, even with the moisture-sensitive Ti alkoxides, alternative solvents those are reported for SrTiO$_3$ precursor synthesis were also taken into the consideration, as an alternative for the toxic 2-methoxyethanol. When we consider alternative solvents for 2-methoxyethanol in similar chemical nature, other glycol ethers such as 2-ethoxyethanol, 2-isopropan oxyethanol, 2-butoxyethanol, and 1-methoxy-2-propanol can be found as popular solvents used in various chemical processes [109]. Among these, 2-ethoxyethanol is also reported as toxic same as 2-methoxyethanol [109~113]. In addition, the acetate esters of 2-methoxyethanol and 2-ethoxyethanol (*i.e.* 2-methoxyethyl acetate and 2-ethoxyethyl acetate respectively) are also reported as toxic [109]. When we consider the solvents in reported SrTiO$_3$ precursors, 1-methoxy-2-propanol could be found as a possible option, where in other chemical industries also it is used as a safer alternative for 2-methoxyethanol [112].

Considering these facts, 3 precursor solutions were prepared under a reader-friendly coding: Chemistry–I, Chemistry–II, and Chemistry–III, as described in table 2–3.

**Table 2–3 : Reader-friendly coding for the 3 precursors used here on in this thesis**

<table>
<thead>
<tr>
<th>Chemistry–I</th>
<th>2-methoxyethanol based precursor used in the previous chapter, reproduced to have qualitative comparison with following 2 precursors.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry–II</td>
<td>Precursor with non-moisture-sensitive Ti alkoxide</td>
</tr>
<tr>
<td>Chemistry–III</td>
<td>Precursor with an alternative for 2-methoxyethanol</td>
</tr>
</tbody>
</table>

The solution syntheses are described in 2.1 in chapter–2.
Chapter 2 — Motivation

2.2 – SrTiO₃ films with substrate dependency

On metal substrates, SrTiO₃ thin film fabrication as a buffer layer has been mainly reported only on nickel [058~061], and nickel-tungsten [076, 077, 084, 086] substrates. Also in our initial experiments, Ni-5at.%W substrates were used for SrTiO₃ thin film fabrication. Following the development of the SrTiO₃ precursor solution prepared by Chemistry–III, textured Cu-33at.%Ni substrates also have been tested for SrTiO₃ deposition, due to their following advantages.

① As a non-magnetic substrate material, Cu alloys would be promisingly beneficial for minimizing the hysteretic losses in coated conductors that are dominated by the irreversible magnetization of the superconducting film and the hysteretic movement of magnetic domains in the ferromagnetic substrates such as Ni/W substrates.
② Cu and commercial Cu alloys can be up to six times less expensive than Ni alloys [027], attributing a foreseeable cost efficiency in the industrial coated conductor applications
③ The ability of serving as a stabilizer whenever a suitable electrical connection is implemented between coated conductor and substrate.
④ Cu alloys have a high yield stress which is necessary for tape handling in real applications.

In all the thin films that we fabricated using our originally developed solution synthesis, significant differences have been noticed between Cu-33at.%Ni and Ni-5at%W substrates. Therefore, further investigations were performed in order to understand the substrate dependency of this SrTiO₃ precursor solution.

2.3 – Further optimizations of SrTiO₃ buffer thin film fabrication

In our work, we were successful in developing an original solution synthesis for SrTiO₃ precursor obtaining c-axis oriented thin films on Cu/Ni textured substrates. Furthermore, it is shown that the copper content of the substrate would be influencing the fine SrTiO₃ orientation probably by the means of oxide formations in the film/substrate interface. In this case, it would be very important to know the window of oxygen partial pressures that would be optimum for the interface oxide formation, in order to achieve an excellent orientation in the final SrTiO₃ thin
Further optimizations of SrTiO$_3$ buffer layers

film. Hence, SrTiO$_3$ thin film fabrication was performed in various different ambient atmospheres, to understand the influence of the oxygen partial pressure.

For the real application as buffer layers for YBCO deposition, the SrTiO$_3$ mono-layers have to show excellent barrier capabilities against metal ion diffusion from the metallic substrate. For this perspective, the SrTiO$_3$ mono-layers have to be as thick as possible, still maintaining excellent coverage and high degree of preferential orientation. Therefore, increasing the film thickness was attempted by increasing the concentration of the precursor solution, and by increasing the withdrawal speed during the dip-coating process.
Chapter — 3

Experimental

3.1 – Solution Synthesis

In our research, dip-coating based CSD method was employed for depositing the SrTiO₃ thin film buffer layers on technical substrates. The solution preparation was carried out in a glove box with Ar atmosphere, due to the moisture sensitivity of the starting chemicals. The solution syntheses are described below under a reader-friendly coding: Chemistry—I, Chemistry—II, and Chemistry—III.

3.1.1 – Chemistry—I

Strontium acetate + Acetic acid + Titanium butoxide + 2-Methoxyethanol

In our initial experiments referring the reported SrTiO₃ work [052, 054, 082, 087], strontium acetate [(CH₃CO₂)₂Sr; Sigma Aldrich] and titanium (IV) butoxide [Ti(O(CH₂)₃CH₃)₄; Sigma Aldrich] were used as Sr and Ti sources. Glacial acetic acid [CH₃COOH; Sigma Aldrich] and 2-methoxyethanol [CH₃O(CH₂)₂OH; Sigma Aldrich] were used as chelating agent and solvent. A rough layout of the solution synthesis is shown in figure 3–1.

Strontium acetate (CH₃COO)₂Sr + Acetic acid CH₃COOH
stirred at 70°C / 24 hours

Titanium (IV) butoxide Ti(OCH₂CH₂CH₂CH₃)₄ + 2-Methoxyethanol CH₃OCH₂CH₂OH
stirred at 70°C / 48 hours

mixed at 1:1 stoichiometric proportions
stirred at 70°C / 24 hours

colourless clear solution
stored / used at RT

Fig. 3–1: Solution synthesis with 2-Methoxyethanol

Strontium acetate was dissolved in glacial acetic acid, placed on a hot plate at 70°C for 24 hours, and continuously stirred using a magnetic stirrer. In a separate bottle, titanium (IV) butoxide was dissolved in 2-methoxyethanol, placed on a hot plate at 70°C for 48 hours, continuously stirring using a magnetic stirrer. Then the strontium solution and the titanium solution were
mixed together in 1:1 stoichiometric proportions, placed on a hot plate at 70°C for 24 hours, continuously stirring using a magnetic stirrer. After completing this synthesis, the final colourless clear solution with a total cation concentration of 0.3 M was left to cool down to room temperature, and used as the SrTiO₃ precursor for dip-coating process.

3.1.2 – Chemistry—II
Strontium acetate + Acetic acid + Titanyl 2,4-pentanedionate + Methanol

This precursor solution that has based on our original idea, was prepared using the reagents: strontium acetate [(CH₃COO)₂Sr] (Sigma Aldrich), glacial acetic acid [CH₃COOH] (Sigma Aldrich), titanyl 2,4-pentanedionate [C₁₀H₁₄O₅Ti] (Alfa Aesar), and anhydrous methanol [CH₃OH] (Sigma Aldrich). A rough layout of the solution synthesis is shown in figure 3–2.

![Diagram of solution synthesis](image)

Fig. 3–2 : Solution synthesis with non moisture-sensitive Ti source

The strontium solution was prepared using strontium acetate dissolved in glacial acetic acid with continuous stirring at 70°C. The titanium solution was prepared using titanyl 2,4-pentanedionate dissolved in anhydrous methanol with continuous stirring at 70°C. Then the final precursor solution with a total cation concentration of 0.4 M was obtained by mixing both sources in 1:1 stoichiometric proportions, with continuous stirring at 70°C for 24 hours. After completing this synthesis, let the final orange-coloured clear solution cool down to room temperature, and used as the SrTiO₃ precursor for dip-coating process.
**Solution synthesis**

3.1.3 – Chemistry–III

Strontium acetate + Acetic acid + Titanium isopropoxide + 1M2P + 2,4-Pentanedione

This precursor solution that has based on our original idea, was prepared using the reagents: strontium acetate [(CH₃COO)₂Sr] (Sigma Aldrich), glacial acetic acid [CH₃COOH] (Sigma Aldrich), titanium (IV) isopropoxide [Ti(OCH(CH₃)₂)₄] (Sigma Aldrich), 1-methoxy-2-propanol [CH₃CH(OH)CH₂OCH₃] (Sigma Aldrich), and 2,4-pentanedione [CH₃COCH₂COCH₃] (Sigma Aldrich). A rough layout of the solution synthesis is shown in figure 3–3.

The strontium source was prepared using strontium acetate dissolved in glacial acetic acid with continuous stirring at 70°C. The titanium source was prepared using titanium (IV) isopropoxide dissolved in 1-methoxy-2-propanol with continuous stirring at 70°C for 48 hours, followed by an addition of 10% vol. of 2,4-pentanedione at room temperature. Then the final precursor solution with a total cation concentration of 0.4 M was obtained by mixing both sources with continuous stirring at 70°C for 2 hours, and then let it cool down to room temperature.

![Diagram](image)

**Fig. 3–3**: Solution synthesis with 1-Methoxy-2-propanol
3.2 – Substrate preparation

In our work, home-made Ni/W and Cu/Ni alloy tapes were prepared respectively from cold-rolled Ni/W ingots and Cu/Ni ingots with the corresponding Ni contents. First, the ingots were mechanically polished using polishing clothes with grain size of 500 and 250μm. The ingots were cold-rolled applying a 5% per-pass-reduction that is supposed to result in a homogeneous deformation across the tape. Two rolling mills with 37.5 mm radius, and 10 mm radius smooth mirror-finished rolls were used for cold rolling. No lubricant was applied during rolling, to minimize the chemical contaminations. The tapes were initially rolled in the first mill to a thickness of 1 mm, and then rolled to the final thickness of 80 μm in second mill.

