T\textsubscript{c} Optimisation of GdBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} Thin Films Grown by Pulsed Laser Deposition

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Abstract. GdBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7} thin films were deposited on single crystalline LaAlO\textsubscript{3}(100) substrates by pulsed laser deposition (PLD) in on-axis geometry. The deposition parameters temperature, laser repetition rate and oxygen partial pressure were optimized with respect to critical temperature \(T\textsubscript{c}\) and self-field critical current density \(J\textsubscript{c}\) of the films. We obtained the best films with a deposition temperature of 910 \(^\circ\)C, an oxygen partial pressure of 0.3 mbar and a laser frequency of 2 Hz. This film had a \(T\textsubscript{c}\) of 93.3 K with a \(\Delta T\textsubscript{c}\) of 0.6 K. The self-field \(J\textsubscript{c}\) at 77 K measured inductively was above 1.5 MA/cm\(^2\).

1. Introduction

YBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\textdelta} (YBCO) is the most widely and thoroughly investigated high-temperature superconductor, and most of the coated conductor development is undertaken on YBCO. However, comparative studies, e.g. [1, 2], on different rare-earth elements showed that the pinning properties depend strongly on the ion radii of the rare earths. Recently, GdBa\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-\textdelta} (GdBCO) is also used for the fabrication of coated conductors and shows promising properties. Especially the 3 K higher transition temperature \(T\textsubscript{c}\) compared to YBCO makes it a better candidate for applications at 77 K. The very similar ionic radii of Gd and Ba result in a higher degree of disorder and, hence, in pinning sites, which further improves the pinning properties, especially at elevated temperatures. This effect is also utilized in mixed-rare-earth films [3].

Feldmann et al. [4] have shown for YBCO that the pinning properties and the \(J\textsubscript{c}\) anisotropy change with the variation of the deposition parameters of the PLD. The main focus laid on the deposition temperature, \(T\textsubscript{dep}\). This paper shows a similar optimisation for GdBCO thin films, where the deposition temperature, the laser repetition rate and the oxygen partial pressure were varied to optimise the superconducting parameters \(T\textsubscript{c}\), \(\Delta T\textsubscript{c}\) and self-field \(J\textsubscript{c}\).

2. Experimental

Pulsed laser deposition (PLD) in on-axis geometry was used for the preparation of our films utilising a commercial GdBCO target with a diameter of 2 cm and LaAlO\textsubscript{3}(100) single crystal substrates. Therefore, a KrF excimer laser was used having a wavelength of 248 nm. The energy density on the target surface was around 2.0 J/cm\(^2\) applying a laser energy of 235 mJ. The distance between target and substrate was set to about 6 cm. The deposition conditions for the GdBCO film were varied in order to optimise the structural and superconducting properties of this material.
In particular, a deposition temperature \( T_{\text{dep}} \) between 870 °C and 930 °C, an oxygen partial pressure \( p \) during deposition between 0.1 mbar and 0.5 mbar (with a constant oxygen flow of 44 sccm) and a laser repetition rate \( f \) between 1 Hz and 10 Hz was used. The deposition rate was kept constant with a value of about 1 Å/pulse. All films were deposited with 3000 pulses, i.e. the final thickness was at around 300 nm. After deposition, the GdBCO films were cooled down in a few minutes to 750 °C and kept at this temperature for 5 minutes. In this time, the chamber was filled with pure oxygen up to a pressure of 400 mbar. Afterwards, the samples were cooled down slowly to room temperature.

The crystalline quality of the GdBCO thin films was checked by X-ray diffraction (XRD) with Co-K\( \alpha \) radiation in Bragg-Brentano geometry. The surface morphology was investigated by atomic force microscopy (AFM) and scanning electron microscopy (SEM). The thickness was verified by AFM on patterned samples. The critical temperature \( T_c \) and the self-field critical current density \( J_c(0) \) were checked by inductive methods. Selected samples were patterned and measured resistively in standard four-point geometry using a Quantum Design PPMS.

3. Results and discussion

3.1. Structural Properties

The XRD scans in Fig. 1 reveal good c-axis oriented growth of GdBCO, as only (00\( l \)) peaks of this compound are present. Additionally, small impurity peaks are visible with the main intensity at \( 2\theta = 59.8° \) and \( 2\theta = 96.3° \), which can not be indexed with GdBCO or other simple oxide phases like Gd\( _2 \)O\( _3 \) or GdCuO\( _2 \). In general, the intensity of the impurity phase increases with higher deposition temperature and higher oxygen partial pressure. In contrast, no general trend was found in the case of changed laser repetition rate (Fig. 1b). Further detailed analysis using transmission electron microscopy (TEM) is required to identify these phases.

Texture measurements revealed a perfect cube-on-cube epitaxial relationship between the LaAlO\( _3 \) substrate and the GdBCO film. No additional a-axis oriented texture component was detected in the corresponding measurements.

