Coherently strained epitaxial YBa$_2$Cu$_3$O$_{7-\delta}$ films grown on NdGaO$_3$ (110)

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YBa$_2$Cu$_3$O$_{7-\delta}$ is a good candidate to systematically study high-temperature superconductivity by nanotechnology using advanced epitaxy. An essential prerequisite for these studies is coherently strained YBa$_2$Cu$_3$O$_{7-\delta}$ thin films, which we present here using NdGaO$_3$ (110) as a substrate. The films are coherent up to at least 100 nm thickness and have a critical temperature of 89±1 K. The $a$ and $b$ lattice parameters of the YBa$_2$Cu$_3$O$_{7-\delta}$ are matched to the in-plane lattice parameters of NdGaO$_3$ (110), resulting in a large reduction of the orthorhombicity of the YBa$_2$Cu$_3$O$_{7-\delta}$. These results imply that a large amount of structural disorder in the chain layers of YBa$_2$Cu$_3$O$_{7-\delta}$ is not detrimental to superconductivity.

The origin of high-temperature superconductivity in the cuprates is one of the biggest and most fascinating challenges in solid-state research. Thin film epitaxy of cuprates superconductors is essential for applications such as superconducting cables and devices. Epitaxial growth is also a vital tool to answer fundamental questions about the nature of superconductivity. For example, the first phase-sensitive determination of the $d$-wave symmetry of the superconducting order parameter was performed by analyzing the spontaneous flux of YBa$_2$Cu$_3$O$_{7-\delta}$ rings grown on a tricrystal substrate, the amount of admixtures to the $d$-wave order parameter symmetry were precisely determined using thin film YBa$_2$Cu$_3$O$_{7-\delta}$-Nb junction technology and a direct correspondence between the critical temperature ($T_c$) and the superfluid density was recently observed in overdoped La$_2$-$x$Sr$_x$CuO$_4$ using high-quality epitaxial thin films.

Moreover, advances in thin film epitaxy such as composition control and layer-by-layer growth monitoring allow for the systematic modification of materials and for artificial materials design. YBa$_2$Cu$_3$O$_{7-\delta}$ is a well-studied cuprate superconductor because of its high critical temperature, the ability to grow high-quality single crystals with effective doping control, and its layered crystal structure where dopants reside away from the CuO$_2$ plane, thus minimizing electron scattering. Therefore, YBa$_2$Cu$_3$O$_{7-\delta}$ is an excellent candidate material for studies by epitaxial modification schemes. An essential prerequisite for such studies is a suitable substrate that results in coherently strained YBa$_2$Cu$_3$O$_{7-\delta}$ films that are single domain together with bulk-like superconducting properties. Here, we demonstrate that YBa$_2$Cu$_3$O$_{7-\delta}$ films grown on NdGaO$_3$ (110) fulfill these requirements.

NdGaO$_3$ has the orthorhombic lattice structure with $a = 5.417$ Å, $b = 5.499$ Å, and $c = 7.717$ Å. Its (110) surface has a rectangular lattice structure with a pseudocubic lattice parameter of 3.85 Å along the (001) direction and a pseudocubic lattice parameter of 3.86 Å along the (110) direction. Atomically smooth surfaces were obtained by a combination of sonication in deionized water, chemical etching with a buffered hydrofluoric acid solution and a two-hour 1000 °C annealing step, similar to the procedure commonly used for SrTiO$_3$. The YBa$_2$Cu$_3$O$_{7-\delta}$ samples were grown by pulsed laser deposition from a stoichiometric target. The growth temperature was 780 °C, the oxygen partial pressure was kept to 0.4 mbar, the target-substrate distance was 5 cm, and the laser fluence was 3 J/cm². After growth, the samples were annealed for two hours at 450 °C in an oxygen atmosphere of 400 mbar. Four samples were grown with thicknesses of 10, 25, 50, and 100 nm. The surface morphology was measured with a Cypher atomic force microscope (AFM) and the X-ray diffraction measurements (XRD) were performed with a Panalytical Empyrean diffractometer in high-resolution mode. We define the out-of-plane component of the momentum transfer $Q_{\text{out}}$ as the component of $Q$ parallel to the (110) direction of the NdGaO$_3$ crystal. The in-plane component of the momentum transfer...
$Q_{in}$ is the component of $Q$ perpendicular to $Q_{out}$ and within the diffraction plane. The film thicknesses were determined using a Dektak surface profiler after etching part of the samples with a phosphoric acid solution. The temperature dependence of the resistance was measured in the van der Pauw geometry using a Quantum Design physical properties measurement system.

