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Pulsed laser deposition synthesis of superconducting (Cu, C)Ba_2CuO_x thin films

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ABSTRACT

(Cu, C)–Ba–O thin films have been deposited at low growth temperature of 450–570 °C by pulsed laser deposition method. A control of CO_2 gas pressure and the growth temperature, usage of $BaCu_yO_x$ pellet target resulted in an expansion of twice *c*-axis length of $BaCuO_2$ structure (2c phase) and a significant rise of conductivity. Measurements of *in-situ* XPS suggest that the 2c phase should be (Cu, C)Ba_2CuO_x [(Cu, C)-1201]. The maximum temperature of onset of the superconducting transition and zero resistance state obtained so far were 60 and 47 K, respectively.

1. Introduction

A crystal structure in high temperature superconducting cuprates (HTS) is constructed by an alternate stacking of charge reservoir layer (CRL) and infinite layer (IL), the number of CuO_2 planes (n) in IL is depend on critical temperature T_c. The superconductors included in a CuO_2 plane ($n = 1$) show lower T_c than that included in some CuO_2 planes ($n > 1$) [1]. Then, the number of CuO_2 planes of almost HTS with $T_c > 60$ K is over two. Multi-layered HTSs, such as $MBa_2Ca_{n-1}Cu_nO_y$ (M = Hg, Tl, (Cu, C), (Cu, Tl), (Cu, V)) [M-12($n-1$)n] include two or more crystallographically inequivalent CuO_2 planes in a unit cell. They have the potentials of less-anisotropic properties and high critical temperature T_c above 100 K, and unique properties [1–3]. In the highest T_c multi-layered Hg-system, Hg-1201 ($n = 1$) has also higher T_c among HTSs included in a CuO_2 plane [4,5]. Therefore, M-1201 superconductors with $T_c > 60$ K have high potentials.

(Cu, C)$Ba_2Ca_{n-1}Cu_nO_x$ [(Cu, C)-12($n-1$)n] are one of promising HTS, because of the non-toxic elements and their potential for high critical temperature T_c above 100 K and low anisotropy, a possibility of multi-component superconductivity in multi-layered HTS with a proper interband coupling [1–3,6–23]. For pursuing these potentials of the Cu- and (Cu, C)-systems, (Cu, C)$Ba_2Ca_0CuO_x$ [(Cu, C)-1201] ($n = 1$), which is a fundamental and simplest structure of (Cu, C)-system, should be fabricated. Then it is important to control a little CO_2 pressure, because these materials sensitive to the carbonate. In this study, we have studied deposition of (Cu, C)-1201 thin films by pulsed laser deposition (PLD). Characterization of their transport properties has been investigated. Crystal structure of specimen grown in little CO_2 mixed atmosphere was $BaCuO_2$ infinite layered structure. The *c*-axis length with increases of CO_2 mixed atmosphere was expanded to twice as long as that of $BaCuO_2$, that was (Cu, C)-1201 structures. The (Cu, C)-1201 films deposited at 500 °C using $BaCu_{0.75}O_x$ target showed superconducting transport, T_c = 60–47 K [14–17].

2. Experiment

Specimen films were grown on (1 0 0) plane of $SrTiO_3$ at temperatures in the range of 450–530 °C by pulsed laser deposition using KrF excimer laser. The used targets were highly dense pellet of $BaCu_yO_x$ (y = 1.0, 0.75, 0.5). The growth conditions were in the following range: reactive pressure = O_2 (3–10 mTorr) + CO_2 (0.01–0.25 mTorr) + Ar (0–80 mTorr); laser power of shot and repetition frequency were in the range of 100–200 mJ/pulse and 0.5–2.0 Hz, respectively. In order to maintain residual gas level of growth chamber constant, we utilized a load–lock system. After the deposition, the films were cooled at room temperature in an oxygen atmosphere, and protection layers were deposited on the specimen before air exposure. Crystal structure of the films was characterized

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by means of *in-situ* reflection high energy electron diffraction (RHEED) and θ–2θ scan of X-ray diffractometry. Their transport properties of (Cu, C)-1201 thin films were characterized by four probe method.

