Deposition of superconducting \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2 \) thin films by pulsed laser ablation

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Abstract. The highest ever superconducting critical temperature \( T_c \) of 120 K has been reported for the compound \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2 \) \( (F-02(n-1)n) \). However, only bulk samples have been synthesized to date and extremely high pressures have been required. Here, the deposition of superconducting \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2 \) films on a \( \text{SrTiO}_3(100) \) substrate was investigated using Nd-YAG pulsed laser ablation under an \( \text{O}_2 \) pressure of 16-19 Pa at a substrate temperature of 740-750 °C. The films exhibited a superconducting onset temperature \( T_{co} \) of 76.5 K and a zero resistance temperature \( T_{ce} \) of 22.5 K. The dominant diffraction peaks matched those reported for \( c \)-axis oriented \( \text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_6(\text{O,F})_2 \) \( (\text{O,F})_2(\text{n}=3) \) bulk samples. However, the \( T_c \) values for the films were much lower than that for the bulk material, even though the ablation target composition was \( \text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_{6+\delta}(\text{O,F})_2 \), which yields the highest bulk \( T_c \) value.

1. Introduction

The dependence of the superconducting critical temperature \( T_c \) for \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2 \) \( (F-02(n-1)n) \) multilayered superconductors on the number of \( \text{CuO}_2 \) planes \( n \) has been reported to be bell shaped for \( n=1\text{-}5 \) and constant for \( n=5\text{-}9 \) \([1,2]\). The highest \( T_c \) of 120 K was reported for \( F-0223 \) \( (n=3) \) \([1]\). \( T_c \) values reported for \( F-0212 \ (n=2) \), \( F-0223 \ (n=3) \), \( F-0234 \ (n=4) \), and \( F-0245 \ (n=5) \) are 90 K, 90-120 K, 70-105 K, and 90 K, respectively \([1-3]\). Figures 1(a) and 1(b) show crystal structures of \( F-0223 \) \( (n=3) \) and \( F-0234 \ (n=4) \), respectively. The \( F-02(n-1)n \) crystal structures are composed of superconducting layers (SCLs) with \( \text{CuO}_2 \) planes \( n \) blocked by \( \text{Ca} \) and charge reservoir layers (CRLs) with a rock salt layer of \( \text{Ba}-(\text{O,F}) \) included with substitutions of \( \text{F}^- \) at apical oxygen sites \( (\text{O}_2^-) \) \([3]\). The carrier concentration in the SCL is controlled by the substitution of \( \text{F}^- \) for an apical \( \text{O}_2^- \) in the CRL \([3]\). Carrier doping on the \( \text{CuO}_2 \) planes of \( F-02(n-1)n \) has been predicted to be so-called self-doping between an electron type outer-\( \text{CuO}_2 \) plane directly under the CRL included with apical \( (\text{O,F}) \) and a hole type inner-\( \text{CuO}_2 \) plane. If \( (\text{O,F}) \) substitutions are optimized, then \( F-02(n-1)n \) superconductors may have the potential to achieve a \( T_c \) that is >120 K with more optimal carrier doping on the inner \( \text{CuO}_2 \) plane by self-doping \([1]\). However, until now, only bulk samples have been synthesized, and extremely high pressures have been required.

We have previously proposed that deposition of \( F-02(n-1)n \) superconducting films with \( T_c > 100 \text{ K} \) may be possible by optimal substitution in the CRLs, if no vacancies are required for optimal carrier
doping and formation of the crystal structure [3]. This is because such high \( T_c \) values are possible for bulk samples, and pulsed laser deposition (PLD) is capable of producing films whose composition, including the number of SCLs and CRLs, and the degree of F substitution, precisely matches that of the target. In the present study, the deposition of superconducting \( \text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_{6+\delta}(\text{O,F})_2 \) \((n=3)\) films on a \( \text{SrTiO}_3(100) \) substrate was investigated using Nd-YAG PLD.

![Figure 1. Crystal structures of (a) \( n=3 \), \( \text{Ba}_2\text{Ca}_2\text{Cu}_2\text{O}_{6}(\text{O,F})_2 \) \((F-0223)\), (b) \( n=4 \), \( \text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{8}(\text{O,F})_2 \) \((F-0234)\) on \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2 \) \((F-02(n-1)n)\).](image)

2. Experimental

Targets of \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O}_{1-y},\text{F}_y)_2 \) \((y=0.8)\) were synthesized with source materials \( \text{BaO}_2, \text{CaF}_2, \text{CuO}, \) and a precursor of \( \text{Ca}_2\text{CuO}_3. \text{Ca}_2\text{CuO}_3 \) was prepared from a mixture of \( \text{CaCO}_3 \) and \( \text{CuO} \) by sintering at 1000 °C for 12 h under an oxygen flow with an intermediate grinding procedure. The starting materials were weighed to achieve a nominal composition of \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O}_{0.2},\text{F}_{0.8})_2 \) and then ground with an agate mortar and pestle in a nitrogen-filled glovebox. The mixture was sintered at 860 °C for 12 h under oxygen flow. The resultant powder was pressed into a ca. 10 mm diameter pellet. The target was reacted in the temperature range of 880-920 °C for 12 h under an oxygen flow.