Figure [1] shows an out-of-plane XRD scan of the 100 nm-thick sample. Next to four substrate peaks, thirteen peaks corresponding to the \{(00l)\} reflections of YBa$_2$Cu$_3$O$_{7-δ}$ are observed. We do not observe peaks corresponding to other orientations of YBa$_2$Cu$_3$O$_{7-δ}$, nor those of secondary phases. Therefore we conclude that the YBa$_2$Cu$_3$O$_{7-δ}$ is single-phase, \{(001)\}-oriented. The $c$-axis lattice parameter is 11.7 Å, in good agreement with the $c$-axis lattice parameter of optimally doped YBa$_2$Cu$_3$O$_{7-δ}$ single crystals. The precise orientation of the films was measured by performing reciprocal space maps around the \{(009)\} reflection for four different values of the azimuthal angle $φ$, as shown in Fig. [2]. The maps also show the NdGaO$_3$ \{(330)\} reflection. The film peak is significantly broadened along $Q_{in}$ in comparison to the substrate peaks for all values of $φ$. For $φ=0^\circ$ ($φ=180^\circ$), the peak center is observed at a larger (smaller) $Q_{in}$ value than that of the substrate peak and the peak shape is asymmetric with a long tail towards larger (smaller) $Q_{in}$ values. In contrast, for $φ=90^\circ$ and $φ=270^\circ$, the film peaks are symmetrical and at the same value of $Q_{in}$ as the substrate peak. This implies the CuO$_2$ planes of the YBa$_2$Cu$_3$O$_{7-δ}$ are oriented at an angle of 0.07 degrees with respect to the crystal lattice of the NdGaO$_3$ substrate. The in-plane projection of the tilt is mostly along $φ=0$. This tilt exactly corresponds to the miscut of the substrate. Therefore the film is oriented with its \{001\} lattice direction parallel to the surface normal vector of the NdGaO$_3$ crystal. The alignment of the YBa$_2$Cu$_3$O$_{7-δ}$ lattice planes with the optical surface of the substrate was also observed for the 50 nm-thick sample. The large peak width along $Q_{in}$ can be due to either mosaicity or a reduction of the in-plane coherence length. The two scenarios can be discriminated by measuring the peak widths at a series of \{(00l)\} peaks. This analysis (data not shown) clearly determined the width to be due to a mosaicity of 0.12° with negligible contribution of a reduction of the in-plane coherence length. In contrast to the thick samples, the two thinner films are oriented such...
that the YBa$_2$Cu$_3$O$_{7-\delta}$ lattice planes are aligned to the NdGaO$_3$ crystal planes, with a peak width smaller than the resolution of the diffractometer, Fig. 2). 

We next turn to the analysis of the in-plane components of the crystal structure. φ-Scans of asymmetric reflections confirmed the epitaxial alignment of all the films with the $a$- and $b$-axes of the YBa$_2$Cu$_3$O$_{7-\delta}$ aligned with the [001] and [1T0] lattice directions of the NdGaO$_3$, respectively. Furthermore, we performed reciprocal lattice maps around asymmetric reflections to study the in-plane crystal structure of the films. Representative maps around the set of YBa$_2$Cu$_3$O$_{7-\delta}$ {109} reflections are shown in Figs. 2a-d. Figure 2f shows the maps of the $t = 100$ nm sample with the in-plane momentum transfer aligned with the NdGaO$_3$ [001], [T10], [00T], and [1T0] lattice directions, respectively. Broad film peaks are observed, indicating a reduced in-plane coherence of the crystal structure compared to that of the substrate, in agreement with the mosaicity described above. The in-plane lattice parameters were extracted from the differences in peak positions with positive and negative in-plane momentum transfer. We find that the film’s in-plane lattice parameters are equal to those of the substrate, $a = 3.85$ Å and $b = 3.86$ Å. Figure 2f shows the maps of the $t = 25$ nm sample. For this sample peaks are observed that are very narrow along the in-plane direction and elongated along the out-of-plane direction. The in-plane momentum transfer of the film peaks is equal to that of the substrate peaks. This agrees well with a thin film that is coherently strained to the substrate, with $a = 3.85$ Å and $b = 3.86$ Å. The in-plane coherence of the film is equal to that of the substrate peaks. We find that the film’s in-plane lattice parameters are equal to those of the substrate, $a = 3.85$ Å and $b = 3.86$ Å. The out-of-plane elongation of the film matches the expectation based on the finite thickness of the film. The unit-cell angles of the YBa$_2$Cu$_3$O$_{7-\delta}$ samples were determined to be 90 degrees by analysing the sets of {109} and {119} reflections. Therefore, all films are orthorhombic.

The morphology of the samples consists of large two-dimensional islands with a height of 12±1 Å, matching the YBa$_2$Cu$_3$O$_{7-\delta}$ $c$-axis lattice parameter. Typically, four different height levels are found within a single terrace of the underlying substrate, indicating that the growth mode of the films is multi-level island growth. Furthermore, some particles with a size of $\sim 10$ nm were found on the surface. These particles, which are tentatively attributed to Y$_2$O$_3$, are commonly observed on PLD-grown YBa$_2$Cu$_3$O$_{7-\delta}$ and were not further investigated as they are not expected to significantly influence the crystal structure and electrical transport properties.

