Preparation of epitaxial La$_{2-x}$Sr$_x$CuO$_4$ thin films for dynamic investigations of epitaxial strain

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Abstract.
Investigations using different single crystalline substrates can only hardly correlate the applied strain with the resulting superconducting properties of thin films directly, since growth conditions and microstructure may severely affect these properties. An alternative approach to study this interaction is the preparation of superconducting films on piezoelectric substrates enabling a dynamical variation of the induced strain by applying an electric field on the substrate. In this work we report on preliminary growth studies of thin epitaxial La$_{2-x}$Sr$_x$CuO$_4$ films on standard and piezoelectric single crystalline substrates. Structural and electrical properties of La$_{2-x}$Sr$_x$CuO$_4$ films on SrTiO$_3$ and SrLaAlO$_4$ substrates using on-axis pulsed laser deposition are shown and compared to films grown in off-axis geometry.

Furthermore, we present the first results of the growth of La$_{1.85}$Sr$_{0.15}$CuO$_4$ on piezoelectric (001) Pb(Mg$_{1/3}$Nb$_{2/3}$)$_{0.72}$Ti$_{0.28}$O$_3$ (PMN-PT) substrates using off-axis geometry. Due to a large lattice mismatch between La$_{2-x}$Sr$_x$CuO$_4$ and PMN-PT substrates a buffer layer is required to match the lattice parameters and to support the growth of high quality films. Structural and superconducting properties of thin films grown epitaxial on a SrTiO$_3$ buffer layer are shown and compared to films grown directly on SrTiO$_3$ substrates.

1. Introduction
Detailed studies revealed that the critical temperature ($T_C$) of high-temperature superconductors (HTSC) can be tuned using hydrostatic pressure. For many compounds compressive pressure in different crystallographic directions has an antipodal influence on $T_C$ [1, 2, 3, 4, 5, 6]. By using uniaxial pressure both effects often nearly cancel, leading to only small changes of $T_C$ [7, 8]. A possibility to avoid this effect is the application of biaxial strain in thin films prepared on substrates with different lattice parameters. Under epitaxial growth conditions the in-plane strain $\epsilon_{ab}$ and the out-of-plane strain $\epsilon_c$ normally have an opposite sign, so the effects in both directions amplify each other. Recent works demonstrated the capability of this procedure [9, 10] using the superconducting compound La$_{2-x}$Sr$_x$CuO$_4$. As a result, $T_C$ values exceeding those of bulk samples were reported.

Unfortunately, the usage of different substrates induces a number of different pre-conditions for the film growth such as chemical termination of the surface or misfit and probably results in a varying microstructure and a different density of defects in the grown layers. Hence the comparability of films deposited on different substrates and especially the $T_C$ derivation in respect of the applied strain is hard to verify independent from these parameters. An elegant solution
for this problem is to grow thin films epitaxially on piezoelectric single crystalline substrates of \( \text{Pb(Mg}_{1/3}\text{Nb}_{2/3})_{0.72}\text{Ti}_{0.28}\text{O}_3(001) \) (PMN-PT). The applied strain in the film can be reversibly and uniformly controlled by the inverse piezoelectric effect of this material. This approach offers the unique feasibility of direct investigation of strain-dependent properties of one and the same sample. Recent works showed that this approach is effective to study various physical properties in dependence of the applied strain [11, 12, 13, 14, 15]. Our goal is to study the dependence of superconducting properties in \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) films on strain. In this paper we report the preliminary results of the fabrication of superconducting \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) thin films on standard single crystal as well as on PMN-PT substrates.

2. Experimental

\( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) films with different thickness were prepared on different substrates using a standard pulsed laser deposition (PLD) setup with two different deposition geometries, a Lambda Physics LPX 305 KrF laser and stoichiometric targets. In the case of on-axis geometry the substrates were fixed with silver glue on the holder and heated prior to deposition up to 750°C in an oxygen atmosphere of 0.3 mbar. Subsequently the films were cooled down after deposition in 0.4 bar oxygen atmosphere.

Alternatively, we used off-axis PLD geometry [14, 16] for the preparation of LSCO films on PMN-PT substrates and standard single crystals. Here, we used typical temperatures of 650–700°C and an oxygen partial pressure of 0.3 mbar. Films, which are deposited under this conditions, typically exhibit a very smooth surface and droplet–free growth [16]. The surface morphology of the prepared layers was investigated using atomic force microscopy (AFM). Standard x-ray diffraction (XRD) measurements were applied using Co K\(_\alpha\) radiation, whereas reciprocal space measurements (RSM) of the area around the (103) substrate peak were carried out for structural characterization using a Phillips XPert MRD Diffractometer with Cu K\(_\alpha\) radiation. Pole Figure measurements confirm the high quality texture of our films. The electrical properties were characterized using a Quantum Design standard physical properties measurement system (PPMS).