The cold rolled tape substrates and the Ni-5at.%W commercial tape substrates with thickness of 80μm [Evico GmbH] were cut into 1 cm × 2 cm pieces and annealed with thermal treatments in a N2-5%H2 reducing gas flow as shown in table 3–1. All the home-made substrates were annealed for the purpose of crystallization to obtain a high bi-axially textured surface, where the commercial textured substrates were annealed for the purpose of removing the oxides possibly formed during the storage. Details of the RTA process are described in section 3.4.

Table 3–1: Ni/W and Cu/Ni substrates used for SrTiO3 thin film deposition

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thermal treatment (RTA) in the N2-5%H2 gas flow</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-5at.%W (commercial tape)</td>
<td>Insert → 900°C / ⅓ hour → quench</td>
<td>To remove oxides</td>
</tr>
<tr>
<td>Ni-5at.%W (home-made tape)</td>
<td>Insert → 700°C / 1 hour → 1100°C / 2 hours → cool</td>
<td>To crystallize</td>
</tr>
<tr>
<td>Ni-5at.%W-5at.%Cu (home-made)</td>
<td>Insert → 700°C / ½ hour → 1050°C / 2 hours → cool</td>
<td>To crystallize</td>
</tr>
<tr>
<td>Cu-45at.%Ni (home-made)</td>
<td>Insert → 1000°C / 1 hour → quench</td>
<td>To crystallize</td>
</tr>
<tr>
<td>Cu-33at.%Ni (home-made)</td>
<td>Insert → 1000°C / 1 hour → quench</td>
<td>To crystallize</td>
</tr>
<tr>
<td>Cu-23at.%Ni (home-made)</td>
<td>Insert → 1000°C / 1 hour → quench</td>
<td>To crystallize</td>
</tr>
</tbody>
</table>

Before coating, all the substrates were ultrasonically cleaned in acetone [CH3COCH3] and / or ethanol [C2H5OH] as listed in table 3–2, and then dried in a flow of N2.
### Dip coating / Spin coating

Table 3–2: Ultrasonic cleaning of the substrates before each thin film deposition

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Time cleaned in acetone [CH₃COCH₃]</th>
<th>Time cleaned in ethanol [C₂H₅OH]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Metal alloy tapes without any deposited film</td>
<td>5 min</td>
<td>5 min</td>
</tr>
<tr>
<td>Metal alloy tapes with a deposited film</td>
<td>—</td>
<td>5 min</td>
</tr>
<tr>
<td>Single crystal substrates</td>
<td>5 min</td>
<td>5 min</td>
</tr>
</tbody>
</table>

3.3 – Dip coating / Spin coating

In our work, a vertically lifting dip coater (KSV Instruments: KSVDCX2) was used for most of the dip coatings with withdrawal speeds of 40 to 150 mm/min. The substrate’s lower end (around 2~5 mm) with a strong increase in film thickness caused by adhering liquid residues after withdrawing from the coating solution, were simply cut off after the coating process.

When applying a coating on CeO₂-coated substrate, spin-coating was employed in order to avoid the contamination of the precursor solution. Only in that experiment, all the coatings were applied using spin-coating in order match the depositing parameters.

In spin-coating technique, typically the substrate to be coated is held in place using a motor-driven vacuum chuck and the coating solution is dispensed on the substrate manually. The substrate is then accelerated to very high angular velocities (300 to 10000 rpm) during which the excess liquid is spun off from the substrate leaving thin uniform coating. Theory behind this coating technique involves the equilibrium between the centrifugal forces created by the rapid spinning and the viscous forces determined by the viscosity of the liquid. The film thickness can be varied by controlling the spin speed and time, as well as the viscosity of the solution. Empirically, it has been observed that the film thickness t is inversely proportional to the square root of the spin speed [104]. For our SrTiO₃ thin film depositions, spin-coater (MTI VTC–100 Vacuum Spin coater) was used with a spinning speed of 4000 rpm for duration of 30 s.
Chapter 3 — Experimental

3.4 – Rapid Thermal Annealing (RTA) process

In our research, single step RTA process was applied for both substrate preparation and film crystallization. Annealings were performed in 2 furnace set-ups as shown in the figure 3-4. For crystallization of home-made Ni/W, Ni/W/Cu and Cu/Ni substrates, a furnace setup was used as shown in setup A, setup A and setup B in the figure 3–4 respectively, where the employed heating profiles are illustrated in figure 3–5, 3–6 and 3–7 respectively.

Fig. 3–4 : Furnace set-ups used for annealing

Fig. 3–5 : Heating profile for the Ni/W home-made substrate crystallization
Rapid Thermal Annealing process

![Graph of heating profile](image1)

**Fig. 3–6**: Heating profile for the Ni-5%at.W-5%at.Cu substrate crystallization

![Graph of heating profile](image2)

**Fig. 3–7**: Heating profile for the home-made Cu/Ni substrate crystallization

In experiments where commercial Ni-5%at.W substrates were used, the tapes were annealed in a N₂-5%H₂ reducing gas flow for removing any oxide layers that could be existing on the substrate surfaces. Annealing was performed in a furnace set-up as shown in the setup B of figure 3–4 employed with a heating profile as shown in figure 3–8.

![Graph of heating profile](image3)

**Fig. 3–8**: Heating profile for the Ni/W commercial tape annealing

All the crystallized substrates were used for dip-coating within 6 hours, minimizing the chance of having oxidized surfaces. Otherwise, the substrates were annealed in N₂-5%H₂ using the heating profile in figure 3–8, in order to remove any oxide layers.
After the coating, followed by a drying step in reducing atmosphere of N₂-5%H₂ for ¼ to ½ hour, the coated samples were annealed in a tubular quartz furnace for single-step heat treatment, allowing the coated film to crystallize.

Depending on the furnace architecture, two heating profiles were employed for annealing the films. The architecture of the furnace setup A of figure 3–4 is not compatible for direct insertions/quenching possibilities. Therefore, in case of annealing of the samples at 950°C in reducing atmosphere of N₂-5%H₂ for 1 hour, the heating profile is applied as shown in figure 3–9.

![Heating profile for the film-annealings in the furnace setup A of figure 3–4](image)

**Fig. 3–9 :** Heating profile for the film-annealings in the furnace setup A of figure 3–4

The furnace setup B of figure 3–4 provides the possibility of inserting/quenching the sample directly into/from the annealing temperature. In a case of an annealing of the samples at 950°C in reducing atmosphere of N₂-5%H₂ for 1 hour, the heating profile is shown in figure 2–10.

![Heating profile for the film-annealings in the furnace setup B of figure 3–4](image)

**Fig. 3–10 :** Heating profile for the film-annealings in the furnace setup B of figure 3–4
3.5 – Oxygen sensing at the RTA process

When fabricating oxide thin films, precise control of the oxygen partial pressure would become a key issue. Therefore in our work, oxygen sensor was utilized as illustrated in the furnace setup A in figure 3–4.

When exposed to different oxygen partial pressures at the outside and inside of the sensor, at a high temperature (\( > 650^\circ\text{C} \)), an EMF \((E)\) is developed which obeys the Nernst equation as shown in equation 3–1, where \( T \) = temperature (in Kelvin) at the sensor, \( R \) = gas constant 8.3144621 \( \text{Jmol}^{-1}\text{K}^{-1} \), \( F \) = Faraday constant \( 9.648534 \times 10^4 \text{ Cmol}^{-1} \), and \((pO_2)_{\text{inside}}\) and \((pO_2)_{\text{outside}}\) are oxygen partial pressures at the inner and outer electrodes respectively, with the higher oxygen partial pressure electrode being positive.

\[
E \ [\text{millivolts}] = \frac{RT}{4F} \log_e \left( \frac{(pO_2)_{\text{inside}}}{(pO_2)_{\text{outside}}} \right) \quad 3–1
\]

If dry air at atmospheric pressure, (21 % oxygen) is used as a reference gas at the inner electrode, it could be written as follows.

\[
E \ [\text{millivolts}] = 2.154 \times 10^{-2} T \log_e \left( \frac{0.21}{(pO_2)_{\text{outside}}} \right) \quad 3–2
\]

Transporting this equation, the final equation could be derived as equation 3–3.

\[
(pO_2)_{\text{outside}}[\text{in Atm}] = 0.215 \times 10^{-2} T \log_e \left( \frac{-46.421E}{T} \right) \quad 3–3
\]

3.6 – Ambient environment at the RTA process

In most of our work, ambient environment in the RTA processes was created with a flow of \( \text{N}_2-5\%\text{H}_2 \). In experiments with different \( O_2 \) partial pressure, films deposited on Ni-5\%W commercial substrates were annealed in a reducing atmosphere containing \( \text{N}_2-5\%\text{H}_2 \), where the ambient oxygen partial pressure was controlled by introducing a small flow of \( \text{N}_2-1\%\text{O}_2 \). To obtain different \( O_2 \) partial pressures on the films deposited on Cu/Ni substrates, annealing was done in a \( \text{N}_2, \text{Ar}-2\%\text{H}_2, \text{N}_2-5\%\text{H}_2, \) or \( \text{N}_2-9\%\text{H}_2 \) flow. The wet \( \text{N}_2-5\%\text{H}_2 \) atmosphere was created by passing
Chapter 3 — Experimental

the wet $N_2$-$5\%H_2$ flow through a water beaker bubbling at room temperature before introducing the flow into the annealing furnace.
Chapter — 4

Characterization Procedures

Throughout our research on SrTiO3 thin film fabrication, several characterization procedures were employed in the view of performing accurate optimizations.

4.1 – Thermogravimetry (TG) / Differential Scanning Calorimetry (DSC)

The behaviour of the precursor materials as a function of temperature was investigated using a DSC/TGA instrument: STA 449C Jupiter [Netzsch]. Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) monitors heat effects associated with phase transitions and chemical reactions as a function of temperature and is a very informative method in physical characterisation of a compound. These experiments have been done using the powders obtained by completely drying the precursor solution in 40°C. And then the dried powders were ground into fine powders in order to decrease the effect of the particle size in the final powder sample. In DSC, the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference used in our experiments was an empty alumina (Al2O3) crucible. The temperature of both the sample and reference was increased at a constant ramping rate of 5°C/min. Measurements were performed up to 950°C in a carrier gas consisting of argon at atmospheric pressure. The gas flow was fixed at 40 ml/min.

