Fabrication of (Cu,C)Ba$_2$CuO$_y$ superconducting thin film by RF magnetron sputtering

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Abstract. We report the superconducting properties of (Cu,C)Ba$_2$CuO$_y$ thin films deposited by RF magnetron sputtering from targets with a nominal composition of Ba$_2$Cu$_{1.5}$O$_y$. The thin films were grown in mixed Ar (5~40 mTorr), O$_2$ (0~1.2 mTorr) and CO$_2$ (0~1.8 mTorr) atmosphere. The epitaxial c-axis oriented thin films with c-axis length in the range between 7.96 Å and 8.82 Å were obtained on SrTiO$_3$ (100) substrates, but superconductivity was observed only for the films which have the c-axis length with 8.01 Å and 8.32 Å. By optimizing deposition conditions, the excellent (Cu,C)Ba$_2$CuO$_y$ thin film with $T_c= 62$K and superconducting transition width $\Delta T_c= 1.5$ K was successfully obtained.

1. Introduction
(Cu,C)Ba$_{2n-1}$Cu$_n$O$_y$ homologous series is one of the most interesting system in the high-$T_c$ cuprate superconductors[1]. The highest $T_c (=120$K) is observed for (Cu,C)Ba$_2$Ca$_2$Cu$_3$O$_y$ (n=3) ((Cu,C)1223). Besides, fourth member (Cu,C)Ba$_2$Ca$_3$Cu$_4$O$_y$ (n=4) ((Cu,C)1234) also has a high-$T_c$ of 118K and shows characteristics of multi-layered superconductors. (Cu,C)1234 has four CuO$_2$ layers, which two inner planes (IP’s) are in optimum-doped state and the other two outer planes (OP’s) are in over-doped state[2]. Since charge carriers are selectively doped into OP’s, $T_c$ of (Cu,C)1234 does not change in the wide range of carrier doping. This feature is consider to be related to high irreversibility field and low anisotropy of (Cu,C)1234[3-5]. However, bulk samples of (Cu,C)-system are synthesized only under high pressure, so far.

(Cu,C)Ba$_2$CuO$_y$ ((Cu,C)1201) superconductor is the first member (n=1) of (Cu,C)-system. This has a simplest crystal structure among the (Cu,C)-system. Superconductivity of
(Cu,C)1201 have been reported on sputtering thin films by H. Adachi et al. [6]. They showed the superconductivity at 40−50 K.

In this study, we report on the thin film growth of (Cu,C)1201 by RF magnetron sputtering method. By controlling deposition parameters, we obtained high quality (Cu,C)1201 thin film with $T_c$ of 62 K and $\Delta T_c = 1.5$ K.

2. Experimental

(Cu,C)Ba$_2$CuO$_y$ thin films were deposited on (100) SrTiO$_3$ (STO) substrates by a RF magnetron sputtering method. Targets with a nominal composition of Ba$_2$Cu$_{1.5}$O$_y$ were used to deposit thin films. The targets were made from a mixture of BaCO$_3$ and CuO. Thin film growths were done by on-axis and off-axis configuration. The distances between the target and the STO substrates for off- and on-axis configuration are 120 mm and 50 mm, respectively. The (Cu,C)-1201 thin films were grown in the temperature range between 520 and 600 °C under Ar (5−40 mTorr), O$_2$ (0−1.2 mTorr), and CO$_2$ (0−1.8 mTorr) atmosphere. Temperature was monitored by an optical pyrometer. The input RF power of 30−80 W were applied for sputtering with the target diameter of 55 mm. After deposition, the samples were cooled down to room temperature in oxygen atmosphere. Typical thicknesses of the films were ~100 nm in the present study. Structure of the films were characterized by X-ray diffraction (XRD) using by a Rigaku RAD-C system for $\theta$ - 2$\theta$ scan and a Phillips X’Pert four-circle diffractometer for omega scan with Cu K-\(\alpha\) radiation. Superconducting properties of the (Cu,C)-1201 films were measured by conventional four probe method. Good electrical contacts were obtained by Au deposition on the film surface. Most of thin films showing superconductivity were obtained by off-axis configuration and RF power of 50 W. We mainly concentrate the results of this growth condition in this report.

