High-Temperature (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ Superconducting Films with Large Irreversible Fields Grown on SrLaAlO$_4$ Substrates by Pulsed Laser Deposition

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Abstract: (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ is a nontoxic cuprate superconducting material with a superconducting transition temperature of about 116 K. Recently, it was found that bulk samples of this material synthesized under high pressure hold the highest irreversibility line among all the superconductors, which is very promising for its application in the liquid nitrogen temperature field. In this work, high-temperature (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ superconducting films with large irreversible fields were prepared on SrLaAlO$_4$(001) substrates by pulsed laser deposition. The substrate temperature during deposition proved to be the most important parameter determining the morphology and critical temperature of the superconductors, with 680 °C considered to be the optimum temperature. X-ray diffraction (XRD) results showed that the (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ films prepared under optimal conditions exhibited epitaxial growth with the a-axis perpendicular to the film surface and the b- and c-axes parallel to the substrate, with no evidence of any other orientation. In addition, resistivity measurements showed that the onset transition temperature ($T_{c,\text{onset}}$) was approximately 116 K, the zero-resistance critical temperature ($T_{c,0}$) was around 53 K, and the irreversible field ($H_{irr}$) was about 9 T at 37 K for (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ films under optimal temperature. This is the first example of the successful growth of superconducting (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ films on SrLaAlO$_4$(001) substrates. This will facilitate high-performance applications of (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ superconducting materials in the liquid nitrogen temperature field.

Keywords: (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ thin film; SrLaAlO$_4$ substrate; pulsed laser deposition; substrate temperature

1. Introduction

Based on their superconducting transition temperature ($T_c$), superconductors can be divided into two categories: Low Temperature Superconductors (LTSS) and High Temperature Superconductors (HTSs). HTSs consist mainly of copper oxide superconductors, iron-based superconductors, and hydride superconductors. Copper oxide superconductors mainly include Tl-Ba-Ca-Cu-O, Hg-Ba-Ca-Cu-O, Bi-Sr-Ca-Cu-O, and RE-Ba-Cu-O [1–4]. The applications of Tl and Hg systems are limited by their toxic elements and the complexity of the manufacturing process. In contrast, the Bi and Y systems have produced three practical high-temperature superconducting material systems: Bi-2212, Bi-2223, and RE-123. The first generation of high-temperature superconducting tapes (1G-HTSs) is based on powder packaging and wire-drawing processes and consists of Bi-2212 and Bi-2223 wires. Bi-2223 has a $T_c$ exceeding 100 K, but its very layered structure and huge anisotropy do not allow a high irreversibility field at the liquid nitrogen temperature [5,6]. In contrast, Bi-2212 has some limitations, such as low critical current density, high void ratio, poor mechanical properties, high production cost, etc., which limit its application range and development prospects. REBCO-coated conductors based on the development of film epitaxy and biaxial texture growth on flexible metal substrates are called second-generation high-temperature...
superconducting tapes (2G-HTSs) [7]. Their biaxial fabric structures eliminate weak-linking at grain boundaries and the defects such as dislocations and vacancies associated with the fabrication of superconducting layers are flux-pinning centres. As a result, the critical current density of REBCO-coated conductors in the liquid nitrogen temperature range is significantly higher than that of other materials, as studies have shown [8–10]. However, the $T_c$ of REBCO superconductors is only about 90 K. In contrast, another cuprate superconductor without toxic elements, (Cu,C)$_2$Ba$_2$Ca$_3$Cu$_4$O$_{y}$ ((Cu,C)-1234), shows structural similarities to HgBa$_2$Ca$_3$Cu$_4$O$_{y}$ [11] with a $T_c$ of about 116 K. At a field of zero, the critical current density $J_c$ reaches $6 \times 10^6$ A cm$^{-2}$ at 4.2 K and $6.5 \times 10^5$ A cm$^{-2}$ at 77 K [12]. Among superconducting materials to date, polycrystalline (Cu,C)-1234 blocks exhibit the highest $H_{irr}$ in the temperature range of liquid nitrogen [12], reaching 15 T at 85 K and 5 T at 98 K, respectively. These excellent properties make the compounds very promising for applications in the liquid nitrogen range and even at higher temperatures. Unfortunately, bulk samples of this material can only be synthesized under high pressure [11–14]. The sample size is typically a few millimeters, which limits its large-scale application.

