The growth of patterned ceramic thin films from polymer precursor solutions
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5.1 Introduction

An advantage of the solution deposition methods, compared to the various vacuum deposition techniques, is the ease to grow oxides of two or more constituting metals in a fixed stoichiometric ratio. Furthermore, the composition of the grown phase can easily be changed by changing the stoichiometric ratio of the metals in the precursor. In this chapter, the growth of lead titanate, PbTiO$_3$, is presented. PbTiO$_3$ is one end member of the solid solution series PbZrO$_3$–PbTiO$_3$ (PZT). PbZr$_{1-x}$Ti$_x$O$_3$ ceramics (single crystals exist only for $x=0$ or $x=1$) are ferroelectric and piezoelectric at room temperature, with the highest dielectric and piezoelectric constants for $x \in [0.46; 0.51]$. This range is also the boundary between the Zr side of the phase diagram, where PZT is rhombohedral, and the Ti side, where PZT has a tetragonal symmetry. Within the $x$-range [0.46; 0.51], a monoclinic PZT phase is stable [61, 62]. Pure PbTiO$_3$ has one of the highest polarizabilities among the perovskite compounds [36] (Appendix A.1 and A.6).

Thin films of PbTiO$_3$ have been prepared by chemical vapor deposition [63, 64], pulsed laser deposition [65, 66], by a sol-gel method from acetates/alkoxides in 2-methoxyethanol [15, 67], from alkoxides in 2-methoxyethanol [68], or acetates/alkoxides in acetic acid (PZT) [12, 16].
5.2 Precursor Preparation

\[ \text{Pb(NO}_3\text{)}_2 \text{ and Ti(NO}_3\text{)}_4 \] in the molar ratio 1:1 were dissolved in DMF and PAA was added. The resulting solution was clear and had a strong orange color. With a weight ratio nitrates:PAA of 1:1.5, the molar ratio of metal cations to carboxylic groups was 0.0761:1 and the molar ratio of positive charges from the Pb\(^{2+}\) and Ti\(^{4+}\) ions to carboxylic groups was 0.4566:1.

5.3 Film Preparation

PbTiO\(_3\) films were manufactured on doped and undoped Si wafers and on doped and undoped SrTiO\(_3\) (001) single crystals cleaned in the way described in Sec. 2.4. The precursor was spin-cast with 1,500–4,000 r.p.m. and dried, yielding clear colorless films. They were heated to 700 °C as described in Sec. 2.7 and held at this temperature for 30 min.

Similarly to the calculations made for ZnO (Sec. 4.3), the theoretical shrinkage of the applied PbTiO\(_3\) precursor film during the high-temperature treatment can be estimated. The thickness of the PbTiO\(_3\) film should be 4.4% of the thickness of the precursor film.

5.4 Analysis

An AFM scan of a PbTiO\(_3\) film, depicted in Fig. 5.1, shows a comparatively rough surface. The composition of the films was confirmed by \(\omega\)-2\(\theta\) scans. For films on Si wafer substrates, the diffractogram has all peaks of PbTiO\(_3\), as shown in Fig. 5.2. In addition to the PbTiO\(_3\) peaks, several other peaks are visible, which could not be identified. They have, however, low intensities. The intensity ratios of the PbTiO\(_3\) peaks are in accordance with those of a powder diffractogram, which indicates that there is no preferential orientation of the film. As described in Sec. 2.8, a high polarizability of a polycrystalline PbTiO\(_3\) film in the direction perpendicular to the film plane is desirable for practical applications. Since \(a_{\text{Si}} \approx \sqrt{2} \cdot a_{\text{PbTiO}_3}\), Si (001) wafers are in principle suitable substrates to grow epitaxially \(\bar{c}\)-axis oriented PbTiO\(_3\) films. Si wafers stored in air are always covered with a thin amorphous SiO\(_x\) layer, which prevents epitaxial growth. In the attempt to grow epitaxial PbTiO\(_3\) film on Si (001) wafers,
the substrates were therefore immersed in HF for several minutes to remove the oxide layer and rinsed with water. Immediately after drying in nitrogen, the substrates were spin-coated with the precursor. The samples were treated in the same way as described above, yielding PbTiO$_3$ films that show the same diffractogram as in Fig. 5.2. No further attempts to epitaxially grow PbTiO$_3$ on Si were made. The reason for the failure to obtain $c$-axis oriented films remains therefore unknown. It is, however, likely that the reactive Si surface oxidizes during the high-temperature treatment before PbTiO$_3$ has formed.

