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Synthesis and superconducting properties of Tl-Ba-Ca-Cu-O films

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SYNTHESIS AND SUPERCONDUCTING PROPERTIES OF Tl-Ba-Ca-Cu-O FILMS

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Abstract

The Tl-Ba-Ca-Cu-O superconducting films were synthesized by sputtering either from a single target or from two oxide targets in a symmetric configuration. Films with zero resistance \(T_c\) of up to 122 K were obtained after various post annealing treatments at 870 ~ 950°C under oxygen atmosphere. We have studied morphology, structure, magnetic and superconducting properties of these films. Films prepared by two different sputtering techniques have similar results which depend mostly on the film compositions and their annealing conditions. We found that the induced magnetic flux in the film decreases rapidly with increasing temperature, indicating the weak flux pinning.

Introduction

Following the initial discovery of superconductivity in the Tl-Ba-Ca-Cu-O system,\(^1\) the highest \(T_c\) (R=0) at 125 K has been observed in the compound of \(Tl_2Ba_2Ca_2Cu_3O_{10}\) (2223). Thin film research on the Tl-based superconductors is particularly important because their \(T_c\)'s (R=0) are much higher than those of the rare earth based \(Y_{1.5}Ba_2Cu_3O_7\) compounds. Furthermore, it is likely to obtain more stable high critical current densities in excess of \(10^5\) - \(10^6\) A/cm\(^2\) at 77 K in the Tl-based system.

Recently, polycrystalline films 0.7 \(\mu\)m thick containing predominantly \(Tl_2Ba_2Ca_2Cu_3O_8\) (2212) phase with \(T_c\) (R=0) at 97 K and a transport \(J_c\) of \(1.1 \times 10^5\) A/cm\(^2\) at 76 K have been obtained by Ginley et al.\(^2\) using electron beam evaporation. Highly oriented films 0.4 \(\mu\)m thick (with the c-axis perpendicular to the film plane) containing nearly a single phase of 2212 as well as having a \(T_c\) (R=0) at 102 K and a transport \(J_c\) of \(1.2 \times 10^5\) A/cm\(^2\) at 77 K have been prepared by Ichikawa et al.\(^3\) using RF magnetron sputtering and a single oxide target. Highly textured c-axis oriented films 2.0 - 4.0 \(\mu\)m thick containing both 2223 and 2212 phases with a \(T_c\) (R=0) at 120 K and a \(J_c\) by magnetic measurement of \(1.5 \times 10^5\) A/cm\(^2\) at 77 K have been reported by Lee et al.\(^4\) using two identical oxide targets in a symmetric RF diode sputtering system.

The ability to produce thin films with the pure high \(T_c\) \(Tl_2Ba_2Ca_2Cu_3O_{10}\) phase not only can further improve \(J_c\)'s at higher temperatures but may also provide a useful material for a fundamental study on the Tl-based superconducting oxides.

In this paper, we discuss the preparation conditions for films with \(T_c\) (R=0) at 122 K. The results of magnetic properties of these films are presented.

Film Growth

The Tl-Ba-Ca-Cu-O films were prepared on MgO(100), Y-ZrO\(_2\) (random orientation) and LaAlO\(_3\) (100) substrates by sputtering either from a single targets or from two oxide target in a symmetric configuration. The details of the sample synthesis have been reported in our previous papers.\(^5\) Due to the volatility of the Tl-oxide, the optimal processing of the Tl-based films requires good control of the Tl-vapor partial pressure. We have used two different methods to control the Tl-vapor partial pressure. One is annealing the film in a sealed gold box with a composite Tl-compound. The other one is annealing the film in a two zone-furnace, in which the Tl-vapor partial pressure is controlled by the zone temperature. The first method is much simpler and the results are reproducible. The second method requires a fine adjustment which we need to study further. The films reported here were prepared by the first method. The annealing steps have been shown to be a crucial determinant of the quality of Tl-based superconducting films.\(^6\) In this study, we show that the films consist of nearly pure \(Tl_2Ba_2Ca_2Cu_3O_{10}\) phase with \(T_c\) (R=0) in the range of 100 K to 122 K and c-axis perpendicular to the film plane were obtained after annealing 870 ~ 895° for up to 3 hours.

The major factors that lead to achieve a higher \(T_c\) than that of the previous study are perhaps due to the better control of Tl-vapor partial pressure and annealing at higher temperature for a longer time. We also observed a substantial improvement in the superconducting properties for films subsequently annealed at low temperature (< 700°C) either in air or oxygen. The detailed study of low temperature annealing will be discussed elsewhere.\(^7\)

Composition, Structure and Processing Conditions

The film compositions were determined by x-ray fluorescence microprobe spectroscopy. A typical composition of as-deposited films is \(Tl_{1.1}Ba_{1.4}Ca_{2.6}Cu_{3.1}O_{10}\). The composition of the as-deposited film was very homogeneous, but the composition of...
the post-annealed film was not homogeneous, especially the Tl and Ca content. As an example, we have tested the stability of Tl in a single crystal. As shown in Figure 1(a), a single crystal with 2223 phase was prepared on a MgO(100) substrate. After we had annealed this crystal at 800°C without providing additional Tl-vapor for 15 minnte, we found that the phase of this crystal was changed, its surface became rough, and its Tl-content was lost completely. Its morphology, as shown in Figure 1(b), is completely different from the original crystal. The Tl content can vary widely depending on the annealing temperature and the duration of the annealing time at the high temperature. The amount of Ba, Ca and Cu in the annealed films was found to be insensitive to the processing conditions if we average over a large area. However, the micro-scale composition of annealed films has some variations which depend on the processing conditions. In order to investigate the effect of the processing conditions on the micro-scale composition, we have prepared two films with similar superconducting and structural properties. The morphology and the composition of the films were studied by scanning electron microscope with energy dispersive x-ray analysis. These films are highly c-axis oriented with mostly (00l) peaks of Tl₄Ba₉Ca₄Cu₄O₁₀ phase as revealed by the x-ray diffraction pattern (as shown in Figure 2). The micrographs of films on Y-ZrO₂ substrates after annealing at 890°C for 3 hours and at 895°C for 1 hour are shown in Figures 3(a) and 3(b) respectively. The films annealed at 890°C for 3 hours had plate-like grains with many small Ca-rich dots on their surface. The composition at different portions is marked in Figure 3(a) and is listed in Table 1.