Since the Differential Scanning Calorimeter is at constant pressure, heat flow dq/dt is equivalent to enthalpy changes which is given by equation 4–1, where q, p, H and t is representing energy, pressure, heat and time respectively.

\[
\left( \frac{dq}{dt} \right)_p = \frac{dH}{dt} \quad \text{4–1}
\]

\[
\frac{\Delta dH}{dt} = \left( \frac{dH}{dt} \right)_{\text{sample}} - \left( \frac{dH}{dt} \right)_{\text{reference}} \quad \text{4–2}
\]

Here Dh/dt is the heat flow measured in mcal sec⁻¹. The heat flow difference between the sample and the reference is calculated by equation 4–2 and can be either positive or negative. In an endothermic process where a transition which absorbs energy, such as most phase transitions, decomposition reactions, dehydrations, reduction reactions, etc. heat is absorbed.
Therefore, heat flow to the sample is higher than that to the reference. Hence $\Delta dH/dt$ is positive. In an exothermic process where the transition which releases energy, such as crystallization, some cross-linking processes, oxidation reactions, and some decomposition reactions, $Dh/dt$ is negative.

Fig. 4–1: Schematic setup of the TG/DSC analysis

The calorimeter consists of a sample holder and a reference holder made of platinum. Under each holder is a resistance heater and a temperature sensor. Currents are applied to the two heaters to increase the temperature at the selected rate. The difference in the power to the two holders, necessary to maintain the holders at the same temperature, is used to calculate $\Delta Dh/dt$. A schematic diagram of a TG/DSC is shown in figure 4–1. A flow of Argon gas is maintained over the samples to create a reproducible and dry atmosphere, also eliminating air oxidation of the samples at high temperatures.

During the heating of a sample, peaks with positive and negative $\Delta Dh/dt$ may be recorded where each peak corresponds to a heat effect associated with a specific process, such as phase transitions, decomposition reactions, crystallization, melting, etc.

In our research, all the analysis results were corrected with the baseline, which was collected on empty the Al$_2$O$_3$ crucibles that were used to contain the powder samples.
4.2 – Infra-red (IR) spectrometry

IR spectrometry is an analytical technique used to qualify and quantify compounds utilizing infrared absorption of molecules. Absorption in the infrared region results in changes in vibrational and rotational status of the molecules. The absorption frequency depends on the vibrational frequency of the molecules, whereas the absorption intensity depends on how effectively the infrared photon energy can be transferred to the molecule, and this depends on the change in the dipole moment that occurs as a result of molecular vibration. As a consequence, a molecule will absorb infrared light only if the absorption causes a change in the dipole moment. Thus, all compounds except for elemental diatomic gases such as N₂, H₂ and O₂, have infrared spectra and most components present in a flue gas can be analysed by their characteristic infrared absorption.

Fig. 4–2: Schematic diagram of the optical setup of an FTIR spectrometer

In a FTIR instrument, a projected beam of IR radiation is divided into two beams by means of a beam splitter. A path difference between the beams is introduced whereupon they are allowed to recombine. In this way, interference between the beams is obtained and the intensity of the output beam from the interferometer can be monitored as a function of path difference using an appropriate detector. An ideal beam splitter consists of a non-absorbing film which transmits 50% of the radiation to the mirror, which is moving back and forth at a constant speed, whereas 50% of the radiation is reflected to the fixed mirror. After being reflected, the
two beams will recombine at the beam splitter where interference between the beams takes place. The complex pattern of overlaid sinusoidal waves of light (in the time domain) is known as an interferogram. This interferogram is converted back to the original frequency distribution (spectrum) by means of a Fourier transform, which is done very rapidly on a PC.

In our work, FTIR spectra were recorded by means of a Bruker Tensor 27 spectrometer coupled to the exhaust line of the TG/DTA device by a transfer line heated to 200°C.

4.3 – X Ray Diffraction (XRD)

In this research, the X-ray diffraction technique was used to characterize the phase content and evaluate the texture of the samples. Initial measurements were performed in a STOE diffractometer with Cu-Kα radiation, backed by a voltage of 40 Kv and a current of 30 Ma, respectively. Further characterization was performed using a BruckerD8 Advanced x-ray diffractometer with a voltage of 20Kv and a current of 20Ma, respectively. The X-rays were generated by a Cu anode producing Cu-Kα₁ and Cu-Kα₂ radiations with wave lengths of 1.5406 Å and 1.5444 Å, respectively, with a relative intensity ratio Kα₂/Kα₁ of 0.5. For most of the θ–2θ measurements at room temperature, the data were collected for a range of θ = 28°~48° at a step size of 0.02° and a scanning speed of 2 s/step.
Texture analysis using X-ray Diffraction has typically been performed via the use of pole figure measurement. Such measurements are typically performed by fixing the $2\theta$ angle (i.e. constant d-spacing) and rocking the sample through $\chi$ (tilt) angles and $\phi$ (spindle) rotations via a Texture Cradle attachment. It consists of a series of $\phi$ –scans (in-plane rotation around the centre of the sample) at different tilt or $\Psi$ –(azimuth) angles, as illustrated in the figure 4–3. The pole figure data are displayed as contour plots or elevation graphs with zero angle in the centre.
4.4 – Synchrotron X Ray Powder Diffraction (SXPĐ)

In our research, the *in-situ* experiments were carried out on powder samples to check the presence / transition of any intermediate phases during the applied thermal treatment. These in-situ experiments were carried out in a BW5 beam line facilitated in the DORIS III Synchrotron facility of Deutsches Elektronen-Synchrotron (DESY) – Hamburg Synchrotron Radiation Laboratory (HASYLAB), in Hamburg (Germany). Positrons at energy of 4.445 GeV were used, that has been stored in the storage ring with circumference of 289 meters. Typically 5 bunches of positrons were stored in DORIS III with an initial beam current of up to 120 Ma. The schematic architecture of the experimental setup at the beamline BW5 is shown in figure 4–4.

![Schematic architecture of the experimental setup at BW5](image)

Fig. 4–4 : Schematic architecture of the experimental setup at BW5

The powder samples were wrapped in nickel foil and clamped in a high-temperature steel holder inserted in a quartz tube. The sample holder assembly was placed in a high-temperature furnace equipped with polymer (Kapton) windows and a stainless steel heat shield with holes for beam entrance and exit. Heat treatment consisted with a heating rate of 5°C/min up to 900°C. During the heat treatment which was identical to the heat profile used in SrTiO3 film
Characterization Procedures

annealing, a constant Ar-5%H₂ flow was introduced to the in-situ furnace. The incident beam was set to 80 keV (λ=0.155 Å), allowing it to penetrate the furnace and the powder sample packed with nickel foil. The diffraction patterns are recorded on an area detector (MAR345). Due to the much higher scattered intensity from the nickel foil, compared to that of the SrTiO₃ powder, a lead pinhole screen is mounted in the right position between the sample and the detector to just hide the diffraction spots from the Ni (200) reflection. Beam size of 1 mm² is used in this experiment, allowing a significant volume of powder to get illuminated. The two dimensional scattering data were handled by the dedicated Fit2D software. The intensity of the signal was normalized to the synchrotron positron beam current value, which varies with time during the experiment.

4.5 – Scanning Electron Microscopy (SEM)

Microstructural investigations were performed using a Supra 35 [Zeiss] Field Emission Gun Scanning Electron Microscope (FEGSEM). The SEM technique utilizes a focused electron beam which is scanned in order to generate an image of the sample’s surface morphology. The spatial resolution of this technique is dependent on the specimen material, beam current, and acceleration voltage. When an electron beam interacts with the specimen material, two of the commonly used signals that are generated; i.e. Secondary Electrons (SE), and the Backscattered Electrons (BSE). The contrast of SE imaging depends mainly on the sample topography while the contrast in BSE imaging is highly dependent on the atomic number and the crystallographic orientation of the sample. In our research, acceleration voltage of 3 Kv was applied for all SEM imaging. And, in-lens field emission mode was used for the high resolution, due to the poor conductivity of the SrTiO₃ thin films.

4.6 – Electron BackScatter Diffraction (EBSD)

In order to investigate on in-plane surface texture of the fabricated thin films, Electron BackScatter Diffraction (EBSD) mapping was performed on selected samples. EBSD patterns are obtained in the SEM by focusing a stationary electron beam on a crystalline sample. The sample is tilted approximately to an angle of 70° with respect to the horizontal plane. When the primary beam interacts with a crystal lattice, low energy loss backscattered electrons are
channelled and are subject to path differences that lead to constructive and destructive interference. If a phosphor screen is placed a short distance from the tilted sample, in the path of the diffracted electrons, a diffraction pattern can be seen. The image is captured using a low-light CCD camera. The bands in the pattern represent reflecting planes in the diffracting crystal volume. Thus, the geometrical arrangement of the bands is a function of the orientation of the diffracting crystal lattice. These EBSD patterns are analyzed by the facilitated software detecting a number of Kikuchi bands using an optimized Hough transform. With a priori information about the candidate phases under the beam, all possible orientations with each phase can be determined with the best fit to the identified phase and orientation. The EBSD patterns are then considered indexed when its orientation and phase are known.

After the analysis, the phase and orientation is visualized by mapping with coloured pixels corresponding to the each scanning point, based on a scale that represents the orientations distribution. If the system was unable to measure the orientation, the corresponding pixel is recorded as a zero-solution. An enormous variety of additional visual and analytical information can be obtained including overall preferred orientation (texture), prevalence and distribution of grains in specific orientations, phase distribution, state of strain and local variations in residual strain, and character and distribution of grain boundaries. Zero-solutions can come from points where no EBSD pattern is available, where overlapping patterns cannot be resolved, or when a new phase is encountered. This also happens when the sample surface deformation is so high that there is no coherent diffraction or when a noncrystalline material is encountered. Overlapping EBSD patterns occur at grain boundaries when the electron beam diameter is large enough to produce the patterns from two grains simultaneously.