3. Results and Discussion

3.1. Preparation of \( \text{La}_{2-x}\text{Sr}_x\text{CuO}_4 \) using on-axis PLD

In the first step we optimized the deposition conditions for \( \text{La}_{1.85}\text{Sr}_{0.15}\text{CuO}_4 \) (LSCO) with respect to the \( T_c \) on \( \text{SrTiO}_3 \) (STO) and \( \text{SrLaAlO}_4 \) (SLAO) substrates. The \( \theta \) 2θ–scan (Fig. 1) confirms a c-axis oriented film growth on both substrates and displays no indication of impurities or misorientations for the film on STO. However, the film on SLAO shows two additional peaks which were identified as \( \text{La}_2\text{O}_3 \). The resulting lattice parameters are about \( c = 13.2 \) Å and \( a = 3.78 \) Å for both films. Pole figure measurements reveal a cube on cube epitaxial relationship between superconductor and substrate.
The measurement of the superconducting properties (Fig. 2) showed a superconducting transition of 26 K for the film on STO and of 28 K for the film on the SLAO substrate, respectively. This result is in good agreement with literature data on thin films prepared with PLD and subsequently treated with oxygen [17, 18].

The superconducting transition shows only a slight dependence on the used substrate which is assumed to be a result of the applied misfit [19]. SLAO ($a = 3.756$ Å) induces compressive strain in LSCO ($a = 3.78$ Å) films whereas STO ($a = 3.91$ Å) leads to tensile strain.

Sato et al. postulated a distinct correlation between the $c$-axis lattice parameter and the superconducting transition temperature analyzing a large number of $La_{2-x}Sr_xCuO_4$ samples with Sr-content $x$ between 0.12 and 0.18 [10]. The interpolation of this data predicts a $T_c$ of 28 K for a $c$-axis lattice parameter of 13.2 Å, which fits to our data, quite well.

Reducing the film thickness reveals a quite different behavior. RSM measurements expose high quality epitaxy and a fully strained 50 nm thick LSCO layer on SLAO with lattice parameters of $a = 3.76$ Å and $c = 13.21$ Å. The $T_c$ is reduced to 20 K on this film compared to 300 nm thick films. In contrast, the lattice parameters of a 50 nm thick LSCO layer on STO is fully relaxed with values of $a = 3.79$ Å and $c = 13.16$ Å, which is almost similar to the 300 nm thick films. However, the resistivity of this layer shows a significant drop at 10 K but does not reach zero at $T = 2$ K.

The results were compared to literature data in order to understand this behavior. Cieplak et al. demonstrated that a maximal $T_c$ of around 28 K can be achieved on both, STO and SLAO substrates in LSCO films prepared by PLD and subsequently treated with oxygen having a thickness above 300 nm. With decreasing thickness also $T_c$ decreases, which results in a $T_c$ of around 20 K for 50 nm thick films on SLAO and nearly zero for films on STO [17]. Similar behavior was reported recently for films prepared by pulsed electron deposition [20].

Cieplak et al. postulated that the reduction of $T_c$ is a consequence of the reduced film thickness but without the observation of the resulting LSCO in-plane lattice parameter [17]. Si et al. demonstrated that a decreasing in-plane lattice parameter results in an increasing $T_c$ of LSCO films subsequently treated with both, molecular oxygen and ozone. Furthermore, an increasing oxygen content of LSCO films using ozone improves the critical temperature. In contrast to that report, our LSCO films on SLAO exhibit a reduced $T_c$ in face of a smaller in-plane lattice parameter compared to 300 nm thick films.

However, LSCO films prepared on SLAO subsequently treated with ozone also exhibit a decreasing critical temperature with decreasing thickness. Thereby, films with thicknesses above 20 nm attain a value of around 40 K, whereas 6 nm thick films exhibit a reduced $T_c$ of 25 K [9]. This critical thickness of 20 nm, which here is defined as
value where $T_c$ starts to decrease, roughly is a factor 10 lower than Cieplak et al. obtained for oxygen treated films. In summary, a higher oxygen content is assumed to decrease the critical thickness of LSCO films due to a higher reactivity of ozone. We confirm that the increased integration of defects during relaxation in thicker films increases the oxygen conductivity of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ and so improves $T_c$ compared to complete strained layers. In contrast to that both LSCO films on STO are fully relaxed independent of the thickness. In that case the reduced $T_c$ is assumed to be a result of the reduced thickness.

