A study of the fabrication and characterisation of high temperature superconductor YBa2Cu3O7 thin films

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Chapter II. Fabrication and characterization of YBa$_2$Cu$_3$O$_{7-x}$ thin films grown on YSZ (100) single crystal substrate using the pulsed laser deposition method

II. 1. Introduction

II. 1. 1. Substrate selection

Three types of single crystal substrate, YSZ (100), SrTiO$_3$ (100), and LaAlO$_3$ (100) were chosen for making Y123 thin films for the work described in this thesis. These three substrates have been widely used for making Y123 films, as they have superior properties over other types of substrates, including chemical compatibility, good thermal expansion matching, lack of reactivity in oxygen-rich ambient conditions, good lattice matching with Y123, and low dielectric loss at high frequency [46]. Some properties of these substrates are shown in table 1.

STO has a rather small lattice mismatch with YBCO (since its lattice constant is 0.3905 nm) and is able to support high quality YBCO films with the-state-of-the-art properties. However, it has a large dielectric δ constant which prohibits its application in microwave applications.

Table 1. Properties of three substrates. Data are extracted from Ref. [46].
LaAlO$_3$ also offers small lattice and thermal mismatches with HTS materials. The pseudocubic lattice constant is 0.5377 nm. The dielectric constant is 24, and $\tan \delta$ is $3 \times 10^{-5}$.

YSZ has fair lattice matching with Y123 and low dielectric loss, however, it has a large lattice mismatch with Y123 compared to STO and LAO substrates, and it should be noted that both YSZ and STO each have a positive lattice mismatch with Y123. However, LAO has a negative mismatch. These differences in lattice mismatch may cause differences in the film growth process and in turn lead to differences in film properties as will be seen in following chapters.

### II. 1. 2. Reported $J_c$ values

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\Delta a/a$</th>
<th>$\Delta b/b$</th>
<th>$\Delta c/c$</th>
<th>$\varepsilon$</th>
<th>$\tan \delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>+3.6</td>
<td>+6.3</td>
<td>+5.8</td>
<td>25</td>
<td>$8 \times 10^{-3}$ (100K, 300GHz)</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>+2.0</td>
<td>+0.7</td>
<td>+0.1</td>
<td>277</td>
<td>$6 \times 10^{-2}$ ((100K,300GHz)</td>
</tr>
<tr>
<td>LaAlO$_3$</td>
<td>-0.9</td>
<td>-2.2</td>
<td>-3.0</td>
<td>24</td>
<td>$3 \times 10^{-5}$ (77K, 5GHz)</td>
</tr>
</tbody>
</table>

The best values of critical current density ($J_c$) at 77 K in zero field reported by different groups [20,46,47,116,117] for the various widely-used single crystal substrates are
summarized in Fig. 1. It can be seen that the $J_c$ values of films grown on the LAO and STO substrates range from $1.0 \times 10^6$ A/cm$^2$ and are higher than that grown on YSZ. However, the best $J_c$ for films grown on MgO is only about $1 \times 10^6$ A/cm$^2$. It has been accepted that films with $J_c$ of about the $1-2 \times 10^6$ A/cm$^2$ grown on different substrates can be regarded as reasonable samples for both fundamental studies and device fabrication.

Fig. 1. The range of the best reported $J_c$ values for Y123 thin films grown on some commonly used substrates. Most of the reported $J_c$ values are in the range below the middle values of each marked area.

The quality of Y123 thin films prepared using the PLD technique is very sensitive to the deposition conditions, such as oxygen pressure, deposition temperature, annealing
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temperature, laser frequency, distance between target and substrate, and laser energy. One has to carry out a large numbers of experiments using various deposition conditions in order to find the best combination of the above mentioned conditions. Therefore, the first part of the thesis work relating to the thin film fabrication using PLD focuses on finding the optimum deposition conditions for pure Y123 films. Then a study of the effects of nano-Ag addition on the performances of Y123 films is presented based on the optimised conditions for Y123 films. This chapter (II) focuses on: Optimising deposition conditions for pure Y123 films, a systematic study of correlations between various deposition conditions and film characteristics performed on films grown on YSZ single crystal substrates. Chapters III-V deal with the effect of nano-Ag particle inclusions on the critical current density and flux pinning for films grown on various single crystal substrates.

II. 2. Experimental

II. 2. 1. Laser deposition system

The PLD system (Fig. 2) used for the present study has the following main features:

1) Spherical chamber with a base vacuum of $1 \times 10^{-7}$ torr.
2) Turbomolecular pump.
3) Compex 301 KrF excimer laser with a wavelength of 248 nm, 25 ns pulse duration, and a frequency of 1-10 Hz.
4) Six target holders allowing multi-layer deposition.
5) Target rotation by an external motor.
6) Substrate temperatures up to 900°C, adjustable by a digital controller.