3. Results and discussion

Fig. 1 shows typical XRD and RHEED patterns of the films grown the $BaCuO_2$ target with whether the addition of CO_2 gas or not. For the films grown at 450 °C without CO_2 gas, some equilibrium phase coexisted, as shown in Fig. 1a. For the films with a small introduction of CO_2 (0.04 mTorr) into the growth atmosphere, epitaxial relationship of Ba–Cu–O [1 0 0]/$SrTiO_3$ [1 0 0], Ba–Cu–O [0 1 0]/$SrTiO_3$ [0 1 0], Ba–Cu–O [0 0 1]/$SrTiO_3$ [0 0 1] were confirmed. The data also showed tetragonal symmetry with lattice constant of a $\sim$3.85 Å and c = 4.05 Å, as shown in Fig. 1b. Though these films had an ideal infinite layer structure, they were highly resistivity ($\rho_{[290\ K]} > 0.1$–$1.0\ \Omega$ cm) and exhibited a negative temperature coefficient of resistivity. Crystal structure and transport properties were drastically changed by the addition of CO_2 gas during the deposition.

Fig. 2 shows a change of XRD patterns of the films grown from $BaCuO_2$ target with an increase of CO_2 gas. In the range of $CO_2 < 0.03$ mTorr, the specimens had the simple infinite layer structure. Further increase of CO_2 gas resulted in the formation of a new phase, which c-axis length was expanded to twice as long as that of the infinite layer $BaCuO_2$ structure. This phase is represented as "2c" phase below. Amorphous $CaCuO_x$ protection layer was deposited on the films before breaking the vacuum, since the 2c phase was chemically unstable. The resistivity of the amorphous protection layers were estimated at over $10^3\ \Omega$ cm. The 2c phase were lower resistivity ($\rho_{[290\ K]} > 10^{-2}\ \Omega$ cm) and exhibited a positive or almost zero temperature coefficient of resistivity, these films did not show superconductivity above 15 K. Table 1 shows a relationship between used $BaCu_yO_x$ (y = 1.0, 0.75, 0.5) target and conductivity of the 2c phase. The maximum conductivity with an order of 10^4 S/cm was achieved in the 2c phase films grown from the $BaCu_{0.75}O_x$ target at a noteworthy low growth temperature around 500–550 °C.

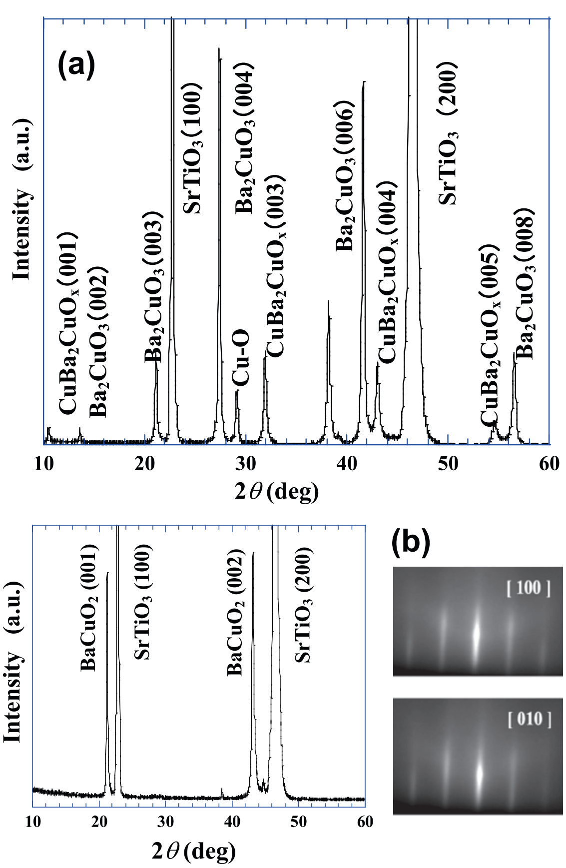

Fig. 1. X-ray diffractogram and RHEED patterns of Ba–Cu–O film grown at 450 °C from $BaCuO_2$ target (a) without CO_2 gas and (b) with a little CO_2 gas (1×10^{-5} Torr). Indices in RHEED patterns show along which electron beam was incident.