3. Results and Discussion

Fig. 1. shows X-ray diffraction patterns of the c-axis orientated (Cu,C)1201 thin films with three different c-axis lengths. By changing deposition condition, we obtained the (Cu,C)1201 thin films with various c-axis lengths ranging from 7.96 to 8.82 Å. These values are almost twice longer than that of infinite layer (IL) BaCuO$_2$ of 4 Å. Since (Cu,C)1201 forms by introducing of CO$_2$ in a sputtering atmosphere, this double periodicity of IL structure is coming from the ordered introduction of carbonate into IL. Thus, considering formation of Ba-(Cu,C)-O charge-reservoir block (CRB) by incorporated carbon, widespread difference (~0.8 Å) of c-axis length
for (Cu,C)1201 thin films should be related to local distortion of crystal structure in the CRB. Such large difference in CRB seems to have great influence on electrical conductivity of CuO$_2$ plane. In fact, superconductivity was observed only in case of the films with c-axis length from 8.0 to 8.3 Å, especially from 8.2 to 8.3 Å.

Fig. 2 shows temperature dependence of resistivity for (Cu,C)1201 thin films grown under various O$_2$ partial pressure of sputtering gas (0.1, 0.3, 0.5, and 0.7 mTorr) normalized at 300 K. Other growth parameters are fixed at a pressure of Ar = 10 mTorr and CO$_2$ = 0.5 mTorr and at substrate temperature (T$_s$) = 560 $^\circ$C. With increase of O$_2$ pressure, resistivity curve changes from semi-conducting like to metallic and their T$_c$ values raise from 20 K to 55 K. These variations of resistivity curves indicate that our films are in under-doped state and introduced oxygen plays as carrier dopant in this system. In a previous work by H. Adachi et al., they showed oxygen annealing effect of resistivity for (Cu,C)1201 films[6]. Their films were in over-doped state and are contrastive to our results. It seems that (Cu,C)1201 thin films is possible to change the entire doping in the range from under-doped to over-doped by variation of oxygen contents like La$_{2-x}$Sr$_x$CuO$_4$.

Fig. 3 shows temperature dependence of resistivity for (Cu,C)1201 thin films grown under various CO$_2$ gas partial pressure (0.3, 0.5, and 0.7 mTorr). These films were grown under sputtering gas pressure of Ar = 10 mTorr and O$_2$ = 0.3 mTorr at T$_s$ = 560 $^\circ$C. The films prepared under CO$_2$ pressure below 0.1 mTorr were not stable in air and color of films changed immediately from black to transparency when the films take out from chamber. This indicate incorporation of carbon into (Cu,C)1201 is important to stabilize their structure. Similar to the case of oxygen pressure dependence, with increase of CO$_2$ pressure, the behavior of resistivity curve varied from semi-conductor to metallic and T$_c$ values are also increased. This indicates that CO$_2$ gas plays not only as stabilizer of (Cu,C)1201 structure but also as oxidizer. In order to optimize the superconductivity of (Cu,C)1201 thin films, it is necessary to control both O$_2$ and CO$_2$ pressure during deposition.

XRD pattern of (Cu,C)1201 thin film grown at optimized growth parameters are shown in
Fig. 4. XRD patterns of (Cu,C)1201 thin film with $T_c=62$K and $\Delta T_c=1.5$K.

Fig. 5. Temperature dependence of (Cu,C)1201 thin film with $T_c=62$K and $\Delta T_c=1.5$K. The inset shows the enlarged portion of the resistivity curve near $T_c$.

Fig. 4 where c-axis orientation of the (Cu,C)1201 film with c-axis length of 8.227 Å can be seen clearly without other impurity phases. The optimized growth conditions are Ar=10 mTorr, O$_2$=1.0 mTorr, CO$_2$=0.4 mTorr, and $T_s=560^\circ$C. Fig.5 shows the temperature dependence of the resistivity for this film. One observes a metallic behavior in the normal state between room temperature and $T_c$. In this study, highest $T_c (=62$K) was observed for this film with sharp transition width $\Delta T_c=1.5$ K. This $T_c$ value is significantly higher than previous reports[6,7].

The crystallinity of the typical (Cu,C)1201 film was studied by employing the $\omega$-scan of (004) reflection of (Cu,C)1201 film. The full width at half-maximum of the rocking curve of (004) reflection was 0.088 degree, indicating high-crystalline quality of the (Cu,C)1201 film.

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4. References

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