Thin film samples were deposited on \( \text{SrTiO}_3(100) \) substrates (STO) using a Nd-YAG PLD system (Pascal PLD-system). F-02\((n-1)n)\) thin films were deposited at a substrate heating temperature \((T_s)\) of 650-800 °C under pure oxygen flow at partial pressures \((P_{O_2})\) of 17-19 Pa for 45-60 min, followed by a cooling process at a rate of 10 °C/min to 400 °C after the oxygen flow was stopped. Other PLD conditions were set as follows: pulsed laser energy density of 80 mJ/cm\(^2\), laser wavelength of 266 nm, pulse frequency of 10 Hz, target-substrate distance of 38 mm. The thickness of the film was calculated based on deposition rates of 0.82, 0.76, 0.70, and 0.64 nm/min at \( P_{O_2} = 16, 17, 18, \) and 19 Pa, respectively. The effective surface area of the films was approximately 5×5 mm\(^2\).

The films were characterized using inductively coupled plasma mass spectrometry (ICP-MS; Agilent 8800ICP-MS) and X-ray diffraction (XRD; Panalytical MRD) with Cu K\( \alpha \) radiation at 45 kV with an emission current of 40 mA. ICP-MS was conducted with a carrier gas volume of 1.03 L/min, an rf power of 1550 W, a sampling depth of 8 mm, 4 mL/min \( \text{H}_2 \) reaction gas, and 300 μL sample uptake. The temperature dependence of the resistivity of the films was measured using the four-probe method (Quantum Design Physical Property Measurement System; PPMS) with a current of 0.1-1 μA applied along the surface. The temperature was varied at a rate of 0.5 K/min.
3. Results and discussion

PLD was conducted using targets with $n=2, 3, \text{ and } 5$ in F-02$(n-1)n$. Films with a superconducting transition were obtained using a target of F-0223, whereas PLD films deposited using other compound targets were insulating or semiconductor-like. However, it is considered that the PLD conditions were not optimized for F-0212 and F-0245, because other conditions, such as $P_{O_2}$ much higher than 20 Pa and $T_s$ lower than 600 °C, were not investigated in this work.

The following results are for the films prepared by PLD using the F-0223 target. PLD conditions such as $T_s$, $P_{O_2}$, and the deposition time were examined first. Comparison with the ICDD database indicated that the XRD patterns for all samples were not consistent with those for cuprate superconductors other than F-02$(n-1)n$. Moreover, no microscopic metallic elements other than Ba, Ca, and Cu were detected by ICP-MS analysis of the film samples. Figure 2 shows XRD patterns for PLD films deposited at $T_s$ of 650-800 °C. Although the film deposited at $T_s=650$ °C was not crystalline, all other films exhibited peaks associated with F-0223 and other phases. The resistivity of the films deposited at 800 and 770 °C was high, and the films displayed insulating and semiconducting characteristics, respectively. In contrast, a superconducting transition was observed for the films deposited at 750 and 740 °C. The F-0223 phase was evident in all samples except that prepared at 650 °C, with the strongest, sharpest peaks being obtained at 800 and 770 °C. The peaks at $2\theta =21.21, 29.31, 37.31, \text{ and } 39.20^\circ$ are associated with the F-0234 phase, whereas that at $2\theta =43.05^\circ$ is due to the F-0245 phase. Figure 2 indicates that the difference in resistivity was probably due to the formation of the insulating F-0234 and F-0245 phases and the under-doped F-0223 phase, when $T_s$ was higher than that for the optimized deposition of F-0223.

Figure 2. XRD patterns for films fabricated at substrate heating temperatures ($T_s$) of (a) 800, (b) 770, (c) 750, (d) 740, and (e) 650 °C.
Figure 3 shows XRD patterns for superconducting samples deposited at $T_s=740 \, ^\circ\text{C}$ and at $P_{O_2}=16$-$19 \, \text{Pa}$, in the non-zero resistivity region at the measurable temperature limits of the PPMS. For all samples, the strongest peaks are associated with $c$-axis oriented F-0223, with some peaks due to the presence of F-0234 and F-0245 impurity phases [1,3]. The strongest peaks are consistent with $(00\ell)$ planes in the F-0223 phase, assuming that the lattice spacing is 0.3642 Å larger than the value of 2.7433 Å for the high-pressure phase. The sample deposited at $P_{O_2}=16 \, \text{Pa}$ has weaker F-0223 peaks than the other samples, although the F-0234 peak intensity is similar. The sample deposited at $P_{O_2}=17 \, \text{Pa}$ has XRD peaks associated with $(006)$, $(0010)$, $(0012)$, $(0014)$, $(0016)$, and $(0018)$ planes in F-0223, and peaks due to $c$-axis oriented F-0234 and F-0245, and the intensity of the $(0010)$ peak is higher than that for the samples produced with a $P_{O_2}$ of 16 and 18 Pa. The intensity of the $(103)$ peak due to the F-0234 impurity phase is highest for the sample produced at $P_{O_2}=18 \, \text{Pa}$. The sample deposited at $P_{O_2}=19 \, \text{Pa}$ exhibits peaks due to $c$-axis oriented F-0223, of which the $(0010)$ peak has the highest intensity. In addition, F-0234 $(0014)$, $(0016)$, and $(0024)$ peaks and an F-0245 $(0014)$ peak are evident.