7) Two gauges measuring the pressure from 1 atm to $10^{-9}$ torr.

**Fig. 2. Schematic diagram of PLD system.** It contains: 1) laser source; 2) optical alignment and focusing system; 3) vacuum chamber; 4) gas controller; 5) target and substrate manipulators; 6) heating system; and 7) viewing windows.

**II. 2.2. Characterisation methods**
A Philips x-ray diffractometer with Cu K$_\alpha$ radiation was used to carry out the crystallinity and texture investigations. The x-ray wavelength was 1.54 Å with a beam size of 3 mm.

Scanning electron microscopy (SEM) experiments were performed on a Hitachi 2000. Some specimens were also examined by scanning electron microscopy in a JEOL JSM 5400 microscope that was operated at 10 kV. No conductive coating was applied. Surface morphologies with detailed surface microstructures were also investigated using optical microscopy and atomic force microscopy (AFM).

The superconducting transition temperatures, $T_c$, for all films were measured by AC susceptibility and the critical current density, $J_c$, was estimated from DC magnetisation hysteresis loops measured over a wide temperature range at 5, 10, 20, 30, 40, 50, 60, 70, and 77 K in external DC fields of up to 5 T parallel to the c-axis of the films using a commercial physical property measurement system (PPMS, Quantum Design).

**II. 2. 3. Study of deposition conditions**

As the superconducting properties of Y123 films are very sensitive to the deposition conditions, many different conditions have been tried. Different variables such as distance between target and substrate (D), deposition temperature ($T_d$), laser energy (E), oxygen pressure ($P_{O_2}$) and annealing temperature ($T_a$) have been investigated in relation to superconducting transition temperatures and their transition widths. The
relationships between variables are plotted in Figs. 3-6 in which only one variable is chosen.

It can be seen that the $T_c$ of films have close relations with those variables. There is an optimum distance ($D$) between target and substrate, which is about 40 cm under other fixed conditions as indicated in the inset of Fig. 3. Oxygen pressure is also very sensitive to $T_c$ for a fixed $D$ of 40 cm and other conditions (Fig. 4). High deposition temperatures seemed to be beneficial to high $T_c$ as revealed in Fig. 5. An appropriate combination of all those conditions was $D = 45$ cm, $T_d = 780\, ^\circ\text{C}$, $E = 300\, \text{mJ/pulse}$, and $T_a = 550\, ^\circ\text{C}$, which led to the best $T_c$ of 90 K, as shown in Fig. 6. Furthermore, the transition widths also became sharp under those optimum deposition conditions.

![Graph showing the correlation between $T_c$ and target-substrate distances](image)

Fig. 3. The correlation between $T_c$ and target-substrate distances with the other conditions fixed: deposition temperature of $720\, ^\circ\text{C}$; laser energy 290 mJ; a annealing temperature $450\, ^\circ\text{C}$; and oxygen pressure 200 mTorr.
Fig. 4. The correlation between $T_c$ and oxygen pressure with the other conditions fixed: target-substrate distance of 40 mm; deposition temperature of 720 °C; laser energy 290 mJ; annealing temperature 450 °C.

Fig. 5. The correlation between $T_c$ and deposition temperature with other conditions fixed: target-substrate distance of 45 mm; laser energy 290 mJ; annealing temperature 600 °C; and oxygen pressure 200 mTorr.
Fig. 6. The correlation between $T_c$ and oxygen pressure with other conditions fixed: target-substrate distance of 45 mm; deposition temperature of 780 °C; laser energy 300 mJ; annealing temperature 550 °C. Note that all the conditions in this graph are different from those indicated in Fig. 4.

Fig. 7 shows the temperature dependence of $T_c$ for some typical samples made using the deposition conditions indicated in Figs. 3-6. Curves 6-8 represent several samples made with a substrate temperature of 720 °C. For a substrate temperature of 780 °C, the $T_c$ gradually raised increased from 40 K (curve 9) up to 89 K (curves 1 and 2) as the oxygen pressures increased from 240 to 350 mTorr. Meanwhile, it can be seen that the transition widths become sharper.
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Fig. 7. Temperature dependence of $T_c$ for some typical samples. Curves 6-8 represent films made with a substrate temperature ($T_s$) of 720 °C, oxygen pressure (PO$_2$) < 240 mTorr, target-substrate distance < 30 mm. Curve 4 and 5 are from samples with $T_d$ of 780 °C and PO$_2$ 240-280 mTorr. Curves 1-3 are from samples with $T_d$ of 780 °C, and PO$_2$ of 300-350 mTorr. Other conditions for samples 1-5: target-substrate distance 40-45 mm; laser energy 300 mJ; annealing temperature 450 °C.