Thin-film deposition methods are sometimes effective in stabilising transient high-pressure phases; Table 1 shows the progress of (Cu,C)-1234 films. The preparation of (Cu,C)-1234 films by pulsed laser deposition (PLD) [15–21], sputtering [22], and molecular beam epitaxy (MBE) [23,24] has been extensively studied. Compared to other methods, PLD has the advantage that there is no segregation of the film components and that the growth conditions can be controlled very well during film growth. Currently, (Cu,C)-1234 films can only be prepared by epitaxy on LaAlO$_3$ (00) single crystal substrates by PLD and on NdGaO$_3$ (001) and SrLaGaO$_4$ (001) single crystal substrates by MBE. In order to produce high-quality (Cu,C)-1234 films, it is important to investigate the effects of different substrates and different deposition temperatures on the epitaxial growth, structural, and electrical properties of (Cu,C)-1234 films. Since the SrLaAlO$_4$ substrate is characterized by high-temperature resistance, it does not react with (Cu,C)-1234 at higher temperatures (475 °C–900 °C). Meanwhile, the lattice constants and thermal expansion coefficients of SrLaAlO$_4$ substrates are similar to those of (Cu,C)-1234 films, which is favorable for the growth of (Cu,C)-1234 films. This paper focuses on trying out the possibility of growing (Cu,C)-1234 films on SrLaAlO$_4$ substrates.

Table 1. The progress of (Cu,C)-1234 films.

<table>
<thead>
<tr>
<th>Method</th>
<th>Film Types</th>
<th>Substrate</th>
<th>$T_c$ onset (K)</th>
<th>$T_c$ (K)</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLD</td>
<td>Ba$_2$Ca$_3$Cu$_2$O$_y$</td>
<td>LaAlO$_3$ (00)</td>
<td>80–100</td>
<td>58</td>
<td>[15–17]</td>
</tr>
<tr>
<td></td>
<td>Ba$_2$Ca$_3$Cu$_2$O$_y$CO$_3$ (Cu,C)-1234</td>
<td>LaAlO$_3$ (00)</td>
<td>110</td>
<td>75</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>(Cu,C)-1234</td>
<td>LaAlO$_3$ (00)</td>
<td>115</td>
<td>78</td>
<td>[19]</td>
</tr>
<tr>
<td></td>
<td>(Cu,C)-1234</td>
<td>LaAlO$_3$ (00)</td>
<td>118</td>
<td>96</td>
<td>[20,21]</td>
</tr>
<tr>
<td>Sputtering</td>
<td>Ba$_2$Cu$_2$O$_y$(CO$_3$)</td>
<td>SrTiO$_3$ (001)</td>
<td>40–50</td>
<td>4.2</td>
<td>[22]</td>
</tr>
<tr>
<td>MBE</td>
<td>(Cu,C)-1234</td>
<td>NdGaO$_3$ (0001)</td>
<td>105</td>
<td>55</td>
<td>[23,24]</td>
</tr>
<tr>
<td></td>
<td>(Cu,C)-1234</td>
<td>SrLaGaO$_4$ (0001)</td>
<td>90</td>
<td>15</td>
<td></td>
</tr>
</tbody>
</table>

In this work, we employed the PLD method to fabricate thin films of (Cu,C)-1234 on SrLaAlO$_4$ substrates by changing the deposition temperature. The purity of the phase, the quality of growth, and superconductivity were investigated using various experimental techniques, including XRD, scanning electron microscopy (SEM)m and a physical property measurement system. Our findings reveal an optimal film temperature of around 680 °C, and the structural, morphological, and physical characterization of these films is also reported.

2. Materials and Methods
2.1. Preparation of the (Cu,C)-1234 Target

The ceramic Ba$_2$Ca$_3$Cu$_2$O$_y$ target was produced using a conventional solid-state sintering process. Reagent grade oxide/carbonate powders, namely BaCO$_3$, CaCO$_3$, and CuO, were
selected as raw materials and weighed according to their stoichiometric ratios. These powders were then added to a 500 mL nylon vessel containing ethanol as solvent and various zirconia beads. The mixed slurry was then ground in a planetary ball mill at 400 rpm for 14 h. After drying at 100 °C for 4 h, the mixture was uniaxially pressed into discs (with a diameter of about 28 mm) and then calcined in a muffle furnace at 860 °C for 12 h. The calcined discs were then ground and ball-milled for 14 h in the same way as before calcination. The slurry was then dried, sieved, and pressed into a disc (with a diameter of about 28 mm and a thickness of about 5 mm) under a pressure of 66 MPa using a dry press. Finally, the Ba$_2$Ca$_3$Cu$_4.2$O$_y$ target was obtained after sintering at 880 °C for 12 h.