By choosing an oxidic substrate, e.g. SrTiO$_3$, the problem of an intermediate layer disturbing the epitaxial growth can be circumvented. The (001) plane of SrTiO$_3$ single crystals matches very well the (001) plane of PbTiO$_3$, as explained in Sec. 2.8. Films on doped and undoped SrTiO$_3$ (001) substrates were made the same way as on Si substrates. Fig. 5.3 shows the $\omega$-2$\theta$ scan of a PbTiO$_3$ film on a SrTiO$_3$ (001) substrate. Only the (00l) peaks of PbTiO$_3$ and SrTiO$_3$ are visible, indicating the expected $c$-axis orientation of the film. However, since (h00) peaks of $a$-axis oriented PbTiO$_3$ coincide with the (00h) peaks of SrTiO$_3$, the amount of possible $a$-axis oriented domains cannot be estimated. With the lattice parameters $a_{\text{SrTiO}_3}=3.905$ Å and $c_{\text{PbTiO}_3}=4.156$ Å (Appendix A.1 and A.6), the lattice mismatch for these domains is $(c_{\text{PbTiO}_3}-a_{\text{SrTiO}_3})/a_{\text{SrTiO}_3}=6.4\%$.

Hsu and Raj [65] find that films thinner than 50 nm consist only of $c$-axis oriented PbTiO$_3$, while with increasing thickness the amount of $a$-axis oriented domains increases to 25% for 350 nm thickness. While the $c$-axis oriented domain ($c_\perp$) is aligned with $c_{\text{PbTiO}_3}\parallel c_{\text{SrTiO}_3}$, for the $a$-axis oriented domains ($a_\perp$) $a_{\text{PbTiO}_3}$ forms an angle of approx. 3.6° with $c_{\text{SrTiO}_3}$ [64–66], as is
depicted in Fig. 5.4 (b). The inclination of $\vec{a}_{\text{PbTiO}_3}$ can be towards any of the four directions [100], [010], [100], [010] of SrTiO$_3$, giving rise to four domains of $\vec{a}$-axis oriented PbTiO$_3$. In Fig. 5.4 (b), only one of the four domains is drawn. An explanation for the inclination of only the $\vec{a}$-axis oriented domains is given by Theis and Schlom [66]. As a consequence, the rocking curve of the SrTiO$_3$ (001) reflection (which has the same d-value as PbTiO$_3$ (100)) shows besides the main peak two smaller side peaks located a few degrees towards lower and higher $\omega$-values.

Rocking curves taken in this work of the SrTiO$_3$ (001) and (002) peaks, had a too small range (ca. 4° in total) to confirm this observation.

Figure 5.2: $\omega$-2$\theta$ scan of a PbTiO$_3$ film on a Si wafer.
5.4 Analysis

Figure 5.3: ω-2θ scan of a PbTiO$_3$ film on a SrTiO$_3$ (001) single crystal.