Our EBSD work was performed on a Zeiss CrossBeam 1540XB™ [Zeiss, Oberkochen, Germany] equipped with an Oxford Instruments Nordlys S™ EBSD detector [Oxford Instruments, Hobro, Denmark]. Oxford Instruments’ [High Wycombe, UK] software was used for EBSD data collection (HKL Fast Acquisition 1.2) and analysis (Channel 5).
Characterization Procedures


In our study, the Cu/Ni diffusion into the SrTiO$_3$ thin films, was investigated through depth profiles using TOF–SIMS measurements. A TOF-SIMS instrument is best described as an extremely sensitive (ppm to ppb) surface mass spectrometer. [105] The SIMS is the mass spectrometry of ionized particles which are emitted from the surface when energetic primary particles bombard the surface. The pulsed primary ions with the energy of 1~25 keV, typically liquid metal ions such as Ga$^+$, Cs$^+$, O$^-$, etc. are used to bombard the sample surface, causing the secondary elemental or cluster ions to emit from the surface. The secondary ions are then electrostatically accelerated into a field-free drift region with a nominal kinetic energy $E_k$ that can be shown as formula 4–3.

$$E_k = eV_0 = \frac{mv^2}{2} \quad 4–3$$

Since $V_0$ is the accelerating voltage, $m$ the mass of ion, $v$ the flight velocity of ion, $e$ its charge, from the above formula it is evident that the ion with lower mass has higher flight velocity than one with higher mass. Thus they will reach the secondary-ion detector earlier. As a result, the mass separation is obtained in the flight time $t$ from the sample to the detector.

$$t = \frac{L}{\sqrt{2eV_0/m}} \quad 4–4$$

The flight time $t$ is expressed by formula 4–4, where $L$ is the effective length of the mass spectrometer. A variety of mass ions are recorded by the detector with the time sequence to give the SIMS spectrum. The resulting mass spectrum contains an overwhelming amount of information, e.g. on contamination, molecular structure, and chemical state of the sample surface. Rastering the primary ion beam over an area of the sample surface enables visualization of the surface chemistry in the lateral plane (imaging). If a sputter gun (removes material from the surface) is used in conjunction with the analysis gun, full 3D information can be obtained, i.e. the vertical distribution of chemistry can be mapped (depth profiling).

In this work, the TOF-SIMS analyses were performed using a TOF-SIMS IV facility [ION-TOF GmbH, Münster, Germany]. 25-ns pulses of 25 keV Bi$^+$ primary ions were bunched to form ion
packets with a nominal temporal extent of < 0.9 ns at a repetition rate of 10 kHz, yielding a target current of 200 Fa. These primary ion conditions were used to obtain mass spectra and depth profiles. Mass spectra were obtained on three different surface locations (100×100 µm²) for 30 s. Depth profiling was performed using an analysis area of 200×200 µm² centered in a sputter area of 300×300 µm². 28 Na of 3 keV Xe⁺ ions was used as sputter ions. Ion images (500×500, 200×200, 100×100, 50×50, and 20×20 µm²) were obtained using ~10 Fa of Bi⁺ ions at a lateral resolution of ~200 nm. For all analyses electron bombardment (20 Ev) was used to minimize charge build-up at the surface. Desorbed secondary ions were accelerated to 2 keV, mass analyzed in the flight tube, and post-accelerated to 10 keV before detection.

4.8 – Atomic Force Microscopy (AFM)

Surface topography was characterized by contact mode Atomic Force Microscopy (AFM) using DS95-50 from DME – Danish Micro Engineering. The images were acquired in tapping mode, 20×20 µm scans at a resolution of 128×128 pixels and at a scan speed of 8 µm/s with the ScanTool software.

This technique utilizes a probe which is brought into contact with the sample material and then scanned across the sample surface. Tapping mode imaging is implemented by oscillating the cantilever assembly at or near the cantilever’s resonant frequency using a piezoelectric crystal. The piezo motion causes the cantilever to oscillate with a high amplitude when the tip is not in contact with the surface. The oscillating tip is then moved toward the surface until it begins to lightly touch, or tap the surface. During scanning, the vertically oscillating tip alternately contacts the surface and lifts off, generally at a frequency of 50,000~500,000 cycles per second. As the oscillating cantilever begins to intermittently contact the surface, the cantilever oscillation is necessarily reduced due to energy loss caused by the tip contacting the surface. The reduction in oscillation amplitude is used to identify and measure surface features.

During tapping mode operation, the cantilever oscillation amplitude is maintained constant by a feedback loop. Selection of the optimal oscillation frequency is software-assisted and the
Characterization Procedures

force on the sample is automatically set and maintained at the lowest possible level. When the tip passes over a bump in the surface, the cantilever has less room to oscillate and the amplitude of oscillation decreases. Conversely, when the tip passes over a depression, the cantilever has more room to oscillate and the amplitude increases (approaching the maximum free air amplitude). The oscillation amplitude of the tip is measured by the detector and input to the controller electronics. The digital feedback loop then adjusts the tip-sample separation to maintain a constant amplitude and force on the sample.

When the tip contacts the surface, the high frequency (50k~500k Hz) makes the surfaces stiff (viscoelastic), and the tip-sample adhesion forces is greatly reduced. Tapping mode inherently prevents the tip from sticking to the surface and causing damage during scanning. Unlike contact and non-contact modes, when the tip contacts the surface, it has sufficient oscillation amplitude to overcome the tip-sample adhesion forces. Also, the surface material is not pulled sideways by shear forces since the applied force is always vertical. Another advantage of the tapping mode technique is its large, linear operating range. This makes the vertical feedback system highly stable, allowing routine reproducible sample measurements.

The images were plane corrected and the line mean function was applied. Roughness calculations were performed with the built-in function.
Chapter — 5
SrTiO$_3$ by novel solution synthesis

5.1 – XRD of SrTiO$_3$ mono-layers

XRD scans from the annealed films deposited on commercial Ni-5at.%W textured substrates using a constant withdrawal speed of $\uparrow$60mm/min. were resulted with the diffraction peaks near $2\theta \approx 32.4^\circ$ and $46.5^\circ$ that correspond to the SrTiO$_3$ (110) and (200) reflections. The thickness of the films measured by ellipsometry was estimated to approximately 80 nm. SrTiO$_3$ thin film fabricated from the originally developed solution (Chemistry–III) on Ni-5at.%W commercial substrates at annealing temperature of 950°C exhibit an excellent c-axis orientation as shown by XRD $\theta$–$2\theta$ scans in figure 5–1.

![XRD scans comparison](image)

Fig.5–1 : XRD $\theta$–$2\theta$ scans of SrTiO$_3$ mono-layers deposited from different SrTiO$_3$ precursors

The SrTiO$_3$ precursor from Chemistry–I was not resulting in any satisfactory orientation this time, even the same recipe was successfully used before as mentioned in the previous chapter. As discussed earlier in 5.2 in this chapter, the poor reproducibility we have been facing when
using this reported precursor can be clearly notable also through this result. Even though a slight c-axis orientation could be observed in the film from the precursor of Chemistry–II, it was not comparable with the film from new developed precursor (Chemistry–III). This SrTiO$_3$ precursor solution was successfully used to achieve SrTiO$_3$ films with large Relative Peak Intensities ($RPI_{(200)} > 85\%$) over 3 months, attributing a ‘practical’ lifetime of 3 months approximately (as shown in table 5–4), where it is stable without any precipitation at least for one year, attributing much longer ‘physical’ lifetime.

<table>
<thead>
<tr>
<th>Precursor</th>
<th>$RPI_{(200)}$</th>
<th>‘physical’ lifetime</th>
<th>‘practical’ lifetime (with $RPI_{(200)} &gt; 85%$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemistry–I</td>
<td>≈ 65 %</td>
<td>≈ 4 months</td>
<td>—</td>
</tr>
<tr>
<td>Chemistry–II</td>
<td>≈ 59 %</td>
<td>≈ 2 months</td>
<td>—</td>
</tr>
<tr>
<td>Chemistry–III</td>
<td>≈ 87 %</td>
<td>≈ 13 months</td>
<td>≈ 3 months</td>
</tr>
</tbody>
</table>

5.2 – Thermal behaviour of the novel SrTiO$_3$ precursor material

The data obtained from TG of the dried powder of Chemistry–III precursor, was plotted with the DSC curve, as shown in figure 5–2. The TG trace of the powder obtained from the SrTiO$_3$ precursor exhibits mass losses at around 250°C, 350°C, and 450°C. In the DSC trace, exothermic peak at 124°C seems to be associated with the boiling of Acetic acid, where the boiling point of acetic acid is 118°C. The endothermic peak seen at 237°C might be due to a reaction occurring in the precursor materials, followed by the decompositions of the organic contents that result with the exothermic peaks seen at 329°C, 358°C and 440°C. Even though the exact reaction, and the organic decomposition could not be identified specifically, it is obvious that the starting material is undergoing a total mass loss of 45\% approximately, during the whole measurement. This reduction is expected to be the result mainly from the decomposition of organic content. The exothermic peak at 920°C might be associated with a decomposition of an intermediate product. In literature on SrCO$_3$, decomposition of SrCO$_3$ is reported near 925°C when heated at 10°C/min heating ramp in argon [114]. Therefore, the exothermic peak at 920°C in our
measurement likely to represent the decomposition of SrCO₃, which might had formed during the decompositions of organic contents.

Fig. 5–2: DSC and mass loss analysis of the powder obtained from the new SrTiO₃ precursor

FTIR spectrums of the evolved gas at several specific temperatures are shown in figure 5–3. Up to 182°C, no peaks could be seen in the FTIR spectrum implying no evidence of IR-detectable gas releases. Based on the references [115, 116] related to IR analysis, an idea on the possible gas releases would be constructed as follows.