2.2. Deposition of the (Cu,C)-1234 Films

With a KrF excimer laser ($\lambda = 248$ nm, COHERENT Compex Pro 205F, Coherent Inc., Santa Clara, CA, USA), the (Cu,C)-1234 films were deposited using the PLD method on SrLaAlO$_4$(00l) substrates with a target-to-sample distance of around 6.5 cm. The laser energy and frequency were 320 mJ pulse$^{-1}$ and 5 Hz. The deposition time was 20 min. The deposition temperature was 650 °C to 720 °C; 30 cm$^3$ min$^{-1}$ of O$_2$ and 20 cm$^3$ min$^{-1}$ of CO$_2$ were separately introduced into the deposition chamber, and the chamber pressure was controlled at 20 Pa during the deposition process. After deposition, the films were slowly cooled down in an oxygen atmosphere of 70 KPa to 500 °C, held at this temperature for 60 min, and then cooled down to room temperature at a rate of 8 °C min$^{-1}$.

2.3. Characterization Techniques

The crystallographic structure and preferential orientation of the (Cu,C)-1234 films were measured by X-ray diffraction (XRD, SmartLab, Rigaku, Tokyo, Japan) with a Cu K$\alpha$ source ($\lambda = 1.541$ Å) and diffraction angles (2$\theta$) from 15° to 60°. The scanning electron microscope images of the (Cu,C)-1234 films were examined using a field emission scanning electron microscope (FE-SEM, HITACHI-SU5000, Tokyo, Japan) in the top view. Electrical resistance measurements were performed with the Quantum Design Instrument PPMS-9 T (Physical Property Measurement System 9 T) using the standard four-probe method.

3. Results and Discussion

Figure 1a shows the XRD $\theta$-2$\theta$ scan of the (Cu,C)-1234 films deposited on SrLaAlO$_4$ substrates at different substrate temperatures. The peaks corresponding to the (100) orientation of the (Cu,C)-1234 films were detected within the substrate temperature range of 660 °C to 710 °C. Whereas the peaks related to the (200) orientation were observed between 650 °C and 710 °C. Figure 1b shows the temperature dependence of the (001) and (002) peak intensities of the (Cu,C)-1234 films. The peak intensity was temperature-dependent. Figure 1 illustrates that the intensities of the (001) and (002) peaks of the (Cu,C)-1234 films decrease notably with rising temperature when the substrate temperature exceeds 690 °C, finally disappearing at 720 °C. Conversely, the intensities of the peaks of BaCuO$_2$ and Ca$_2$CuO$_3$ show a significant increase with temperature. The peak intensities of (001) and (002) of the (Cu,C)-1234 films increase significantly with temperature when the substrate temperature is below 680 °C. Conversely, the peak intensities of BaCuO$_2$ and Ca$_2$CuO$_3$ decrease significantly with increasing temperature. The XRD spectra show weak Ca$_2$CuO$_3$ peaks and BaCuO$_2$ peaks, which could be unreacted particles in the Ba$_2$Ca$_3$Cu$_4.2$O$_y$ target.

Fitting the $\theta$-2$\theta$ diffractograms revealed that the $a$-axis lattice constant of the (Cu,C)-1234 thin film is 3.859 Å, which is very close to the bulk $a$-axis lattice constant of 3.860 Å [12–14]. In addition, the (Cu,C)-1234 thin film had a black surface with an almost metallic lustre.