The surface morphology of the grown samples was studied in detail using SEM and AFM measurements. The dependence of the GdBCO surface structure on the laser repetition rate is shown as one example in Fig. 2. A typical pinhole structure was observed on all samples similar to YBCO films grown by standard PLD [5]. Additionally, an elongated substructure is visible, which seems to be closely related to the pinholes and has a distinct orientational relationship towards the single crystalline substrate. This substructure is more pronounced at higher laser repetition rates.

![XRD scans](attachment:image.png)

**Figure 1.** XRD scans for GdBCO films in dependence of: (a) the oxygen partial pressure \( (T_{\text{dep}} = 910°C, f = 5 \text{ Hz}) \); (b) the laser repetition rate \( (T = 910°C, p = 0.3 \text{ mbar}) \).
Figure 2. SEM pictures of the GdBCO surfaces for samples deposited with a laser repetition rate of:
(a) 1 Hz, (b) 2 Hz, (c) 5 Hz and (d) 10 Hz ($T_{\text{dep}} = 910^\circ \text{C}$, $p = 0.3$ mbar).

The origin of this feature is still unsolved as the existence of a significant a-axis oriented component was ruled out in the x-ray measurements. Therefore, more detailed structural analysis using TEM cross sections is necessary. The sample with $f = 1$ and 2 Hz (Fig. 2a and b) show a lot of smaller precipitates at the surface. They are in the range of 100 nm, presumably Gd oxide or CuO particles.

3.2. Superconducting Properties
The superconducting properties of the prepared sample series were determined using inductive as well as resistive measurements. Figure 3 shows the resistively measured superconducting transition in dependence on the different deposition parameters. The data in Figure 3a indicate that the highest critical temperature $T_c$ for the GdBCO thin films was achieved with a value of $T_c = 93.5$ K for a deposition pressure of 0.3 mbar ($T_{\text{dep}} = 910^\circ \text{C}$, $f = 5$ Hz). At the same time, the transition curve of this film is sharper compared with the other samples. It was also found that the $T_c$ decreases monotonously with increasing laser repetition rate (Fig. 3 (b)). This indicates that the development of an optimal structure requires sufficient time between the laser pulses. This is especially important for GdBCO because a high deposition rate usually leads to an increased ionic disorder, which in general decreases $T_c$.

Finally, an optimal deposition temperature of 910°C was found (Fig. 3c). This temperature is rather high, compared with literature data. Miyachi et al. [2] deposited GdBCO on MgO (100) substrates at a deposition temperature of 850°C and Song et al. [6] on SrTiO$_3$ (100) at 810°C, and Li et al. [7] with sputtering on LaAlO$_3$ (100) at 820 °C, all more than 60 °C lower than for our films.
Figure 3. Superconducting transition measured resistively for GdBCO films deposited at different: (a) oxygen background pressures; (b) laser repetition rates; (c) deposition temperatures.

Figure 4 shows the deposition temperature dependence of the critical temperature for $f = 5$ Hz and $p_{\text{dep}} = 0.3$ mbar. A strong dependence of $T_c$ on temperature with a distinctive maximum at 910 °C is visible. Compared with the ablation of YBCO thin films this is an increase in deposition temperature of about 100 K [5].

As shown in Fig. 4, $\Delta T_c$ was minimised for the deposition temperature about $T = 910$ °C. Furthermore, $p = 0.3$–0.4 mbar and $f = 2$ Hz lead to minimised transition widths. Remarkable is the small optimisation window for most of the deposition parameters: We obtain for example with a deposition temperature of 870 °C only a $T_c = 91.25$ K and a $\Delta T_c = 3.55$ K. Also a change in pressure from 0.3–0.4 mbar to 0.1–0.2 mbar, $\Delta T_c$ increases from 0.8–0.9 K to 1.9–2.1 K. The same range is seen in the frequency series, but the small number of samples between 1 Hz and 10 Hz does not allow a more precise quantitative investigation.

Figure 5 shows the dependence of the deposition temperature on the critical current density $J_c$ as an example of the dependence of $J_c$ on different deposition parameters. $J_c$ is roughly $T_{\text{dep}}$ independent with a value of around 1.5 MA/cm², however with a little enhancement for the highest and lowest deposition temperatures. The comparison with the maximum values of YBCO thin films [8, 9] shows smaller values, probably because of the precipitates as seen in Fig. 2.

These particles are dispersed randomly; the superconducting current must find its way in a percolative process, and the superconducting cross-section is diminished. Nevertheless, the superconducting transitions and the $J_c$ values around 1.5 MA/cm² provide evidence for good epitaxial
growth of these thin films. However, $J_c$ has to be improved by minimising the number of precipitates. One possibility is a variation in the target stoichiometry as shown by Lee et al. [9].

4. Summary
The best superconducting properties are obtained for a deposition temperature of 910 °C, an oxygen partial pressure of 0.3 mbar, and a laser frequency of 2 Hz. For these conditions we obtain a $T_c$ of 93.3 K with a $\Delta T_c$ of 0.6 K. The XRD measurement shows a good c-axis orientation of all films, the surface analysis has resulted in an inhomogeneous film with an interesting orthogonal substructure of an unknown phase within the film. For future, e.g. studies of the pinning properties and the anisotropy behaviour, a reduction of these secondary phases is necessary.

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