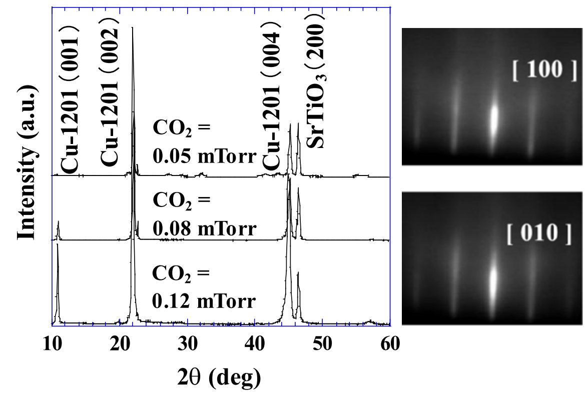

Fig. 2. Change of X-ray diffraction patterns of the Ba–Cu–C–O films as a function of pressure of CO_2, and typical RHEED patterns of them.

In-situ XPS measurement of the 2c phase showed a rather high concentration of CO_3 groups. The ratio of carbon in the CO_3 group to Cu was in the range 20–30%. XPS results also showed that the Cu/Ba ratio of this phase was lower than that in the infinite layer $BaCuO_2$ (Cu/Ba = 1.0). The metallic transport properties of this phase mean that there was structural perfection of the CuO_2 planes in this phase. Also, comparison of the valence band spectra of the 2c phase superconducting films with different T_c and $SrCuO_2$ reveals that the superconductivity of the 2c phase films should be induced by hole-doping and better hole-dopability than $SrCuO_2$ [15]. Moreover, in comparison of the valence band spectra of the 2c phase superconducting films with T_c = 42 K and other HTS, the position of the (Cu, C)-1201 specimen almost coincided with that of YBCO [15]. This suggests the presence of a heavily doped (Cu, C)–O charge reservoir structure in the high T_c 2c phase films, like Cu–O chains in YBCO. Therefore, one of the most possible structures should be an alternative stacking of CuO_2 and (Cu, C)–O layers separated by a Ba–O one. In the (Cu, C)–O layer, almost half of Cu sites would be substituted with CO_3. These results suggest that the 2c phase structure should be (Cu, C)Ba_2CuO_x [(Cu, C)-1201] = [(Cu, C)–O–BaO–CuO_2–BaO–(Cu, C)–O]. Therefore, the XRD peak that appeared at 2θ around 11° was assigned as the (0 0 1) diffraction peak of the (Cu, C)-1201 phase. In the case of using $BaCu_{0.5}O_x$ target, the structure would be $BaCuO_2(CO_3)_x$ that was reported by Koller et al. [18].

In the target–substrate spacing D = 30 mm, decrease of P_{Ar} means an increase of growth rate mainly due to the reduction of scattering of the ablated species by the atmospheric gases. I(0 0 1)/I(0 0 4) showed a bow-shape dependence on P_{Ar}; in the high region of P_{Ar}, I(0 0 1)/I(0 0 4) increased with a decrease of P_{Ar}. Though further decrease of P_{Ar} increased growth rate more,

Table 1
Relationship between used $BaCu_yO_x$ (y = 1.0, 0.75, 0.5) target and conductivity of the 2c phase films.

Cu/Ba	Resistivity (Ω cm)
1.0	10^{-1}–10^{-2}
0.75	10^{-3}–10^{-4}
0.5	>1.0