Figure 4 shows the temperature dependence of the resistivity for samples produced under various conditions. All samples exhibited a superconducting onset temperature ($T_{co}$), with the highest value of 81.6 K being obtained for that produced with a $T_s$ of 750 °C and a $P_{O_2}$ of 17 Pa. Figures 4(a) shows $T_{co}=37.8 \, \text{K}$ for a sample deposited at $P_{O_2}=16 \, \text{Pa}$ and $T_s=740 \, ^\circ\text{C}$. In addition, the samples produced with $T_s=740 \, ^\circ\text{C}$ and $P_{O_2}=17$ and 19 Pa exhibited $T_{co}$ of 76.5 and 70.7 K, $T_c$ of 47.8 and 38.7 K, and zero-resistance temperature ($T_{ce}$) of 22.5 and 19.0 K, respectively. The $T_c$ values were much lower than that for the bulk material, even though the ablation target composition was Ba$_2$Ca$_2$Cu$_3$O$_{6+\delta}$(O,F)$_2$, which yields the highest $T_c$ for the bulk [1].
Figure 4. Temperature dependence of resistivity for samples deposited under conditions of (a) \( PO_2 = 16 \) Pa and \( T_s = 740 \) °C, (b) \( PO_2 = 17 \) Pa and \( T_s = 740 \) and 750 °C, and (c) \( PO_2 = 19 \) Pa and \( T_s = 740 \) °C.

Figure 5. \( PO_2 \) dependence of (a) resistivity at 300 K and (b) \( T_{co} \) (upper or only inverted triangle), \( T_c \) (middle), and \( T_{ce} \) (lower) for superconducting films.

Figures 5(a) and 5(b) show the \( PO_2 \) dependence of the resistivity at 300 K and the \( T_{co} \), \( T_c \), and \( T_{ce} \) values for the superconducting films. The resistivity and \( T_{co} \) results suggest that the samples deposited at \( PO_2 = 17 \) and 19 Pa contain different phases. Electrical conductivity is observed for the F-0223 phase sample prepared with \( PO_2 = 17 \) Pa (Figure 3(b)), although there is a considerable amount of scatter in the data points for the resistivity and transition temperatures, which indicates a lack of repeatability from sample to sample. In contrast, for the F-0223, F-0234, and F-0245 multiphase samples prepared with \( PO_2 = 19 \) Pa (Figure 3(d)), there is a higher degree of repeatability. For samples prepared with \( PO_2 = 17-19 \) Pa, the molar composition was determined to be \( \text{Ba:Ca:Cu} = (0.4-2):2:5 \) from ICP-MS analysis, which indicates a lower Ba content than that typically found in F-0223 and F-0234. All of the films had \( T_c \) values that were lower than that for the bulk. This may be because, although \( c \)-axis oriented F-02(\( n-1 \))\( n \) films were formed, the F-0223 was the normal-pressure phase, and other phases such as F-0234 and F-0245 were also present. In addition, defects such as intergrowth in the layered structure may be present. Balestrino et al. [4] attributed the decrease of \( T_c \) for \( (\text{BaCuO}_2)_2/(\text{CaCuO}_2)_m \) superlattices, relative to the bulk \( T_c \), to the high degree of disorder in the artificial structure and the not yet optimized chemistry of the \( \text{BaCuO}_2 \) in CRL block. Similarly, in this present work, the intergrowth in the layered structure and the lower \( T_c \) are probably due to a deviation from the typical growth conditions for \( \text{BaF}_2 \) layers in the CRLs with F-0223 and F-0234 phases.

4. Summary

Superconducting \( \text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n}(\text{O,F})_2 \) thin films were deposited on \( \text{SrTiO}_3(100) \) substrates using Nd-YAG pulsed laser ablation under \( O_2 \) partial pressures of 16-19 Pa and at substrate temperatures of 740-750 °C. The films had \( c \)-axis orientation and a typical sample exhibited a \( T_{co} \) of 76.5 K and a \( T_{ce} \) of 22.5 K.

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