Table 1. The film composition at various portions

<table>
<thead>
<tr>
<th>Portion</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate-like</td>
<td>Tl₁.sBa₁₅Ca₂.oCu₁₃.oO₂</td>
</tr>
<tr>
<td>Plate-like</td>
<td>Tl₁.sBa₁₅Ca₂.oCu₁₃.oO₂</td>
</tr>
<tr>
<td>Dot</td>
<td>Tl₁.sBa₁₅Ca₂.oCu₁₃.oO₂</td>
</tr>
<tr>
<td>Dot</td>
<td>Tl₁.sBa₁₅Ca₂.oCu₁₃.oO₂</td>
</tr>
<tr>
<td>Rod-like</td>
<td>Tl₁.sBa₁₅Ca₂.oCu₁₃.oO₂</td>
</tr>
</tbody>
</table>

The morphology of the film annealed at 890°C for 1 hour is shown in Figure 3(b). The plate-like grains were connected much closer than that of the previous film. The composition of this film is Tl₁.sBa₁₅Ca₂.oCu₁₃.oO₂ and it does not change from place to place. However, we still observe many submicron Ca-rich dots in the plate-like grains.

**Transport, Flux Trapping, and Granularity**

The superconducting and transport properties were measured by the standard four-point measurement using a dc method by switching the polarization of the applied current during the measurement. Critical current densities (Jc's) were measured in the van der pauw configuration with and without a lithographic patterning. Figure 4 shows the data of resistance versus temperature of the film annealed at 895°C for 1 hour. This
film have a $T_c$ onset at 130K and a $T_c$ ($R=0$) at 122K. The $J_c$'s at zero magnetic field is about $10^4$ A/cm$^2$.

We found the superconducting transition temperature of our films with Tl$_2$Ba$_2$Ca$_2$Cu$_3$O$_{10}$ phase vary from 100K to 122K, and it is very sensitive to the processing conditions. The $J_c$'s of the films prepared on Y-ZrO$_2$ and MgO substrates were in the range of $10^3$ to $10^4$ A/cm$^2$ at 77K. The $J_c$'s of the films prepared on SrTiO$_3$ and LaAlO$_3$ substrates were in the range of $10^8$ A/cm$^2$ to $10^9$ A/cm$^2$ at 77K.

The magnetic properties of the films were studied by using SQUID magnetometer. The diamagnetic shielding and Meissner effect data were shown in Figure 5. The diamagnetic shielding data was obtained after cooling in zero field, followed by applying a field of 20 Oe and taking data on warming. The Meissner effect data was measured on cooling in an applied field of 20 Oe. The diamagnetic shielding and Meissner signals at 6K are estimated to be 30% and 15% of those for a perfect diamagnetic of the same shape and volume, respectively. The low values of the diamagnetic shielding and the Meissner signals indicate a serious film-substrate interactions or a substantial portion of non-superconductor in the film.

Figure 6 shows a magnetization curve at 6K for the film annealed at 895°C, the applied fields were up to ±55 kOe and were perpendicular to the films' surface. Analysis of these data using the standard Bean method indicates a critical current density of $7.5 \times 10^4$ A/cm$^2$ at 6K under 55 kOe$^{11}$. $J_c$ of $7.5 \times 10^5$ A/cm$^2$ at 6K and $4.2 \times 10^4$ A/cm$^2$ at 77K under zero field were obtained for this film. The flux trapping data, as shown in Figure 7, was obtained after cooling in the applied field. The induced flux in the film decrease rapidly with increasing temperature. This clearly indicates the weak flux pinning at higher temperature. The flux trapping data correspond to the $J_c$ function of temperature at zero field. This rapid decrease in $J_c$, which is similar to that of some YBa$_2$Cu$_3$O$_y$ granular films, may be due to the granular nature of these films$^{12}$. 
Superconducting films of Tl-Ba-Ca-Cu-O have been prepared by sputtering. Films with zero resistance $T_c$ of up to 122 K were obtained after various post annealing at 850°C for 1 hour to 3 hours. The composition of films is not very homogenous in sub-micrometer scale. The critical current at 77 K of these films are in the $10^3$ A/cm² to $10^4$ A/cm² range, which is much smaller than that of the films prepared on SrTiO₃ and LaAlO₃ substrates. The low critical current density in these films are likely due to the granularity in these films.

Summary

Fig. 6 Magnetization versus field curve at 6 K for the film annealed at 695°C for 1 hour. The magnetic field was applied normal to the film surface.

Fig. 7 Flux trapping versus temperature for the film annealed at 895°C for 1 hour. This data were obtained after cooling in the applied field of 50 kOe, removing the field and taking the data on warming in zero field.

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References