At 232°C, the peaks at 1762 cm⁻¹ and 1797 cm⁻¹ would be corresponding to the C=O stretch of the carbonyl groups in the sample. This would be due to a start of an evaporation of an ester and residual acetic acid. This ester would be a product in the dried powder, where a possible esterification occurred between acetic acid and 1-methoxy-2-propanol in this powder’s originating precursor solution.
Fig. 5–3 : FTIR analysis of the evolved gases from the SrTiO₃ powder during the thermal treatment. (\(a\) : C=O symmetric stretch in acetic acid \(e\) : C=O vibrations in an ester \(c\) : C=O vibrations in CO₂ \(p\) : C=O vibrations in 2,4-pentanedione \(m\) : –O–CH₃ vibrations in 1M2P)

Even after the normal boiling point of acetic acid 118°C, the –COOH ligand would exist in the powder as residual acetic acid. After 294°C, peaks appearing at around 2358 cm⁻¹ could be identified as CO₂ releases that could be associated with decompositions of the organic components that would exist in the dried powder. Increased peak intensities at 1762 cm⁻¹ and 1797 cm⁻¹ at 294°C would be due to a partial decomposition and also the further evaporation of the ester and residual acetic acid. This seems to be further facilitated until 324°C showing a growth especially in the peak at 1797 cm⁻¹. At 324°C, a peak at 1238cm⁻¹ becomes very significant, which corresponds to –CH₃ rock vibrations which are expected to appear in 1187~1248 cm⁻¹. Therefore a release from –CH₂–O–CH₃ fragment of 1-methoxy-2-propanol would be occurring in the sample.
Thermal behaviour of the SrTiO₃ precursor material

At 385°C, this peak gets decreased while the CO₂ peaks at 2358 cm⁻¹ is very high. This is probably associated with the mass loss occurring at 350°C. This can be thought as a start of a decomposition of the resulting product left after evaporation steps. Peak from 1737 cm⁻¹ would be expected as a C=O group that is released from 2,4-pentanedione. At 463°C, this release is still occurring with a small increase of the peak at 1737 cm⁻¹. Even the normal boiling point of 2,4-pentanedione is 140°C, the presence of that legend still until 463°C suggests that the 2,4-pentanedione would probably be strongly bonded in the solution. Since this might correspond to the mass loss at 450°C, a decay of a metal organic compound might be possible, which associate to the decomposition of C=O groups in the metal organic salt. Intense CO₂ peaks at 2358 cm⁻¹ at 923°C could be thought as a CO₂ release occurring from the decomposition of SrCO₃, corresponding to the exothermic peak at 920°C in the DSC trace.

The key effective performance of this SrTiO₃ precursor is thought to be mainly due to the combination of titanium isopropoxide + 1-methoxy-2-propanol + 2,4-pentanedione, where the chemical structures were schematically shown in figure 5–4. In solution, the chemical reactivity of metal alkoxides towards hydrolysis and condensation mainly depends on the steric hindrance of alkoxide groups [117]. The isopropoxide groups are expected to be effective to form bridges between titanium cations on the film surface because the steric hindrance is relaxed due to the reduced number of alkoxide groups per titanium cations [060]. But, under the alcohol exchange reactions, a new organic network is expected to be formed with the alcohol ligand coming from the 1-methoxy-2-propanol or 2-methoxyethanol. As shown as in figure 5–5, exchange reaction with a secondary alcohol like 1-methoxy-2-propanol would result in much complex network, compared to an exchange reaction with a primary alcohol like 2-methoxyethanol.
Fig. 5–4: Schematic reference of the ingredient chemicals in the Strontium solution (upper row) and the Titanium solution (lower row).

Fig. 5–5: Alcohol exchange of Ti isopropoxide with 2-methoxyethanol (upper row) and 1-methoxy-2-propanol (lower row).

In figure 5–5, the resulting molecules from 1-methoxy-2-propanol would be thought to have a higher steric hindrance in the molecules due to their –CH₃ ligands, compared to the steric hindrance in the result from 2-methoxyethanol.

With the addition of a strong complexing ligands such as β-diketonates like 2,4-pentanedione, and acids like acetic acid, metal-oxo polymers are known to be formed while some of the ligands are still bonded to the titanium, as illustrated as in figure 5–6 [118]. And, it is also
known that the addition of acetylacetone leads to an increase in the coordination number of the metal in the precursor [122].

Fig. 5–6: Moderation of Titanium alkoxide by 2,4-Pentanedione as a complexing ligand.

Based on these reference, the resulting organic networks in our precursor would also be much complex, possibly ending up with complicated 3 dimensional network. Therefore, resulting molecules from 1-methoxy-2-propanol (shown in figure 5–5) with higher steric hindrance, would be thought to end up with complicated metal-organic network. Higher spatial hindrance could limit the mobility of the molecules, supporting to form a stable alignment in the final metal-organic network in the wet (dip-coated) film. During the steps of drying and decomposition, organic content would be thought to get disappeared, possibly leaving a homogeneous metal atomic matrix in the amorphous film. That kind of homogeneous metal atomic network would be a beneficial influence for achieving a good crystallographic orientation during the process of crystallization.
Chapter 5 — SrTiO₃ by novel solution synthesis

5.3 — Synchrotron studies of the precursor materials

Following results were achieved from the in-situ experiments performed on powder samples of Chemistry–III precursor to check the presence / transition of any intermediate phases. A synchrotron diffraction pattern obtained from the SrTiO₃ powder heated at 880°C for ¼ hour, is shown in figure 5–7. Figure 5–8 shows the radially integrated Synchrotron diffraction scans from the SrTiO₃ powder recorded at different temperatures during the in-situ thermal treatment.

Fig. 5–7: Synchrotron diffraction patterns from the SrTiO₃ powder obtained at 880°C during the in-situ thermal treatment

There are no any significant intermediate phases seen during the in-situ synchrotron session. Although an intermediate phase of SrCO₃ was expected based on the TG/DSC analysis in chapter–5, absence of any SrCO₃ peaks suggests that this SrCO₃ phase might be forming as an amorphous state. The growth of the SrTiO₃ (110) and (200) peaks seems to start at around 615°C, suggesting this as the starting temperature of SrTiO₃ crystallization.
Synchrotron studies of the precursor materials

Fig. 5–8: Radially integrated Synchrotron diffraction scans from the SrTiO$_3$ powder recorded at different temperatures during the *in-situ* thermal treatment.

5.4 – Conclusion

A new precursor solution for SrTiO$_3$ buffer layers has been successfully developed with the reagents of strontium acetate + acetic acid + titanium isopropanoxide + 1-methoxy-2-propanol + 2,4-pentanedione. The SrTiO$_3$ precursor solution has a ‘practical’ lifetime of several months, where it is stable at least for one year, having much longer ‘physical’ lifetime compared to the other precursors. Furthermore, the SrTiO$_3$ precursor solution is less toxic in comparison to highly toxic 2-methoxyethanol, TFA or methanol, which is commonly used for this kind of precursor solution preparation [053, 059, 060, 067, 068, 078].
Chapter — 6

SrTiO$_3$ films with substrate dependency

6.1 – SrTiO$_3$ thin films on different templates (buffer, metal tapes, single crystals)

XRD $\theta$–2$\theta$ scans of the deposited films on five different suitable templates (Ni-5at.%W, CeO$_2$ buffered Ni-5at.%W, Y-ZrO$_2$, LaAlO$_3$, Cu-33at.%Ni) are shown in figures 6–1 ~ 6–4. SrTiO$_3$ grown on the Cu-33at.%Ni tape substrate (figure 6–1) shows a good c-axis orientation of the SrTiO$_3$ grains. Here it is notable that the film thickness is thinner than the films fabricated by dip-coating using a withdrawal speed of $\uparrow 60$mm/min., where the thickness of the spin-coated films measured by ellipsometry was estimated to approximately 40 nm. SrTiO$_3$ grown on the Ni/5at.%W substrate and CeO$_2$ buffered Ni-5at.%W substrate (figure 6–2) resulted in unsatisfactory out-of-plane orientation.

SrTiO$_3$ c-axis orientation on the Y/ZrO$_2$ single crystal substrate (figure 6–3), was the worst among these tried substrate selection, as shown by the higher SrTiO$_3$ (110) peak. SrTiO$_3$ grown on the LaAlO$_3$ single crystal substrate (figure 6–4) shows an excellent out-of-plane orientation indicating a sharp c-axis oriented growth of the SrTiO$_3$ grains.
Fig. 6–1: SrTiO$_3$ thin film on Cu-33at.%Ni tape substrate

Fig. 6–2: SrTiO$_3$ thin film on Cu-5at.%Ni tape substrate

Fig. 6–3: SrTiO$_3$ thin film on Y/ZrO$_2$ single crystal substrate

Fig. 6–4: SrTiO$_3$ thin film on LaAlO$_3$ single crystal substrate
SrTiO₃ films with substrate dependency

Table 6–1: Lattice mismatch of each template with SrTiO₃

<table>
<thead>
<tr>
<th>Substrate / Template</th>
<th>Lattice constant</th>
<th>Mismatch with SrTiO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-5at.%W</td>
<td>0.3523 nm</td>
<td>−10 % (cube-on-cube)</td>
</tr>
<tr>
<td>CeO₂ buffered Ni-5at.%W</td>
<td>0.5411 nm</td>
<td>39 % (cube-on-cube)</td>
</tr>
<tr>
<td></td>
<td>0.3826 nm (diagonal)</td>
<td>−2 % (cube-on-diagonal)</td>
</tr>
<tr>
<td>Cu-33at.%Ni</td>
<td>0.3582 nm</td>
<td>−8 % (cube-on-cube)</td>
</tr>
<tr>
<td>Y-ZrO₂</td>
<td>0.5101 nm</td>
<td>31 % (cube-on-cube)</td>
</tr>
<tr>
<td></td>
<td>0.3607 nm (diagonal)</td>
<td>−8 % (cube-on-diagonal)</td>
</tr>
<tr>
<td>LaAlO₃</td>
<td>0.3793 nm</td>
<td>−3 % (cube-on-cube)</td>
</tr>
</tbody>
</table>

The lattice mismatch between each substrate template and SrTiO₃ is shown in table 6–1. The lattice parameter difference between SrTiO₃ and CeO₂ for a cube-on-cube growth is very large. In the reported literature about CeO₂ growth on Ni substrates [079], CeO₂ epitaxial growth is found to be rotated by 45° with respect to Ni to adjust the lattices. If this cube-on-diagonal epitaxy is occurring also in the case of SrTiO₃ on CeO₂, the diagonal of the CeO₂ lattice is expected to match with the SrTiO₃ unit cell with a low lattice mismatch of −2%. However, the XRD results shown in figure 6–2 suggest that the weak c-axis oriented SrTiO₃ growth on CeO₂ would not supported by such mechanism.

