The growth of patterned ceramic thin films from polymer precursor solutions
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CHAPTER 2

Film Synthesis

The manufacture process applied in this work for the (potentially) superconducting Bi2212 and Y123 has been described before by von Lampe and coworkers [18, 19, 22]. In this work, the recipe was used with small modifications. For the other ceramic materials, the process was adapted accordingly.

2.1 Chemicals

The following chemicals were used to make the precursor solutions:

- N,N-Dimethylformamide (DMF), 99 %, Acros, Geel, Belgium.
- 2-Methoxyethanol, 98 %, Merck, Darmstadt, Germany.
- Al(NO$_3$)$_3$·9H$_2$O, 98+ %, Aldrich.
- Ba(NO$_3$)$_2$, 99 %, Aldrich.
- Ba(NO$_3$)$_2$, 99.999 %, Aldrich.
- Bi(NO$_3$)$_3$·5H$_2$O, 99.99+ %, Aldrich.
- Bi(NO$_3$)$_3$·5H$_2$O, 98+ %, Fluka.
- Ca(NO$_3$)$_2$·4H$_2$O, 99.99+ %, Aldrich.
- Cu(NO$_3$)$_2$·2.5H$_2$O, 98 %, Aldrich.
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- Cu(NO$_3$)$_2$·2.5H$_2$O, 99.99 %, Aldrich.
- Pb(NO$_3$)$_2$, 99+ %, Aldrich.
- Sr(NO$_3$)$_2$, 99+ %, Aldrich.
- Sr(NO$_3$)$_2$, 99.995 %, Aldrich.
- Sr(NO$_3$)$_2$, 99+ %, Fluka.
- Ti(NO$_3$)$_4$, 99.9+ %, Aldrich.
- Y(NO$_3$)$_3$·4H$_2$O, 99.99 %, Aldrich.
- Zn(NO$_3$)$_2$·6H$_2$O, 98+ %, Aldrich.
- Poly(acrylic acid) (PAA), $M_w$=2 kg/mol, Aldrich.
- Poly(methacrylic acid) (PMAA), $M_w$=82.4 kg/mol, Polymer Standards Service, Mainz, Germany.
- Poly(methacrylic acid), $M_w$ unknown, self-made (see Appendix C).

2.2 Precursor Preparation

Precursor solutions were made in the following way: The constituting metals were dissolved as nitrates in DMF or 2-methoxyethanol (in the case of some Bi2212 precursors). If the oxidic phase consisted of more than one metal, the corresponding nitrates were dissolved in the correct stoichiometric ratio, i.e. the same molecular ratio as in the final oxidic phase. For Y123, for example, the ratio is $x$ mol Y(NO$_3$)$_3$·4H$_2$O : $2x$ mol Ba(NO$_3$)$_2$ : $3x$ mol Cu(NO$_3$)$_2$·2.5H$_2$O. When the nitrates were fully (or almost fully) dissolved either PAA or (for some HTSC precursors) PMAA was added. The molecular structure of these polyacids is described in Appendix B. This procedure yielded clear viscous solutions that were stable from several months up to more than a year. Eventually they turned opaque as some of the metals precipitated or the solutions formed a gel. In the first case, when the solution became cloudy, the precursor was unsuitable for film growth because of its lack of homogeneity in chemical composition, in the second case it had unsuitable mechanical properties (i.e. it was too viscous). The weight ratios
(all nitrates):polymer:solvent was approx. 0.65:1:2 (HTSC precursors) or 1:1:2 (other precursors).

2.3 Substrate Materials

The following materials were used as substrates:

1. Microscope cover slips from glass (SiO$_2$:B, thickness: 0.1 mm, refractive index n(546 nm)=1.5255, n(588 nm)=1.5231, Menzel Glasbearbeitungs- werk GmbH & Co. KG, Braunschweig, Germany). At the glass transition temperature the plates wet other materials and soak into the underlying sample carrier ceramic. This temperature was approx. 630 °C. Small deformations in the form of bending occurred, however, already at lower temperatures.

2. SrTiO$_3$ (001) single crystal plates, polished (10×10×1 mm$^3$, edges along [100] directions, TBL-Kelpin, Neuhausen, Germany). The crystal structure of SrTiO$_3$ is described in Appendix A.1. For some experiments substrates of Nb-doped SrTiO$_3$ were used (Crystal GmbH, Berlin, Germany) that had the same orientation and dimensions as the undoped substrates. The doping rate was 0.20 mol%, the conductivity was 0.03 Ω·cm.

3. LaAlO$_3$ (001) single crystal plates, polished (10×10×1 mm$^3$, edges along [100] directions in the pseudocubic setting, TBL-Kelpin, Neuhausen, Germany). For the crystal structure of LaAlO$_3$ see Appendix A.2.