Analyzing the relationship between the peak intensities of the XRD peaks (100) and (200) of the (Cu,C)-1234 films and the substrate temperature, it can be concluded that the substrate temperature has a great influence on the crystalline quality of the films. This is because at a low substrate temperature, the atoms adsorbed on the substrate surface have a lower energy and a poorer ability to migrate on the substrate surface and are covered by other atoms before they reach the ideal nucleation position [25,26]. This leads
to more defects in the film and poorer film orientation and crystal quality. As the substrate temperature increases, the residence time of the deposited atoms on the substrate decreases, but the diffusion rate and the total accessible area of diffusing atoms increase. This favors the nucleation and growth of the film and reduces the defects during film growth, which improves the crystal quality of the (Cu,C)-1234 films.

Figure 1. (a) The XRD θ-2θ scan of the (Cu,C)-1234 films deposited on SrLaAlO$_4$ substrates at different substrate temperatures; (b) the temperature dependence of the (001) and (002) peak intensities of the (Cu,C)-1234 films.

The phi-scans and the omega-scans make it possible to determine the quality of the (Cu,C)-1234 thin film. Figure 2 shows the omega and phi scan spectra of the (Cu,C)-1234 films deposited on SrLaAlO$_4$ films. The φ-scan of the (Cu,C)-1234 (104) film in Figure 2a shows four peaks at 90° intervals, indicating that the film is orientated and grew. As shown in Figures 1 and 2, the (Cu,C)-1234 thin film is purely a-axially orientated and exhibits good crystalline quality. The in-plane and out-of-plane half-height widths of 0.39° and 2.09°, respectively, indicate that the (Cu,C)-1234 films are epitaxially grown on SrLaAlO$_4$ substrates.

Figure 2. (Cu,C)-1234 thin film with a substrate temperature of 680 °C: (a) (104) phi scan curves in-plane; (b) (100) omega scan curves out-of-plane.
The critical temperature and the critical current density of superconducting materials are strongly dependent on the surface morphology of the materials. In order to clarify the morphology of the (Cu,C)-1234 films, the surface morphology was analyzed by SEM. Figure 3 shows SEM images of the (Cu,C)-1234 films prepared at different substrate temperatures. Figure S1 shows SEM images of the SrLaAlO$_4$ substrate. As can be seen in Figure 3, the surface of the (Cu,C)-1234 films is free of cracks at different temperatures. At substrate temperatures of 650°C, 660°C, and 670°C, there are only a few rice-like (Cu,C)-1234 grains on the surface of the film; as the temperature increases, the rice-like (Cu,C)-1234 grains gradually increase and show a continuous shape, and the (Cu,C)-1234 grains are perpendicular to each other and show a twin structure with 90°. The 90°-orientated twin structure is a typical feature of this material [23,24]. However, when the substrate temperature reaches 720°C, the surface of the film becomes wrinkled and the (Cu,C)-1234 grains disappear completely. The combination of the above experimental results shows that 680°C is the optimal substrate temperature for the epitaxial growth of (Cu,C)-1234 films.

Figure 3. SEM images of the (Cu,C)-1234 films grown on SrLaAlO$_4$(001) substrates at different substrate temperatures.
Figure 4 shows the temperature dependence of resistivity for the (Cu,C)-1234 film with a deposition temperature of 680 °C under zero magnetic field, with the red line in the figure showing $dR/dT$. Figure 4 shows that the samples exhibit metallic properties until the superconducting transition occurs. In this work, $T_{c\text{onset}}$ was determined using the point of deviation from the linear range of the metal as a criterion and $T_c$ was determined using the point of $dR/dT = 0$ as a criterion; $T_{c\text{onset}}$ was about 116 K, $T_c$ was about 60 K, and $T_{c0}$ was about 53 K. The $T_{c0}$ of the epitaxially grown (Cu,C)-1234 films were low and not as good as those of the (Cu,C)-1234 blocks prepared by the high-pressure method. One of the reasons for this could be that the process of producing (Cu,C)-1234 films on SrLaAlO$_4$ substrates is not optimal and there is still a certain amount of non-superconducting phases, such as Ca$_2$CuO$_3$ and BaCuO$_2$, which need to be further explored and optimized to improve the superconducting properties of the (Cu,C)-1234 films, including the deposition temperature, CO$_2$ flow rate, and composition of the target materials and other parameters. The second reason could be that the fabricated (Cu,C)-1234 films are $a$-axis oriented, i.e., the $a$-axis is perpendicular to the film surface, and there is a mutually perpendicular 90° twinning structure within the surface. Later attempts can be made to grow (Cu,C)-1234 with $c$-axis orientation to overcome this twinning problem. The third reason could be the non-uniform distribution of oxygen content in the (Cu,C)-1234 films, which can be solved by post-annealing the (Cu,C)-1234 films under an oxygen atmosphere.