In these results, it is evident that the solution from Chemistry–III is resulting good c-axis orientation only on Cu-33at.%Ni and on LaAlO₃ single crystal, among the selected template materials, showing a strong substrate dependency for the epitaxial growth of SrTiO₃. When compared to the reported SrTiO₃ buffer layers [059, 060] on Ni substrates, our SrTiO₃ layer on Cu-33at.%Ni exhibits no undesired (110) SrTiO₃ reflection.
Chapter 6 — SrTiO$_3$ films with substrate dependency

6.2 — SrTiO$_3$ thin films on different Cu/Ni substrates

The XRD $\theta$–2$\theta$ scans of the deposited films on Ni-5at.%W, Ni-5at.%W-5at.%Cu, Cu-45at.%Ni, Cu-33at.%Ni, and Cu-23at.%Ni substrates using dip-coating with a withdrawal speed of ↑100 mm/min. are shown in figure 6–5. The SrTiO$_3$ films grown on Cu-23at.%Ni and Cu-33at.%Ni have the best c-axis orientations. Even though all the used substrates were high cube-textured substrates, it seems that the Ni-5at.%W and Ni-5at.%W-5at.%Cu substrates are not constituting a good crystallographic support for the SrTiO$_3$ grain orientation. In Cu/Ni substrates, specific copper contents seem to be optimum for the strong c-axis orientation.

It is known that higher copper contents in the Cu/Ni substrates result in a higher sensitivity to copper oxidation due to the very high diffusivity of Cu ions through CuO/Cu$_2$O and the
SrTiO$_3$ thin films on different Cu/Ni substrates

consequent inability of the native metal oxide to be self-protective especially at YBCO processing conditions [027]. When the coated film is annealed in a reducing atmosphere of N$_2$-5%H$_2$ flow, a very slight oxidation might occur, forming a sparse oxide layer just in the interface between the Cu/Ni substrate and the SrTiO$_3$ film. Several possibilities of different oxides could be thought of as shown in table 6–2. The calculated lattice mismatches between Cu/Ni lattice parameters [120] and SrTiO$_3$ are shown in table 6–3.

Table 6–2 : Possible oxides that could be formed in the film/substrate interface

<table>
<thead>
<tr>
<th>Cu/Ni oxide composition</th>
<th>Lattice constant</th>
<th>Mismatch with SrTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>0.4177 nm</td>
<td>6.97 %</td>
</tr>
<tr>
<td>Ni$<em>{0.95}$Cu$</em>{0.05}$O</td>
<td>0.4179 nm</td>
<td>7.01 %</td>
</tr>
<tr>
<td>Ni$<em>{0.90}$Cu$</em>{0.10}$O</td>
<td>0.4182 nm</td>
<td>7.08 %</td>
</tr>
<tr>
<td>Ni$<em>{0.80}$Cu$</em>{0.20}$O</td>
<td>0.4188 nm</td>
<td>7.25 %</td>
</tr>
<tr>
<td>Ni$<em>{0.75}$Cu$</em>{0.25}$O</td>
<td>0.4191 nm</td>
<td>7.34 %</td>
</tr>
<tr>
<td>CuO</td>
<td>0.4245 nm</td>
<td>8.71 %</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>0.4269 nm</td>
<td>9.34 %</td>
</tr>
</tbody>
</table>

Table 6–3 : Calculated lattice mismatches between Cu/Ni substrate and SrTiO$_3$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Cu/Ni composition</th>
<th>Lattice constant</th>
<th>Mismatch with SrTiO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-23at.%Ni</td>
<td>Cu$<em>{0.77}$Ni$</em>{0.23}$</td>
<td>0.3590 nm</td>
<td>– 8.07 %</td>
</tr>
<tr>
<td>Cu-33at.%Ni</td>
<td>Cu$<em>{0.67}$Ni$</em>{0.33}$</td>
<td>0.3581 nm</td>
<td>– 8.29 %</td>
</tr>
<tr>
<td>Cu-45at.%Ni</td>
<td>Cu$<em>{0.55}$Ni$</em>{0.45}$</td>
<td>0.3561 nm</td>
<td>– 8.81 %</td>
</tr>
</tbody>
</table>

When comparing the lattice mismatches of Cu/Ni substrates and Ni$_x$Cu$_{1-x}$O oxides with SrTiO$_3$, it is notable that the reported XRD data of all the Ni$_x$Cu$_{1-x}$O (0.75 ≤ x ≤ 1) oxide components [121] are showing a lower lattice mismatch with SrTiO$_3$. Even if CuO has a slightly larger mismatch with SrTiO$_3$, there might be a sub lattice / intermediate arrangement existing, which
supports a lower lattice mismatch with the SrTiO₃ film. One possibility for this intermediate arrangement might be thought as a Cu–O arrangement as seen in CuO (1̅01) atomic plane.

In a CuO crystal structure as shown in the Figure 6–6, the shortest distances between Cu and O atoms can be calculated as 0.1950 nm [121]. Hence, if we consider a CuO sublattice (green parallelogram) with 2 times that distance, the width/length (0.3900 nm) of that sublattice will perfectly match with the SrTiO₃ lattice (pink square) with a mismatch of 0.0128%.

Even if the CuO was formed in a different orientation a similar sublattice would be found with a length within a deviation of = 0.0141% considering $\cos \beta$, since the $\beta = 9.9653^\circ$ in this monoclinic structure. Even in that case, the lattice mismatch with the SrTiO₃ lattice would be remained in a very small figure of 0.0163%.
SrTiO$_3$ thin films on different Cu/Ni substrates

Fig. 6-6: Schematic illustration of a SrTiO$_3$ lattice (pink) fitting into the a sublattice (green) in the CuO (1̅01) atomic plane. Cu atoms: Green, O atoms: Grey.

Therefore, if a slight oxidation yields to a thin CuO arrangement in the interface between Cu/Ni substrate and SrTiO$_3$ film, it would be thought as the possibility that enhance the epitaxial growth of SrTiO$_3$ grains in an excellent orientation on Cu/Ni substrate.

6.3 – Conclusion

Among our SrTiO$_3$ film depositions on 7 different substrates using the precursor Chemistry–III, good out-of-plane orientation could be achieved only on Cu-23at.%Ni, Cu-33at.%Ni and on LaAlO$_3$ single crystal, among the selected template materials, showing a strong substrate dependency for the epitaxial growth of SrTiO$_3$. The small lattice mismatch between LaAlO$_3$ single crystal and SrTiO$_3$ is expected to facilitate the SrTiO$_3$ growth. Fine orientation of SrTiO$_3$ grains grown on Cu-33at.%Ni substrate is thought to be backed by a possibility of a sheer oxidation of the Cu/Ni substrate in the substrate-film interface.
Chapter—7

Further optimizations of SrTiO$_3$ buffer thin film fabrication

7.1 – SrTiO$_3$ thin films fabricated under different O$_2$ partial pressures

Figure 7–1 shows the XRD $\theta$-2$\theta$ scans of SrTiO$_3$ thin films fabricated on Ni-5at.%W commercial textured substrates using a withdrawal speed of $\uparrow$100 mm/min with precursor of chemistry–III in the reducing gas atmospheres.

![XRD θ-2θ scans](image)

Fig.7–1 : XRD θ-2θ scans of SrTiO$_3$ mono-layers deposited on Ni-5at.%W commercial textured substrates, and annealed at different oxygen partial pressures

The oxygen partial pressures shown in figure 7–1 were derived from equation 2–4, based on the Nernest equation, as mentioned in 2.5 in chapter–2. Annealing in higher oxygen partial pressures resulted in no crystallized SrTiO$_3$ phase, due to the oxidation of the Ni/W alloy which can be identified mainly by the peak at $2\theta \approx 30.0^\circ$ in the XRD θ-2θ scan, corresponding to the (111) peak of NiWO$_4$. In that XRD plot, peaks appearing at $2\theta \approx 33.2^\circ$ and $2\theta \approx 45.2^\circ$ could not be identified.
In contrast, SrTiO$_3$ thin films fabricated on Cu-33at.%Ni alloy textured substrates at annealing temperature of 950$^\circ$C in the reducing gas atmospheres exhibit a good crystallographic orientation as shown by XRD $\theta$-2$\theta$ scans in figure 7–2.

Annealing in pure N$_2$ did not result in any crystallized SrTiO$_3$ phase, due to the oxidation of the Cu/Ni alloy which could be identified by the $2\theta \approx 37.1^\circ$ and $2\theta \approx 43.3^\circ$ peaks in XRD $\theta$-2$\theta$ scan, corresponding to the (111) and (200) peaks of Ni$_x$Cu$_{100-x}$O respectively. An exact reference for the oxide corresponding to the Cu/Ni ratio used in the present alloy could not be found. Nevertheless, published values for Cu/Ni oxides closely corresponding to our substrate are shown in table 7–1. Therefore, these two peaks resulted in the figure 7–2 are expected to be the (111) and (200) peaks of Ni$_{0.33}$Cu$_{0.67}$O respectively.
Table 7–1: Reference for Ni\textsubscript{x}Cu\textsubscript{100−x}O peaks from XRD powder diffraction data [121]

<table>
<thead>
<tr>
<th>Cu/Ni oxide composition</th>
<th>(111) peak of 2θ</th>
<th>(200) peak of 2θ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni\textsubscript{0.75}Cu\textsubscript{0.25}O</td>
<td>37.122</td>
<td>43.130</td>
</tr>
<tr>
<td>Ni\textsubscript{0.80}Cu\textsubscript{0.20}O</td>
<td>37.153</td>
<td>43.166</td>
</tr>
<tr>
<td>Ni\textsubscript{0.90}Cu\textsubscript{0.10}O</td>
<td>37.213</td>
<td>43.237</td>
</tr>
<tr>
<td>Ni\textsubscript{0.95}Cu\textsubscript{0.05}O</td>
<td>37.238</td>
<td>43.266</td>
</tr>
</tbody>
</table>

Films annealed in other gas atmospheres \textit{i.e.} in reducing gas atmospheres, resulted in diffraction peaks near \(2θ \approx 32.4°\), and 46.5° that correspond to the (110), and (200) reflections of SrTiO\(_3\).