4. Si wafers from Si (001) single crystals, polished (thickness: 675(15) µm, p-type, B-doped, conductivity: 8.12-11.82 Ω·cm, Wafernet GmbH, Eching, Germany). As obtained, the wafers were covered by an amorphous, thin, isolating oxide layer which was removed in some cases by dipping the wafer into an HF solution for several minutes, followed by a rinse in reverse osmosis (RO) water and blowdrying in nitrogen. The crystal structure of Si is described in Appendix A.3. For the samples which required a conductive substrate strongly B-doped Si (001) wafers were used (thickness: 300(25) µm, conductivity: 1-2 mΩ·cm, Virginia Semiconductor, Fredericksburg, USA).
2.4 Substrate Cleaning

The following cleaning procedure was developed: The substrate was fixed on a hot stage (by means of vacuum), which was set to ca. 130 °C, and a fine jet of CO$_2$ crystals was moved systematically over the entire surface to blow off larger dust particles by impact and to dissolve organic molecules adhered to the surface. The water contact angle of a Si wafer cleaned in such a way was approx. 5°. The second cleaning step was plasma-etching in an air plasma (5·10$^{-2}$ mbar, Harrick Plasma Cleaner PDC-002, Harrick Scientific Corporation, Ossining, USA) for ca. 5 min. After this treatment the water contact angle of a Si wafer was less than 2°.

This cleaning procedure deviated from the procedure used by von Lampe and coworkers [23] who heated the substrates to approx. 900 °C in air for several hours. The newly developed cleaning method gave satisfactory results (see below) in a much shorter time. The main objective of substrate cleaning is to remove (macroscopic) dust particles and (microscopic) organic molecules from the substrate surface. Dust mainly affects the aesthetic appearance of the film and for the patterned films disturbs the pattern only locally. Contamination with organic molecules is much more severe, since it can result in the poor wetting of the substrate by the precursor solution. The consequence can be a partial or even complete detachment of the film during the drying process, which follows the coating process and which is always associated with a shrinkage of the film. If the precursor film wets the substrate well enough, this shrinkage occurs in vertical direction only, since the film adheres well to the substrate. If the wetting is poor, the shrinking film will locally detach from the substrate, leading to cracks in the film or even a complete lift-off of the film.

2.5 Spin-casting and Drying

Homogeneous films were made by spin-casting. Immediately after cleaning, the substrates were spin-coated with the precursor solution (PWM32 spincoater, Headway Research Inc., Garland, USA) with varying velocities. Since DMF and 2-methoxyethanol evaporate only very slowly at room temperature, the spinning time was rather long: 20-30 s. This yielded clear precursor films that typically showed a rim of higher thickness along the edge of the substrate. If
the spin-coating time was too short, the rim material tended to flow back to 
the areas of homogenous thickness. In some cases a weak lateral variation of 
the interference color could be observed, indicating a small thickness gradient 
of the precursor film.

Immediately after spin-casting, the films were dried by placing the samples 
onto a hot stage set to 80 °C for several minutes. During this step most of the 
solvent was removed from the film. The precursor films were then ready for 
high-temperature processing (see Sec. 2.7).

In some cases (Y123 and Bi2212 precursors) fast drying was crucial to ob-
tain a homogenous, crack-free precursor film. Otherwise cracks formed when 
heating the films and, together with a poor substrate cleaning, the films might 
detach from the substrate. Furthermore, it occurred that inorganic material 
precipitated shortly after spin-casting when the sample was kept at room tem-
perature. Once the drying procedure was established for the superconductor 
precursors, it was also applied to all other spin-cast precursor films in this 
work.

2.6 Micromoulding

To manufacture a patterned precursor film, which yields a patterned inorganic 
film after high-temperature processing (see following chapter), several methods 
can be considered. Patterning in an electric field with a patterned electrode 
placed above the spin-cast film is one possibility [24]. Another method is to 
print a self-assembling monolayer (SAM) of octadecyltrichlorsilane (OTS) onto 
the substrate, thereby locally modifying the surface energy. After spin-casting 
and drying, a precursor film (tantalum-ethoxide in ethanol) adheres better 
to the non-SAM covered parts of the substrates. By softly rubbing the film, 
the precursor can be removed from the printed areas. This way a patterned 
precursor film was obtained, which could be transferred into a patterned oxidic 
film (of Ta₂O₅) [25]. Apart from the poor adhesion of a precursor on OTS, the 
dewetting of a polymer solution from OTS covered substrates can be employed. 
Experiments on gold-covered substrates with Y123 precursors have shown that 
the patterning of a precursor solution is possible but no superconducting films 
have been obtained [26].