Figure 5a shows the resistance versus temperature curves of the (Cu,C)-1234 films at different external fields, and the inset shows $dR/dt$ at different magnetic fields. Figure 5a shows that the (Cu,C)-1234 films have a $T_{c0}$ value of about 53 K and a $\Delta T_c$ value of about 36 K at zero field. The high $\Delta T_c$ value indicates that the superconducting grains are poorly bonded to each other and the quality of the film needs to be optimized. As shown in Figure 5a, the $T_c$ value of the samples gradually decreases with the increase of the magnetic field, and the $\Delta T_c$ value gradually increases with the increase of the magnetic field. The upper critical field $H_{c2}$ and the $H_{irr}$ of the (Cu,C)-1234 films were determined using 90% $R_n$ and 0.1% $R_n$ as the criterion, and the results are shown in Figure 5b. As can be seen in Figure 5b, it is also difficult to observe a significant change in the $T_{c\text{onset}}$ when the magnetic field is increased to 9 T, indicating that there is a large upper critical field $H_{c2}(0)$ in the
zero-temperature limit. We have not yet observed the \( H_{irr} \) at the temperature of liquid nitrogen, but the \( H_{irr} \) reached 9 T at 37 K. The main reason for the low \( H_{irr} \) of this film is the presence of a certain amount of heterogeneous phases, the 90° twin structure, etc., in the prepared film, which can significantly affect the superconducting properties, so the quality of the film needs to be further improved.

![Diagram](image_url)

**Figure 5.** (a) Temperature dependence of the resistivity at zero field and under magnetic fields of \( H//a \) for the (Cu,C)-1234 films; the inset shows \( dR/dT \) at different magnetic fields. (b) Upper critical field and \( H_{irr} \) determined by the criterion of 90% and 0.1% of the normal state value for the (Cu,C)-1234 thin film. Red circles show \( H_{c2} \) and blue squares show \( H_{irr} \).

4. Conclusions

Epitaxial growth of (Cu,C)-1234 films on SrLaAlO\(_4\)(00) single crystal substrates was successfully achieved for the first time through PLD. This study highlights the significant impact of deposition temperature on the quality of growth and surface morphology of (Cu,C)-1234 films, identifying the optimal deposition temperature as 680 °C. The peak intensity of (Cu,C)-1234(00) exhibits a non-linear relationship with deposition temperature, showing an initial increase followed by a decrease, while the number of grains follows a similar trend. The in-plane and out-of-plane textures of the (Cu,C)-1234 films grown at the optimal temperature are measured at 2.09° and 0.39°, respectively, with a \( T_{c\text{onset}} \) of around 116 K, a \( T_{c0} \) of approximately 53 K, and a \( H_{irr} \) of 9 T at 37 K. These findings provide valuable insights for further research into the growth mechanism of (Cu,C)-1234 films, with potential implications for the large-scale production and practical utilization of (Cu,C)-1234 superconductor materials.

An investigation concerning the growth of (Cu,C)-1234 films on different substrates is in progress. With further research on the phase formation mechanism and process conditions of (Cu,C)-1234 films prepared by PLD, the superconductivity of the film can be significantly enhanced. There is potential for the epitaxial growth of c-axis oriented (Cu,C)-1234 films in the near future, maximizing the performance of (Cu,C)-1234 superconducting materials. This could lead to the development of high-performance, low-cost, and reliable high-temperature superconducting strips by combining this technology with second-generation high-temperature superconducting strip technology. The future prospects for these new (Cu,C)-1234 high-temperature superconducting strips are very promising and could greatly contribute to the advancement of superconducting materials.
Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/cryst14060514/s1, Figure S1: SEM images of SrLaAlO$_3$ substrates.

Author Contributions: Z.L. and C.C. conceived and executed the project. Y.L. performed the thin film deposition and XRD, SEM, and R-T measurements; analyzed the data; and wrote the manuscript with the help of P.Z. and J.H. Z.L. analyzed the data and reviewed the manuscript. C.C. provided funding support for the project and reviewed the manuscript. All authors have read and agreed to the published version of the manuscript.

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