Based on the (110), (111), and (200) reflections of SrTiO\(_3\), the Relative Peak Intensities \(RPI\) as an orientation factor for the (200) SrTiO\(_3\) peak, was calculated using formula 4–1, and used for comparison between the films annealed in Ar-2%H\(_2\), N\(_2\)-5%H\(_2\), N\(_2\)-5%H\(_2\)+N\(_2\)-0.01%O\(_2\), wet N\(_2\)-5%H\(_2\), and N\(_2\)-9%H\(_2\). Figure 7–3 shows the influence of the oxygen partial pressure \(p(O_2)\) of the annealing atmosphere, on the (200) orientation of the SrTiO\(_3\) thin films. The \(p(O_2)\) values for oxygen partial pressure were calculated based on the Nernst equation as introduced in chapter–2. In this graph, circles represent the data obtained on Ni-5sat.%W substrates and the diamonds represent the data obtained on Cu-33at.%Ni substrates. The colours are representing the ambient atmosphere used for annealing.

Even at a specific gas composition N\(_2\)-5%H\(_2\), the actual oxygen partial pressures \(p(O_2)\) resulted in distributed values mainly due to the uncertain amount of leakage in the annealing system. Although the careful attempts were taken to keep the same tightness when closing the annealing tube, practically it is difficult to assure an accurate tightness. And, the \(p(O_2)\) values could be calculated only after reaching the elevated temperatures, hence they are not adjustable after starting the annealing process.
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Fig. 7–3: The orientation factor $RPI_{(200)}$ of SrTiO$_3$ thin films annealed in different p(O$_2$) atmospheres.

Based on these results within the attempted oxygen partial pressure window, it is evident that low oxygen partial pressures are most favourable for a high orientation factor, in both N$_2$-5%H$_2$ and N$_2$-9%H$_2$ environments.

To further characterise the crystallographic texture of the films that used for the XRD scans of figure 7–2, EBSD scans of the corresponding films (corresponding to the data points indicated with arrows in figure 7–3) annealed in N$_2$-5%H$_2$ and N$_2$-9%H$_2$ environments are shown in figure 7–4. The fraction of the cube texture component of the 2 films determined considering orientations within $15^\circ$ from the ideal \{001\}<100> orientation, amounts to 64.7% and 86.7% respectively. These values are smaller than the relative peak intensities ($RPI_{(200)} = 90.1\%$ and

---

4 Circles represent the data obtained on Ni-5at.%W substrates, and the diamonds represent the data obtained on Cu-33at.%Ni substrates, where the filled colours are representing the ambient atmosphere used for annealing. The 5 different annealing atmospheres \textit{i.e.} N$_2$-5%H$_2$, N$_2$-5%H$_2 +$ N$_2$-0.01%O$_2$, wet N$_2$-5%H$_2$, Ar-5%H$_2$, and N$_2$-9%H$_2$ are represented by dark blue, green, light blue, orange, and red respectively. The 2 films of the corresponding data points that indicated with arrows are further investigated in the following pages.
SrTiO$_3$ thin films under different $O_2$ partial pressures

90.7% respectively) mainly because biaxial orientation is considered in the EBSD scans, where XRD measurements represent only c-axis orientation. Nevertheless, XRD data attributes an integrative information from broader part of the film, in contrast the surface sensitive information of a selected area was attributed by EBSD scans.

In figure 7–4, EBSD scan of the film annealed in N$_2$-9%H$_2$, shows bluish colour majority, implying that the deviation angle from the ideal cubic texture is very close to 0°. In contrast, many more deviations from the cubic texture can be seen in the EBSD scan of the film annealed at N$_2$-5%H$_2$, showing the presence of some unfavourable texture components in the film.

Fig. 7–4 : EBSD maps (step size of 0.03 μm, covering an area of 12 μm ×12 μm in the rolling plane) of SrTiO$_3$ thin films annealed in different ambient environments i.e. N$_2$-5%H$_2$ (left) and N$_2$-9%H$_2$ (right). Color reference/scale: Deviation angle from the cube texture [0° to 65°]

These results clearly emphasize the importance of the lower $O_2$ partial pressure during crystallization for obtaining a high degree of cube texture in the film surface. The film annealed in N$_2$-9%H$_2$ was further investigated in terms of surface morphology using SEM as shown in Figure 7–5.
Accoding the left image in Figure 7–5, the SrTiO₃ grains are seen to be grown in sizes of 100 to 200 nm. Both images show that the film is covered homogeneously with a fine porous-free microstructure, suggesting a promising buffer template for further YBCO deposition.

It is notable that the lower O₂ partial pressures minimize the oxidation of the Cu/Ni substrate during the annealing process, probably forming a sparse atomic arrangement of CuO at the film–substrate interface, which would facilitate an optimum SrTiO₃ epitaxial growth as suggested in the end of previous chapter. In contrast, in higher O₂ partial pressures at high temperatures, Cu/Ni substrates would be easily covered with a thicker oxide phase interlayer of Ni₀.₃₃Cu₀.₆₇O which would not such supportive for the SrTiO₃ film’s epitaxial growth. Therefore, lower O₂ partial pressures are thought to be very beneficial for obtaining optimum conditions for that sparse atomic arrangement of CuO, resulting a fine SrTiO₃ epitaxial growth.
Thickness improvement of the SrTiO₃ mono-layers

7.2 – Thickness improvement of the SrTiO₃ mono-layers

7.2.1– Increasing the concentration of the precursor solution

The developed precursor solution mentioned in the previous chapters has a total cation concentration of 0.4 M. Attempts at obtaining more concentrated precursors with 0.5 M, 0.6 M, and up to 0.8 M were made many times. The final solutions after mixing the two separate Sr and Ti solutions were not stable, nevertheless the preparation of the strontium solution (Strontium acetate + Acetic acid), and titanium solution (Titanium isopropoxide + 1-Methoxy-2-Propanol + 2,4-Pentanediene) was successful. For example, during the stirring process at 70°C after mixing, the 0.5 M precursor solution got precipitated after around ¼ hour. After mixing, even if the stirring process was carried out at room temperature, the 0.5 M precursor solution got precipitated after around 24 hours. When we consider the ‘physical’ lifetime (as introduced in 5.1.1 in chapter─5) of the film fabrication, a duration of 24 hours would not be acceptable as a practical time limit, when comparing the ‘practical’ lifetime of the 0.4 M solution. Therefore, practically the highest possible concentration for the SrTiO₃ precursor solution by Chemistry─III is believed to be around 0.4 M.

7.2.2– Increasing the withdrawal speed at the dip-coating process

When increasing the withdrawal speed, mainly 2 technical issues have to be considered very carefully. First and the most fundamental issue could be the technical limitation of the speed of the dip-coater. Even though, a higher speed would be applied using e.g. a gear system, the second issue i.e. the gravitational draining in the entrained wet thick coating would eventually limit the film thickness. Figure 7─6 shows the XRD θ-2θ scans of SrTiO₃ thin films deposited on Cu-33at.%Ni substrates and crystallized at an annealing temperature of 950°C in N₂-5%H₂ reducing gas atmosphere. The (200) SrTiO₃ orientation factors of the films coated at ↑100 (film─A) and ↑150 mm/min (film─B), were 91% and 93% respectively based on equation 4─1, revealing an excellent c-axis orientation.
Chapter 7 — Further optimizations of SrTiO₃ buffer thin film fabrication

Figure 7–6: XRD θ-2θ scans of SrTiO₃ mono-layers deposited on Cu-33at.%Ni textured substrates, using a coating speed of ↑100 (film–A) and ↑150 (film–B)

Figure 7–7 and 7–8 show the XRD φ-scans and ω-scans of the SrTiO₃ thin film coated at ↑150 mm/min (film–B), and the Cu-33at.%Ni textured substrate respectively. According to the φ-scans of figures 7–7 and 7–8, it is evident that the FWHM (Δφ) value for the film is 2.2° larger than that of the substrate, suggesting that the in-plane-texture can be further improved. The out-of-plane texture of the film is comparable with that of the substrate. Still it is obvious that the SrTiO₃ growth had achieved a good biaxial orientation.
Thickness improvement of the SrTiO$_3$ mono-layers

Fig. 7–7: XRD $\varphi$-scan (left) and $\omega$-scan (right) of the SrTiO$_3$ film–B coated at $\uparrow$150 mm/min

Fig. 7–8: XRD $\varphi$-scan (left) and $\omega$-scan (right) of the Cu/Ni substrate
Chapter 7 — Further optimizations of SrTiO$_3$ buffer thin film fabrication

The surface morphology of both films were characterized using SEM as shown in Figure 7–9, and Figure 7–10. All the SEM images show a complete coverage of the mono-layer.

![SEM images of film–A – SrTiO$_3$ film coated at ↑100 mm/min](image)

Figure 7–9 : SEM images of film–A – SrTiO$_3$ film coated at ↑100 mm/min

This fine coverage over the Cu/Ni substrate is expected to be acting as a fine protective layer for the substrate, preventing it from oxidization during the YBCO deposition stages where the coated substrate is exposed to oxygen containing ambient atmospheres.

When compared to the SEM images of film–A, the thicker film (film–B) resulted in unidentified ‘snow-like’ artefacts homogeneously distributed over the SrTiO$_3$ grains. At the highest achievable magnification as seen in figure 7–10, it is evident that these artefacts are completely different from a porous structure.
Thickness improvement of the SrTiO$_3$ mono-layers

Since the sizes of these artefacts are ranging around 20–40 nm, the need of an extremely high resolution would be foreseen for further investigations.