Finally, we checked the electrical properties of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ films for different Sr-doping content. The results are summarized in Fig. 3. The films show a typical characteristic compared to reported films, also prepared by PLD with oxygen atmosphere [17]. The referred films with $x = 0.1$ and $x = 0.15$ exhibit $T_c$ values of 22 K and 28 K, respectively, which are very close to ours. Cieplak et al. proved a stoichiometric transfer of the ablated material by comparison of the dependence of $T_c$ and $x$ for the used target versus deposited $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ film. Compared to films prepared with ozone generally exhibit higher $T_c$ values [10] and also exhibit a superconducting transition at $x = 0.25$. This suggests that our films still have oxygen vacancies.

### 3.2. Growth of LSCO films using off-axis PLD

PLD in off-axis geometry is the preferred technique in our case for the application of the sensitive 0.3 mm thick PMN-PT substrates, as they don’t need to be fixed with silver glue which reduces the danger of damaging the sample during unmounting. Even small cracks lead to the risk of destroying the sample while applying an electrical field during the study of the dependence of the functional properties on strain.

In the first step, we deposited LSCO films on STO to compare the crystal structure and the superconducting properties to samples prepared by on-axis PLD. The standard XRD scan of off-axis samples often shows additional peaks, which are most probably generated by $\text{La}_2\text{O}_3$ precipitations (Fig. 4(a)). Annealing the sample subsequently deposition for 10 h in 400 bar oxygen reduces these precipitations but does not improve the critical temperature, which is with $T_c = 21$ K for sample (a) and 19 K for sample (b), respectively, slightly smaller compared to samples prepared with on-axis PLD (Fig. 5(b)). RSM measurements confirm similar structural properties for both films compared to on-axis samples and therefore suggest a comparable growth behavior using off-axis PLD. In the case of sample (b), the lattice parameters are $a = 3.78$ Å and $c = 13.21$ Å.

In the next step we prepared LSCO films directly on PMN-PT substrates. PMN-PT has a monoclinic structure with only very tiny distortions regarding a cubic structure ($a = 4.02$ Å). Unfortunately, the larger misfit compared to films on STO substrates leads to a completely
different growth behavior. Standard XRD scans and pole figure measurements reveal a large fraction of a-axis oriented LSCO besides the c-axis oriented grains. Therefore these films show a low (<5 K) or even no superconducting transition. A possible solution for this problem is the deposition of a buffer layer to reduced the misfit. This technique is commonly adapted for the preparation of buffered YBa$_2$Cu$_3$O$_7$ coated conductors [21, 22] and was already realized with SLAO for the LSCO–STO system [18]. The growth of a STO layer on PMN–PT substrates was successfully demonstrated by Bilani-Zeneli et al. [23].

XRD scans confirm a precipitation free cube on cube growth of STO on PMN–PT resulting in lattice parameters of $a = 3.92$ Å and $c = 3.91$ Å for STO which is in good agreement with other works [23]. The pole figure of the STO (110) peak, displayed in Fig. 6(a), verifies the high texture quality without misorientations. This data approve that STO is an adequate buffer layer, which reduces the lattice parameter and offers significantly better preconditions for the further deposition of LSCO layers.

The XRD scan of a LSCO film deposited on the STO-buffered PMN–PT substrate (Fig. 4(c)) shows no indication of misorientation. Similar to films directly prepared on STO, the scan contains only minor additional peaks, which might arise from La$_2$O$_3$ precipitations. The structural parameters of $a = 3.78$ Å and $c = 13.21$ Å are close to LSCO film prepared directly on STO. In the pole figure (Fig. 6(b)) two different peaks are visible. Besides the (103) LSCO (outer peak) the (011) PMN–PT peak is found, which is caused by almost similar 2Θ values of both peaks. The $T_c$ value with about 17 K (Fig. 5(a)) is somehow is smaller compared to films directly on STO. Further optimization is necessary to improve the superconducting properties on PMN–PT.

4. Summary

La$_{2-x}$Sr$_x$CuO$_4$ films were deposited successfully on different single crystals. A clear thickness dependence was found for LSCO using on-axis PLD, which is more pronounced for STO. LSCO layers deposited on STO using off-axis geometry exhibit slightly smaller $T_c$ values compared to layers deposited by on-axis geometry. The large misfit of the PMN–PT substrates requires the application of a buffer layer resulting in c-axis oriented LSCO layers. We showed the efficiency of STO as buffer layer for the deposition of LSCO layers leading to a superconducting transition of about 17 K. Further investigation is necessary to optimize the LSCO films and study the superconducting transition in dependence of biaxial stain.
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