The method chosen for patterning precursor films in this work was mi-
cromoulding. Patterned stamps of poly(dimethylsiloxane) (PDMS) were pro-
duced (see Appendix D) with a structure height of approx. 900–950 nm. Compared to clean substrates, the surface energy of the PDMS is much lower, causing the precursor film to adhere preferentially to the substrate and not to the stamp. Directly prior to usage, dust particles were blown off the stamps by air or nitrogen. Two ways of micromoulding were tested, but only one of them was successful. In a first attempt, the stamps were pressed into as-cast Bi2212 precursor films, either immediately after spinning or after placing them for a few minutes onto a hot stage (see Sec. 2.5). The films were solidified at an elevated temperature on the hot stage for 1 to 30 min underneath the stamp. Eventually the PDMS stamp was carefully peeled off the film and the sample, that often showed the interference colors of light diffraction, was transferred to the tube furnace for the high-temperature treatment. This yielded, however, only poorly patterned Bi2212 films. Nowhere on the film, the elevated lines of Bi2212 were fully separated from each other (similar to Fig. 8.2 (d)). In other words, the film thickness between the lines was finite. The reason for this finding is that the PDMS stamp cannot be fully pressed down to the substrate after spin-casting the film, since the film viscosity is too high after most of the solvent has evaporated.

Therefore, a second method was tested, in which a droplet of the precursor was placed onto the substrate and the PDMS stamp was pressed into it. The viscosity was then low enough to allow the precursor to flow from underneath the protruding parts of the stamp to the receded parts or to the edges. Sample and stamp were placed onto a hot stage set to 80 °C before the stamp was removed. As a rule of thumb, one can note that the longer the stamp remained on the sample, the smaller was the amount of film area that attached to the stamp upon removing it. Leaving the stamp on the substrate for 5 min gave rather poor results, while samples on which the stamps were left for 50 min had the best reproduction of the stamp pattern (Fig. 8.2). After the stamp had been lifted off, the sample was transferred to the tube furnace for subsequent high-temperature processing\(^1\). Micromoulding has been used to produce patterned films of Si-glass [20, 21, 27] or organic Zr/Si-glass [28]. Micromoulding in capillaries has been used to manufacture lead zirconate titanate [12, 16].

\(^1\)Instead of solidifying the precursor film underneath the stamp and removing the stamp prior to the high-temperature treatment, it was also tried to leave the stamp on the film and pyrolyse it together with the precursor. This yielded films of unidentifiable composition and with very poorly replicated patterns. Replacing the PDMS stamps by poly(butadiene) stamps (see [26] for details) provided no improvement.


2.7 Polymer Degradation and Metal Oxidization

After drying the spin-cast or micromoulded films, the samples were transferred into a preheated tube furnace (80°C). An air flow through the furnace was applied to ensure a sufficient partial oxygen pressure and to remove solvent vapours and all gaseous products of the high-temperature treatment. The purpose of this treatment was to transform the precursor film into a ceramic, inorganic film. To achieve this, the following processes have to take place: The solvent has to evaporate entirely from the precursor film, the polymer has to degrade and the degradation products have to be removed from the film. Finally, the metals have to be oxidized and the oxide has to crystallize to its final phase.

For the polymers used in this study (PAA and PMAA), the thermal degradation in a nitrogen atmosphere was investigated by thermogravimetric analysis (TGA). The TGA curves are shown in Fig. 2.1. PMAA loses 90% of its weight at 450°C and degrades completely at approx. 650°C. The PAA weight decreases to ca. 10% at 500°C and remains stable up to 700°C. For a degradation in an air atmosphere, however, it is likely that all polymers degrade fully at temperatures above 550°C (PMAA [29]) and 575°C (PAA [30]). The main degradation of the polymers takes place in the temperature range from ca. 200°C to 500°C (Fig. 2.1). To avoid damage of the film caused by too rapid polymer degradation, the heating rate of the samples was reduced in this temperature range. The samples were heated in the following sequence:

1. From 80°C to 200°C with 10°C/min.
2. From 200°C to 500°C with 5°C/min.
3. From 500°C to the final temperature $T_{\text{max}}$ with 10°C/min.
4. Constant temperature $T_{\text{max}}$ for 30 min (superconductors) or 90 min (other phases).
5. From $T_{\text{max}}$ to room temperature. At temperatures above approx. 700°C, the cooling rate was 10°C/min, below 700°C it was lower.

Since Ba easily forms Ba(CO$_3$)$_2$, (which is stable to above 1000°C,) in the presence of free carbon and oxygen, the recipe was slightly modified for the manufacture of Y123 films. The degradation process was carried out in
a nitrogen atmosphere. When the temperature had reached $T_{\text{max}}$, the gas flow was changed to oxygen and the oxygen flow was maintained until the temperature was below 300 °C.