TOF-SIMS imaging was performed on the substrate surfaces (uncovered parts) of film–A and film–B. The film surfaces did not show any distinct features. Figures 7–11 and 7–12 display selected extracted ion images obtained over a 200×200 µm$^2$ surface area on the substrates of film–A and film–B respectively. These images have fixed intensity scales, which means that the intensity for a particular element can be compared between samples.

As seen through the higher image contrasts of film–B (figure 7–11) compared to those of film–A (figure 7–10), the impurity intensities of the film–B’s substrate are much more intense with respect to the homogeneous distribution compared to film–A’s. The elevated intensities of the impurities make it possible to see that the intensities are especially elevated at the substrate grain boundaries.
Fig. 7–10: TOF-SIMS ion images (200×200 µm²) of substrate surface of film–A. The intensity scale is fixed for each element.

Fig. 7–11: TOF-SIMS ion images (200×200 µm²) of substrate surface of film–B. The intensity scale is fixed for each element.

Here the relative intensities between different elements do not correspond to difference in concentration of the corresponding ions. Different elements have different response factors, i.e. a small concentration can cause a very intense signal and a high concentration can cause a low
signal intensity. The response from a certain element is dependent of the chemical environment, i.e. an element intensity can vary between different chemical phases. It is the physical properties of the matrix that affects the signal intensities. In these figures 7–10 and 7–11 the individual substrate grains have different intensity. The reason is that the surface of the substrate grains have different physical properties, which is caused by different crystallographic orientations. And, it is evident that Ni and Cu exhibit the same behaviour in regard to lateral distribution of signal intensity, which is the expected observation.

Figure 7–12: TOF-SIMS ion images (20×20 µm²) of substrate surface of film–B.

The intensity scale is fixed for each element.

The images in Figure 7–12 are the corresponding images at a smaller lateral scale (20×20 µm²), and they clearly confirm that the impurity intensities are elevated at the edges of substrate grain boundaries. The elevated intensity could be enrichment, but it could also be due to the presence of oxide (i.e. matrix effect). Oxides tend to increase the signal intensity of all other present species.
To appraise the surface topography of the thickest film *i.e.* film–B, AFM tapping mode scans were utilized. Figure 7–13 shows 8.43×8.43 μm scan acquired at a scan speed of 8 μm/s.

![AFM scan of the film–B, i.e. the SrTiO₃ film coated at ↑150 mm/min](image)

Figure 7–13: AFM scan of the film–B, *i.e.* the SrTiO₃ film coated at ↑150 mm/min

The surface roughness of the film was calculated using several independent scans on different positions of the film. The root mean square (rms) value ranged from 5.2 to 8.0 nm, where the substrate roughness amounted to ≈ 16 nm. Rms average was in the ≈ 4.2~5.7 nm range for this SrTiO₃ mono-coating. This is comparable with the reported work [086] on a SrTiO₃ layer grown on SrTiO₃ seed layer on Ni/W substrates, where rms average = 4.31 of the final bi-layer. Since the lower surface roughness is required for YBCO deposition [094], the results we achieved can be considered as a fine surface smoothness that would be favourable for YBCO deposition.
Depth profiles of the SrTiO₃ mono-layers

7.3 – Depth profiles of the SrTiO₃ mono layers

Figure 7–14 and 7–15 show the depth profiles obtained by employing the TOF/SIMS technique using an analysis area of 200×200 μm² centred in a sputter area of 300×300 μm². These plots show the ⁸⁸Sr, ⁵⁸Ni, ⁴⁸Ti, ⁶³Cu, and ¹⁶O signals as a function of the sputter time, which is proportional to the depth. All the signals were normalized based on the maximum intensity of each signal. Since the sputtering was carried out using a constant Xe⁺ ion beam, the sputtered depth can be

![Graph showing depth profiles](image)

Fig. 7–14 : Bi⁺ ion depth-profile of the SrTiO₃ film (film A) coated at ↑100 mm/min on Cu/Ni
relatively comparable with the sputtering time. As expected, three regions could be identified in both samples, i.e. the film region, a transient interface region, and the substrate region. In the film region, a fairly homogeneous distribution of Sr and Ti was found in both films, indicating a good distribution of Sr and Ti over the whole SrTiO$_3$ film thickness. In the transient region corresponding to the film/substrate interface, the $^{88}$Sr and $^{48}$Ti signals decrease exponentially, while the $^{58}$Ni and $^{63}$Cu signals are increasing. In the deeper region, the $^{58}$Ni and $^{63}$Cu signals start to show a homogeneous distribution indicating the presence of Ni and Cu.

Here, considering the intersection of the $^{48}$Ti and $^{58}$Ni signals, a rough idea of the film/substrate interface could be derived. In both depth profiles, the region that is seen left side of the interface is film region, where the substrate region is represented by right side. Then it is clearly notable that the film–B has thickness increment of at least 80% in respect to the thickness of film–A. When considering the film region starting from the film/substrate interface, it is evident that the traces of $^{58}$Ni and $^{63}$Cu are drastically decreasing through the film region, indicating the obstruction of Ni and Cu diffusion coming from the substrate. But, Cu/Ni diffusion seems to get almost terminated at a broader region within the film region, nevertheless small traces of $^{58}$Ni
Depth profiles of the SrTiO$_3$ mono-layers

and $^{63}$Cu are still present near the mid-point of the film region in the film–A. In film–B, which is the thickest film, it is more obvious that the Cu/Ni diffusion is getting terminated at a thickness-region lower than the film thickness. Therefore, the SrTiO$_3$ mono-layers deposited with withdrawal speed of ↑150 mm/min would be safely applied on Cu/Ni substrates as a promising chemical barrier.

7.4 – Conclusion

In our optimizations of SrTiO$_3$ mono-layers on Cu-23%at.Ni substrates using the precursor Chemistry–III, the films annealed at lower O$_2$ partial pressures resulted with better biaxial texture. With the highest practically achievable concentration for the Chemistry–III precursor i.e. 0.4 M, thicker SrTiO$_3$ mono-layers deposited by using a withdrawal speed of ↑150 mm/min at dip-coating could achieve a thickness of (200 ± 50) nm. These films found to have a porous-free, crack-free and smooth morphology with an excellent biaxially textured surface. The thickness of these SrTiO$_3$ mono-layers was thick enough to stop the nickel and copper diffusion from the Cu/Ni substrate.
Chapter — 8

Summary

In our research the main focus was on the development of SrTiO$_3$ single buffer layers based on environmentally safe chemicals, avoiding conventional precursors that use toxic and hazardous chemicals such as 2-methoxyethanol, and trifluoroacetic acid (TFA). A new precursor solution for SrTiO$_3$ buffer layers has been successfully developed with the reagents of strontium acetate, acetic acid, titanium isopropoxide, 1-methoxy-2-propanol and 2,4-pentanedione. Using this precursor with dip-coating, high cube-textured SrTiO$_3$ mono-layers were reproducibly obtained on Cu-33at.%Ni tapes using single step annealings at 950°C in N$_2$-5%H$_2$ ambient flow. Based on the c-axis texture of the SrTiO$_3$ films annealed in different oxygen partial pressures, higher orientation factors were achieved in the both films annealed in N$_2$-5%H$_2$ and N$_2$-9%H$_2$ respectively. Furthermore, EBSD scans highlighted the importance of the lower O$_2$ partial pressures during crystallization for obtaining higher degree of cube texture in the film surface. As the highest practically achievable concentration for the developed precursor i.e. Chemistry–III precursor was 0.4 M, the thickness improvement of the SrTiO$_3$ mono-layers were attempted by increasing the withdrawal speed at dip-coating. These layers with (200 ± 50) nm thickness were found to have a pore-free and crack-free morphology in SEM observations, with an excellent biaxially textured surface as seen in EBSD analysis. According to the AFM scans, the surface roughness was found to have an rms average of 4.2~5.7 nm range, exhibiting a smooth surface morphology. TOF-SIMS depth profile of the SrTiO$_3$ mono-layer deposited using a withdrawal speed of ↑150 mm/min at dip-coating on Cu-33at.%Ni tapes, revealed that the Cu/Ni diffusion is getting terminated at a thickness-region lower than the film thickness.
Chapter — 9

Conclusions and Outlook

9.1 – Conclusions

A new precursor solution for SrTiO₃ buffer layers has been successfully developed with the reagents of Strontium acetate + Acetic acid + Titanium isopropoxide + 1-Methoxy-2-Propanol + 2,4-Pentanedione. The SrTiO₃ precursor solution has a ‘practical’ lifetime of several months, where it is stable at least for one year, having much longer ‘physical’ lifetime. Furthermore, the SrTiO₃ precursor solution is less toxic in comparison to highly toxic 2-methoxyethanol, TFA or methanol, which is commonly used for this kind of precursor solution preparation [053, 059, 060, 067, 068, 078]. Using this precursor with dip-coating, high cube-textured SrTiO₃ mono-layers with (200 ± 50) nm thickness were reproducibly obtained on Cu-33at.%Ni tapes using single step annealings at 950°C in N₂-5%H₂ ambient flow. These layers were found to have a porous-free, crack-free and smooth morphology with an excellent biaxially textured surface. The thickness of these SrTiO₃ mono-layers was thick enough to stop the nickel and copper diffusion from the Cu/Ni substrate. Hence, the developed high quality buffer layers are expected to be acting as efficient diffusion barriers.
9.2 – Experimental Outlook

In order to achieve a biaxially textured buffer layer with a fine coverage, that also act as an efficient diffusion barrier, a sufficient thickness has to be achieved using multi-coatings or by a single-coating. To assure a cost efficient fabrication in CSD based industrial reel-to-reel setups, single-coatings are desired, due to the simplicity of the process, compared to multi-coatings. The simple annealing process combined with a relatively high film thickness per single coating is expected to be very advantageous in reel-to-reel applications. Hence, our developed SrTiO$_3$ mono-layers are expected to be acting as efficient diffusion barriers and also as an alignment arbitrator for following growth of biaxially textured YBCO nanostructure. Therefore, YBCO depositions should be performed in order to test the feasibility of the developed SrTiO$_3$ mono-layers. And, then a real application in a reel-to-reel setup should be done, in order to link to a real industrial potential.
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