Generally speaking, the key factors for achieving films with high $T_c$ and narrow transitions are deposition temperature, oxygen pressure, the distance between target and
substrate, and laser fluence. It should be noted that the optimum conditions found for making high quality Y123 films and used in the thesis work are in the range reported by other groups [20,46,47,118,119]. As indicated in Fig. 3, the $T_c$ is very sensitive to the substrate-target distance. The optimum distance under the conditions given in this figure is around 40 mm. Taking into account both the distance and oxygen pressure, a distance of 45 mm was found to produce the best quality Y123 films used in these thesis studies. A picture of the plume recorded during deposition is shown in Fig. 8.

Fig. 8. An optical image showing the shape of the visible plume resulting in the best films.
II. 2. 4. Surface Morphology by AFM

An extensive study on the morphology of surfaces of films has been carried out using AFM to gain detailed information about the surface microstructures. It was found that the microstructures are very sensitive to the laser frequency and substrate temperature, but not to the oxygen pressure, when the other deposition conditions such as substrate-target distance, laser energy, annealing temperature, and deposition time, are fixed. Fig. 9 shows a comparison of AFM images for two films made using different oxygen pressures of 200 (a) and (b) and 170 mTorr (c) and (d) with the same conditions of substrate temperature of 720 °C, laser frequency of 3 Hz, and annealing temperature of 500 °C. It can be seen that both films exhibited similar morphologies with almost the same grain sizes and densities. The grain sizes ranged between 100-500 nm and the density of these grains were about $7 \times 10^6$ /cm$^2$, roughly estimated from the two dimensional AFM images as shown in Fig. 9(a) and (c).

If the substrate temperature was increased to 780 °C, with oxygen pressure of 200 mTorr and the other conditions unchanged, the surface morphology changed considerably, with the grain sizes significantly increased up to 3 µm. All the grains seemed to be well connected as seen in the three dimensional AFM images shown in Fig. 10 (d) and (e). These results clearly imply that high substrate temperatures enhanced the grain growth of Y123. However, some smaller particles are found to be embedded in the matrix of large grains as shown in Fig. 10 (a) and (c). These particles
are presumably formed due to the segregation of Y211 phase because of the high temperature of the substrate.

Fig. 9 (a)

Fig. 9 (b)
Fig. 9 (c).

Fig. 9 (d).

Fig. 9 AFM images for two films made using different oxygen pressures of 200 (a,b) and 170 mTorr (c,d) with the same conditions of substrate temperature of 720 °C, laser frequency of 3 Hz, and annealing temperature of 500 °C.
Fig. 10 (a)

Fig. 10 (b)
Fig. 10 (c).

Fig. 10 (d)
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Fig. 10 (e)

Fig. 10 (f)

Fig. 10. 2D and 3D AFM images with various magnifications of a typical film made at a substrate temperature of 780 °C, frequency of 3 Hz, oxygen pressure of 200 mTorr and other conditions unchanged. The small grains indicated by the arrows in (a) and (c) are Y211 particles.
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Fig. 11(a)

Fig. 11(b)
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Fig. 11(c)

Fig. 11 (d)

Fig.11. Typical AFM images of two films made using the following conditions; frequency 6 Hz, $T_d$ of 770 °C, target-substrate distance 40 mm, but with different oxygen pressures of 200 (a,b) and 250 mTorr (c,d).
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The quality of the deposited films is, above all, determined by the crystallinity of the lattice and the surface smoothness. The generation of particulates during the PLD process is one of the most important features affecting the smoothness of the resulting films. These particulates can be classified as those with small droplets and those with large irregular-shaped out-growth as indicated in the above AFM images.

For the performance of films in terms of critical current density and flux pinning, deposition conditions should be aimed at reducing grain sizes, which could be controlled by using a relatively high frequency of laser shots. However, if the frequency is too high, it could cause poor c-axis alignment of Y123 grains as a result of very fast growth rates. According to these experiments, it was found that a frequency of 6 Hz gives the best results in terms of grain sizes and c-axis orientation, along with better superconductivity.