### 2.8 Epitaxy

The critical current densities $j_c$ (Sec. 3.4) of Y123 and Bi2212 are strongly anisotropic. Within the crystallographic $\vec{a}\vec{b}$-plane they are higher than perpendicular to it [31, 32]. For practical applications of thin films, high values of $j_c$ within the film plane are desirable. The crystallites that form these films have therefore to be oriented with their individual $\vec{a}\vec{b}$-planes parallel to the substrate surface (or film plane). Their individual $\vec{c}$-axes have to be normal to the substrate surface, i.e. the out-of-plane orientation has to be a $\vec{c}$-axis orientation. Furthermore, it is desirable that the individual crystallites also have the same in-plane orientation. The critical current density strongly decreases with an increasing tilt or twist angle between the lattices of adjacent crystal-
2.8 Epitaxy

lites [33]. The critical current density within the film plane is the highest for a $\vec{c}$-axis oriented film with a strong in-plane orientation of the crystallites, lower for a $\vec{c}$-axis oriented film without in-plane orientation and the lowest for a film of randomly oriented crystallites.

The easiest way to achieve both the out-of-plane orientation and the in-plane orientation is by letting the crystallites grow epitaxially (Greek $\epsilon\pi\tau$-: at, on, upon, $\tau\alpha\xi\iota\sigma$: arrangement). The two-dimensional lattice of a single crystal surface that matches closely the two-dimensional lattice of the superconductor $\vec{a}\vec{b}$-plane, causes, for energetical reasons, the superconducting phase to grow with the $\vec{a}\vec{b}$-plane parallel to the substrate surface plane. Furthermore, the $\vec{a}\vec{b}$-plane has an in-plane orientation such that its lattice points coincide with lattice points of the substrate surface. This is depicted in Fig. 2.2, where the lattice points of the (001) plane of cubic SrTiO$_3$ are drawn as white circles\(^2\). The lattice points of the (001) plane of orthorhombic Bi2212 and orthorhombic Y123 are drawn as black circles in the upper and lower half of the image, respectively. The lattice of Bi2212 is rotated by an angle of 45° around the $\vec{c}$-axis with respect to the SrTiO$_3$ lattice, since the $\vec{a}$- and $\vec{b}$-axis of Bi2212 are approx. by a factor of $\sqrt{2}$ longer than the $\vec{a}$-axis of SrTiO$_3$. The crystal lattice parameters of all three materials are summarized in Appendix A. For both superconductors, the lattice mismatch with SrTiO$_3$ is very small, compared to other potential substrate materials [34]. When choosing a suitable substrate material, the most important aspects to consider are the matching of the lattice parameters at room temperature and the matching of the thermal expansion coefficients. The best substrates to fulfil both these requirements are SrTiO$_3$ (001) and LaAlO$_3$ (001) [34]. They were therefore used in this work as substrates for the superconductor films, but also for some of the PbTiO$_3$ films. The direction of the spontaneous electrical polarization of tetragonal PbTiO$_3$ is parallel to the $\vec{c}$-axis. In this work PbTiO$_3$ films were grown with the aim to achieve a strong polarizability perpendicular to the film plane. The highest polarizability per film thickness is achieved with $\vec{c}$-axis oriented films. Because $a_{\text{PbTiO}_3}$ is nearly identical to $a_{\text{SrTiO}_3}$, the (001) plane of SrTiO$_3$ is very suitable as a substrate for $\vec{c}$-axis oriented PbTiO$_3$ films.

All Y123 and Bi2212 films, which were always prepared on SrTiO$_3$ or LaAlO$_3$, and all PbTiO$_3$ films prepared on SrTiO$_3$ showed epitaxial growth.

\(^2\)In cubic crystals, the (001) plane is identical to the (100) plane. For simplicity in the evaluation of the x-ray experiments, the first labeling was chosen in this work.
Only for some of the Y123 films x-ray diffractograms indicate the presence of small amounts of non-oriented material. Thus, whenever a lattice plane of the film material was commensurate with the lattice of the substrate surface, epitaxial growth took place. While no research had been done on this topic, it is interesting to speculate about the growth process taking place during the high-temperature treatment. After the polymer is pyrolyzed, the metals form an intermetallic phase [23]. This intermetallic phase can either first oxidize and then crystallize, or oxidize and crystallize at the same time. In any case the crystallization can take place in two possible ways: 1. The crystals grow randomly oriented and undergo a subsequent reorientation process, leading to the epitaxial orientation. In this scenario, ions from crystallites with a random orientation would diffuse to crystallites having grown at a seed on the substrate surface and possess thus epitaxial orientation. 2. In a more likely scenario, only crystallites with epitaxial orientation grow on the substrate surface and a reorientation step is therefore superfluous. The question, which of the two growth processes takes place could be answered by taking in-situ diffractograms of the film during the high-temperature treatment.
Figure 2.2: Epitaxy. The lattice of the (001) plane of SrTiO$_3$ (white circles) nearly coincides with the lattice of the $\overline{ab}$-plane of Bi2212 (upper half, black circles) and Y123 (lower half, black circles).
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