The temperature dependence of the resistivity of all samples is shown in Fig 3. The room-temperature resistivity is $\sim 350 \mu\Omega$ cm, the temperature dependence of the resistivity is linear for $T > T_c$, and $T_c = 89\pm 1$ K for the films with $t \geq 25$ nm. These results are in good agreement with the resistivity of optimally doped YBa$_2$Cu$_3$O$_{7-\delta}$ single crystals, albeit with a factor of two higher resistivity[17,18]. The thinnest sample, in contrast, has a room temperature resistivity of 700 $\mu\Omega$ cm, a sublinear $\rho(T)$, and a reduced $T_c$ of 80 K. The reduction of $T_c$ in thin YBa$_2$Cu$_3$O$_{7-\delta}$ samples is commonly observed[19].

We start the discussion of the crystal structure of the films and its implications with the observation that the films are untwinned and $c$-axis oriented. Earlier reports mention predominantly $a$-axis oriented films for YBa$_2$Cu$_3$O$_{δ}$ on NdGaO$_3$ at growth temperatures below 570 °C and fully $c$-axis oriented films grown above 800 °C[20,22]. Moreover, YBa$_2$Cu$_3$O$_{7-\delta}$ thin films on perovskite oxides are generally twinned with up to four different structural variants[23,24]. The amount of variants can be reduced to two by anisotropic strain using the NdGaO$_3$ (001) crystal orientation[25] or to one by choosing a suitable miscut of the substrate[26]. Earlier experiments with NdGaO$_3$ (110) resulted in four structural variants[23,24]. The in-plane coherence of a thin film depends on the initial growth and is limited by anti-phase boundaries[27,28]. The absence of twinning in our films and the $c$-axis orientation is therefore probably explained by an enhanced surface diffusivity due to the chemical substrate preparation resulting in a singly terminated surface. Control experiments using substrates with mixed termination yielded samples with significantly reduced structural quality. However, the general advances in thin-film growth techniques made in the last decades, such as the minimization of impurities and homogeneous ablation of the target, are also expected to be beneficial to the quality of the films.

The alignment of YBa$_2$Cu$_3$O$_{7-\delta}$ with respect to the optical surface of the substrate is commonly observed[29,30]. The large $c$-axis lattice parameter of YBa$_2$Cu$_3$O$_{7-\delta}$ does not match well with the small step-height of the NdGaO$_3$ terraces. The tilt of the YBa$_2$Cu$_3$O$_{7-\delta}$ crystal structure prevents the necessity of anti-phase boundaries occurring at the stepedges, thereby reducing the energy of the film. The tilt, however, also
implies a larger substrate-film interface energy as the chemical bonds have to adjust to large local strain fields. The balance of these energies explains why the tilt occurs for the thicker films, but not for the thinner films.

These YBa$_2$Cu$_3$O$_{7-\delta}$ thin films have an unusual strain state. On average, NdGaO$_3$ (110) is close to being lattice matched and therefore no biaxial strain is present. However, a significant uniaxial strain component is present that compresses the $b$-axis and extends the $a$-axis, thereby reducing the orthorhombicity of the YBa$_2$Cu$_3$O$_{7-\delta}$ from 0.018 to 0.002. This strain state cannot directly be compared to that of YBa$_2$Cu$_3$O$_7$ single crystal subject to uniaxial stress$^{[30]}$, because in our case the stress is applied when the YBa$_2$Cu$_3$O$_7$ is cooled through the tetragonal to orthorhombic phase transition at high temperature. During the cooling process, the films remain clamped to the substrates. The orthorhombic-tetragonal phase transition is related to the formation of the CuO chains in the crystal structure. Since the strain state is observed for films with a large thickness, it is very likely that the structure is stabilized by a significant reduction of CuO chain formation. A strain-induced change in oxygen stoichiometry would result in a change in $T_c^{[29]}$, contrary to the observations. Therefore, the oxygen stoichiometry of the films has to be similar to that of optimally doped single crystals and the lack of CuO chains implies most of the oxygen ions in the chain layer are randomly distributed between bonds in the $a$ and $b$ lattice directions. The behavior of these YBa$_2$Cu$_3$O$_{7-\delta}$ films thus implies that a large amount of structural disorder in the chain layers of YBa$_2$Cu$_3$O$_{7-\delta}$ is not detrimental to superconductivity.

In conclusion, we have shown that YBa$_2$Cu$_3$O$_{7-\delta}$ grows coherently strained on NdGaO$_3$ (110) with thicknesses up to 100 nm. The critical temperature is 89 K for $t \geq 25$ nm. For $t \geq 50$ nm, the $c$-axis lattice parameter tilts in the direction of the normal to the optical surface of the substrate. These results show that YBa$_2$Cu$_3$O$_{7-\delta}$ grown on NdGaO$_3$ (110) is a promising cuprate for systematically studying the superconductivity of the high-$T_c$ cuprates by materials modification using advanced epitaxy. The combination of high $T_c$ and reduced orthorhombicity implies a large amount of structural disorder in the chain layers of YBa$_2$Cu$_3$O$_{7-\delta}$ is not detrimental to superconductivity. Finally, coherently strained YBa$_2$Cu$_3$O$_{7-\delta}$ thin films are expected to be beneficial to superconducting electronic devices, such as grain-boundary Josephson devices.

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