Figure 5.4: Epitaxial alignment of $\vec{a}$- and $\vec{c}$-axis oriented PbTiO$_3$ on SrTiO$_3$ (001). Without twinning, the lattices of all domains would be parallel to the SrTiO$_3$ crystal lattice (a). In reality, the lattices of the $\vec{a}$-axis oriented domains are tilted by ca. ±3.6° around SrTiO$_3$ [100] and [010] (b). This gives rise to a displacement of the reflections of these four domains.
To confirm both in-plane and out-of-plane orientations, a texture scan of the \{101\} reflections (the strongest ones) of the sample was taken (see also footnote on page 26 for labeling), which is shown in Fig. 5.5. The sample was aligned on the 4-circle-diffractometer such that at $\varphi=0^\circ$ the SrTiO$_3$ [100] direction was in the plane of diffraction. Only four peaks are present in the texture scan, located approx. at $\varphi=0^\circ; 90^\circ; 180^\circ; 270^\circ$. This proves that the $\vec{c}$- and $\vec{a}$-axis oriented PbTiO$_3$ has grown epitaxially: $\vec{a}_{\text{PbTiO}_3}\parallel\vec{a}_{\text{SrTiO}_3}$ and $\vec{b}_{\text{SrTiO}_3};\vec{c}_{\text{PbTiO}_3}\parallel\vec{c}_{\text{SrTiO}_3}$ in the case of $\vec{c}$-axis oriented PbTiO$_3$. In the case of $\vec{a}$-axis oriented PbTiO$_3$ was $\vec{a}_{\text{PbTiO}_3}\approx\parallel\vec{c}_{\text{SrTiO}_3}$ and $\vec{c}_{\text{PbTiO}_3}\approx\parallel\vec{a}_{\text{SrTiO}_3}$ and $\vec{b}_{\text{SrTiO}_3}$. The peak positions in the texture scan (Fig. 5.5) in terms of $\psi$ are not quite clear due to the elongation of the peaks caused by the beam profile. Fig. 5.6 shows the intensity distribution of the four peaks from Fig. 5.5 in more detail. Fig. 5.7 shows the peaks of a second PbTiO$_3$ film grown on a doped SrTiO$_3$ (001) substrate. The second sample was prepared similarly to the first epitaxial PbTiO$_3$ film. The only difference was that the spin-coating velocity was 2,000 r.p.m. instead of 3,000 r.p.m. Nevertheless the peaks have much lower intensities, indicating a lower film thickness or lower amount of crystalline PbTiO$_3$. Note that in Fig. 5.6 the intensities are given in counts per 1.5 seconds, in Fig. 5.7 they are given in counts per 3 seconds. The tilt of the $\vec{a}$-axis oriented PbTiO$_3$ domains does not only give rise to the appearance of side peaks in the rocking curve of the SrTiO$_3$ (001) reflection, caused by the PbTiO$_3$ (100) reflection as described e.g. by Hsu and Raj [65]. It should also give rise to four additional \{101\} peaks in a texture scan, located
Figure 5.6: The peaks of the PbTiO$_3$ \{101\} texture scan of Fig. 5.5 in detail. The center of the $\varphi$ ranges are (a) $\varphi=0^\circ$, (b) $\varphi=90^\circ$, (c) $\varphi=180^\circ$, (d) $\varphi=270^\circ$. The stepwidth in $\psi$ was $1^\circ$. 
Figure 5.7: The peaks of a PbTiO$_3$-\{101\} texture scan of a PbTiO$_3$ film on doped SrTiO$_3$ (001) in detail. The center of the $\varphi$ ranges are (a) $\varphi=0^\circ$, (b) $\varphi=90^\circ$, (c) $\varphi=180^\circ$, (d) $\varphi=270^\circ$. The stepwidth in $\psi$ was 0.4$^\circ$. 
Table 5.1: FWHMs of rocking curves and $\phi$ scan peaks.

<table>
<thead>
<tr>
<th>Rocking curves</th>
<th>$\phi$ scan</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.84^\circ$</td>
<td>$0.88^\circ$</td>
</tr>
</tbody>
</table>

at $\psi=45^\circ-3\cdot1.8^\circ=39.6^\circ$, while the {101} peaks of $\bar{c}$-axis oriented PbTiO$_3$ are located at $\psi=45^\circ+1.8^\circ=46.8^\circ$, as can be seen in Fig. 5.4 (b). Due to the poor resolution of the 4-circle-diffractometer in the $\psi$ direction, when a line profile primary beam was used, these peaks overlap in the texture scan of PbTiO$_3$ {101}. However, in Fig. 5.6 it can be seen that the maxima of the peaks are located at $\psi=43^\circ$ (note that the stepwidth in $\psi$ was $1^\circ$), which is a strong indication for the presence of a certain amount of $\bar{a}$-axis oriented PbTiO$_3$. The peaks in Fig. 5.7, on the other hand are located approx. within the $\psi$ range [45$^\circ$; 48$^\circ$]. Due to the low intensities, their positions are, however, not very clear. The latter finding would be in agreement with the observation in Ref. [65] that thinner films contain less $\bar{a}$-axis oriented PbTiO$_3$, if one assumes that the film of Fig. 5.7 has a lower thickness than that of Fig. 5.6. This assumption is supported by the lower peak intensities.