Typical AFM images of two films made using those conditions: frequency 6 Hz, $T_d$ of 770 °C, and target-substrate distance 40 mm, but with different oxygen pressures of 200 and 250 mTorr are shown in Fig. 11. It is obvious that the high frequency resulted in smaller grain sizes compared to low frequency even though the same substrate temperature of 770 °C were used (see Fig. 10). Note that the scan sizes are quite different for Fig. 10(f) and Fig. 11. This was caused by the high growth rate because of the high rate of laser shots, as anticipated. Again, different oxygen pressures seemed to make little differences in the morphologies as seen in Fig. 11 (b) and (c).
II. 2. 5. Surface morphology study by SEM

According to observations by SEM, no significant differences in surface morphologies were found for all the films prepared under different oxygen pressures, in agreement with the AFM images. Typical SEM surface morphologies of films corresponding to those in Fig. 11 (AFM) are shown in Fig. 12. The most prominent types of particulates on YBCO thin films, such as droplets with smooth surfaces, droplets with granular surface, spherically shaped features, target fragments, and pinholes, are illustrated in these images. It can be seen that the surfaces of films seemed to be dense (Fig. 12(a)) but with numerous visible white spots, which were determined to be Ba-rich particles by EDS. Under high magnifications (Fig. 12(b) and (c)), irregular holes with sizes of 100-300 nm can be seen, and white spots are found on the top of the films, similar to what is commonly present in Y123 films made using the PLD technique. It is likely that these white particles originate from targets. The crystallinity of the film is improved when particulates are formed since the films are separated into two phases: the precipitates and the crystal matrix.
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Fig. 12(a)

Fig. 12 (b)
II. 2. 6. Characterizations by X-ray diffraction

c-axis or (00l) orientations of Y123 grains have been observed for all the films produced under different deposition conditions. Fig. 13 shows the typical XRD patterns for some films made under different conditions grown on YSZ (100) single crystal substrates, as indicated in Figs. 9-12. It should be noted that the substrate temperatures of 720 and 780 °C were used for the samples shown in (a)-(d) and (e), respectively. It can be seen that all these films exhibited Y123 single phase because all the diffraction peaks belong to those of Y123 as indicated by the indexed peaks, in
addition to a peak from the substrate, except for the sample shown in (a), which was made under the same deposition conditions as the other samples, but without post-annealing processing. Extra peaks, mainly from (102) and (012) of Y123 and from the Y211 phase are present in this sample. This indicates that post-annealing plays an important role in the degree of texture of the films. Furthermore, high substrate temperatures are beneficial to a high quality of crystallinity. This is manifested by a strong diffraction intensity for sample (e) made with the high substrate temperature of 780 °C as compared to other samples made at the low substrate temperature of 720 °C. The ratio of peak intensities of (003)/(006) (\(R = I(003)/I(006)\)) for sample (e), having a \(T_c\) of 89 K with a sharp transition is greater than 1 (\(R>1\)), while \(R\) is much less than 1 (\(R < 0.5\)) for other samples, which also showed low \(T_c\) values of 0 – 65 K and very wide transitions as seen from curves 4-9 in Fig. 7. Therefore, it is believed that the \(R\) values are closely related to the quality of the films in terms of the \(T_c\) and the transition widths. We found that if the \(R\) was close to 1, the \(T_c\) was high and transition was accordingly sharp, as will be seen for all the high quality films grown on other single crystal substrates of LaAlO\(_3\) and SrTiO\(_3\) that are to be presented in the later chapters.

II. 3. Summary

Because the superconductivity of Y123 compound is very sensitive to the oxygen content, the deposition conditions are crucial for making high quality Y123 thin films using the PLD technique. It has been found that a wide range of deposition conditions resulted in a good c- alignments, which was easily obtained. However, the values of \(T_c\)
Fig. 13. Typical XRD patterns for films prepared under different conditions, as indicated in Figs. 9-12 grown on YSZ (100) single crystal substrates. Substrate temperatures of 720 and 780 C were used for the samples shown in (a)-(d) and (e), respectively. Peaks marked with * are non-(00l) peaks.
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and the transition widths are highly dependent on several important conditions, such as laser fluency, oxygen pressure, substrate temperature, and distance between target and substrate. Only a proper combination of these conditions could lead to high quality films. In this work, we found that $T_d$ should be around 780 °C, 300 mJ/pulse, $D_{s-t}$ about 45 mm, and PO$_2$ 300-400 mTorr for making good quality films. Films made under these conditions have 100% (100) orientation with $T_c$ of 89K and sharp transition widths of 1 K. These conditions have been used for making all other films relating to the effect of nano-silver dot additions on the flux pinning that are to be presented in the following chapters.