To investigate the quality of the alignment of the $\bar{c}$-axis oriented PbTiO$_3$ crystals, rocking curves of the (001) and (002) reflections of film and substrate were taken (Fig. 5.8 (a)). In Fig. 5.8 (b), a single $\phi$ scan, extracted from the texture scan in Fig. 5.5 ($\psi=46^\circ$), is depicted. Table 5.1 lists the FWHMs of the rocking curves and of the peaks of the $\phi$ scan. The rocking curves are significantly broader than those of PbTiO$_3$ films grown by chemical vapour deposition ($0.1^\circ$) [64], and also the peaks of the $\phi$ scan are somewhat broader than reported for films grown by pulsed laser deposition ($0.4^\circ$) [66].
Figure 5.8: Rocking curves (a) and \(\{101\}\) \(\varphi\) scan (b) of a \(\text{PbTiO}_3\) film on a \(\text{SrTiO}_3\) (001) single crystal.

The SEM image of the film in Fig. 5.9 shows crystallites with rather round corners and edges, locally forming a continuous film with pores. These pores have comparatively sharper corners and straighter edges. The edges of the pores run more or less in the two directions indicated by the two white lines drawn in the upper right corner of Fig. 5.9. These two directions are parallel to the edges of the \(\text{SrTiO}_3\) substrate, i.e. the [100] and [010] direction of \(\text{SrTiO}_3\), which is in accordance with the epitaxial orientation found before. It can be concluded that \(\text{PbTiO}_3\) has mainly developed the \(\{100\}\) faces (i.e. (100), (010), (\(\overline{1}00\)), and (0\(\overline{1}0\))), forming a tetragonal prism, and the \(\{001\}\) faces (pinacoids). The ap-
pearance of the PbTiO₃ crystallites differs from that of the Bi2212 crystallites shown e.g. in Fig. 7.1. It is remarkable that the edges of the pores (or “negative crystals”) are so much straighter than those of the PbTiO₃ crystallites.

To summarize, PbTiO₃ films have been grown non-epitaxially on Si wafers and epitaxially on SrTiO₃ (001) substrates. The epitaxial films consist of domains of \( \vec{a} \)- and \( \vec{c} \)-axis oriented PbTiO₃.

5.5 Patterned Films of Lead Titanate

For practical applications of PbTiO₃ films, such as data storage or piezo actuators, patterning of the film can improve the suitability, as described in Ref. [69] for magnetic data storage, or even be necessary. Patterned films of PZT have been prepared by a sol-gel process in combination with micromoulding in capillaries (MIMIC) [12, 16]. This method is restricted to “open” structures, where all elevated features of the film are linked to each other. The micromoulding process used in this work, however, allows also patterns of isolated high features such as columns. The PbTiO₃ precursor films were patterned by micromoulding as described in Sec. 2.6. The patterned precursor films were heated in the same way as spin-cast films, which yielded line- and column-patterned PbTiO₃ films. The composition was confirmed by \( \omega\)-2\( \theta \) scans. The films were imaged by light microscopy and AFM (Fig. 5.10).
Figure 5.10: Patterned films of PbTiO$_3$ on Si wafers, imaged by light microscopy ((a) and (b)) and AFM ((c) and (d)). Below (c) and (d), height profiles of the two AFM scans are shown. The parameters, as defined on page 45, are for the line pattern: $a=2.26 \, \mu\text{m}$, $d=1.25(8) \, \mu\text{m}$, $h=90(5) \, \text{nm}$. For the column pattern they are: $a=1.95 \, \mu\text{m}$, $d=1.49(6) \, \mu\text{m}$, $h=115(10) \, \text{nm}$. 