Pulsed Laser Deposition Synthesis and Photoemission Study of Superconducting Ba-Cu-O Thin Films

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Abstract. Ba-Cu-O films have been grown by pulsed laser deposition. Investigation of their transport properties and characterization of electronic structure by in-situ photoemission spectroscopy have been carried out. The films grown at 450 ~ 480 °C from BaCuO 2 target had simple infinite layer structure with lattice parameter of a and c about 0.385 and 0.405 nm, respectively. Conductivity of these films were, however, poor. Usage of BaCu 0.75Ox target and addition of CO 2 into the growth atmosphere resulted in an expansion of c-axis length up to 0.810 ~ 0.835 nm and a significant rise of conductivity. This structure is represented as “2c”. For the 2c phase, conductivity above of 103 S/cm was achieved by adjusting their growth temperature in the range of 500 ~ 530 °C. Most of the highly conductive 2c phase showed superconductivity. The maximum temperature of onset of the superconducting transition and zero resistance state obtained so far were 60 and 47 K, respectively. Finite spectral weights at Fermi level were successfully observed in in-situ photoemission spectra of the 2c phase. In valence band region, a prominent peak with u 3d character located at a binding energy around 1.6 eV. Though this low binding energy suggested a rather high hole concentration of mobile holes were around middle of 1021 cm-3 range. These results about electronic structure indicate a coexistence of conventional CuO 2 planes and distorted ones. The latter structure might play charge-reserving blocks, though some portions of holes should localize in them. Correlations between the properties and electronic structure are to be discussed.

1. Introduction

In multi-layered high temperature superconducting cuprates (HTS), such as HgBa2Ca12Cu24Ox, TlBa2Ca12Cu24Ox, Cu12Ba2Ca12Cu24Ox and (Cu, C)3Ba2Ca12Cu24Ox, carrier distribution among crystallographically non-equivalent CuO2 planes can be varied. This new degree of freedom results in unique properties, including a coexistence of high temperature superconductivity and antiferromagnetism within single unit cell [1], robustness of almost optimum critical temperature against over-doping [2], and so on. In a group of multi-layered HTS of which charge reservoir blocks
contain Cu ions, a widely controllable conductivity of the reservoirs leads a potential for tunability of transport properties along c-axis. The multi-layered HTS, especially Cu- and (Cu, C)-systems, therefore, provide a suitable platform to investigating change of electronic structure of the HTS and to explore novel properties such as multi-component superconductivity at high temperature [3].

Usefulness of artificial superlattice technique for preparation of series of the multi–layered HTS has been demonstrated by Balestrino et al. [4, 5]. In previous works, we also have studied (AE)CuO$_2$ [AE = alkaline-earth] infinite layer films and their superlattices. Up to now, $T_{c\text{-onset}}$ of 58 K has been achieved in [SrCuO$_2$]/[BaCuO$_2$]$_3$ superlattice [6]. There were, however, a wide spread in the obtained properties, so for. Study about doping efficiency of these films has indicated that precise control of the Ba-Cu-O blocks should be a key for systematic study of their superconducting properties.

In the present study, we have performed a deposition of Ba-Cu-O films by pulsed laser deposition. Characterization of their electronic structure by in-situ photoemission spectroscopy and transport properties has been also carried out. Cu-poor samples grown in O$_2$-CO$_2$ mixed atmosphere, of which c-axis parameter is twice as long as that of simple infinite layer structure, exhibits $T_{c\text{-onset}}$ up to 60 K. The in-situ photoemission measurement of the superconducting films reveals a similarity of their electronic structure to YBa$_2$Cu$_3$O$_7$ [YBCO]. The spectra also suggest a heavy injection of holes and possibility of localization of major part of the holes.

2. Experiments

Specimen films were grown on (001) plane of SrTiO$_3$ at temperatures in the range of 450 ~ 530 °C by pulsed laser deposition using KrF excimer laser. The growth was performed under 0 ~ 2.4 % CO$_2$ + O$_2$ reactive gas and Ar gas mixture atmosphere. Partial pressure of the reactive and Ar gases were 0 ~ 5 mTorr and 0 ~ 55 mTorr, respectively. In order to maintain residual gas level of growth chamber constant, we utilized a load-lock system. Highly dense pellets of BaCuO$_2$, BaCu$_{0.75}$O$_x$ and BaCu$_{0.5}$O$_x$ were used as targets. For preparing films with a composition in between those of the targets, alternative deposition from two targets was adopted. An amount of deposited atoms during one cycles was 0.2 atomic layer or less. Crystal structure of the films was characterized by means of in-situ reflection high energy electron diffraction (RHEED) and $\theta$-2$\theta$ scan of X-ray diffractometry. Their electronic structure and chemical bond nature were investigated by means of photoemission spectroscopy without exposing them to air, where vacuum bessel ( <1x10$^{-8}$ Torr) was utilized for sample-transfer. Temperature dependence of resistivity was measured by standard four probe method.

3. Results and discussion

Figure 1 shows typical XRD and RHEED patterns of the films grown from the BaCuO$_2$ target without CO$_2$. Epitaxial relationship of Ba-Cu-O [100] // SrTiO$_3$ [100], Ba-Cu-O [010] // SrTiO$_3$ [010], Ba-Cu-O [001] // SrTiO$_3$ [001] were confirmed. The data also showed tetragonal symmetry with lattice constant of a ~ 3.85 Å and c~4.05 Å. Though these films had an ideal infinite layer structure, they were highly resistive (0.1 ~ 1.0 Ωcm) 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. Figure 2 shows a change of XRD patterns of the films grown from the BaCuO$_2$ target with relative pressure of CO$_2$ to O$_2$ $P_{CO_2}$ in the film growth. In the range of $P_{CO_2}$ below 0.6 %, the specimens had the simple infinite layer structure. Further increase of $P_{CO_2}$ resulted in a development of another phase; in this phase, the fourfold azimuthal symmetry was maintained, and c-axis length was expanded to almost twice as long as that of the infinite layer structure. This phase is represented as “2c” phase.
below. Since the 2c phase was chemically unstable, the specimen films, which were initially black, easily got transparent by short-time exposure to air. Measurements of transport properties performed immediately after the sample taking out, however, revealed a low resistivity of 2c phase not higher than few mΩcm. To avoid the chemical degradation, amorphous CaCuO₂ or Au protection layers were deposited in-situ. Temperature dependence of resistivity and zero resistance temperature $T_{c(0)}$ of 2c phase were characterized by using the protected specimens. Though temperature coefficient of the 2c phase containing films grown from the BaCuO₂ target were positive or almost zero, these films did not show superconductivity above 10 K.

Systematic survey of the preparation conditions revealed one of the keys for improving transport properties is a precise control of Cu/Ba ratio and $R_P$.$CO_2$. The maximum normal state conductivity with an order of $10^4$ Ωcm was achieved in the 2c phase films grown from the BaCu₂₀.₇₅Oₓ target at 500 ~530°C. Hole measurements of these films showed that major carrier of these films was hole, and that its concentration reached as high as $1.9x10^{21}$ cm⁻³. Figure 3 (a) shows temperature-resistivity characteristics of the 2c phase film coated with the CaCuO₂ layer. A sharp drop of resistance started around 60 K. Constant residual resistance below 47 K should be due to the protecting layer. Figure 3 (b) shows temperature dependence of resistance of the same kind of 2c films covered with in-situ amorphous CaCuO₂ layers (a) and Au one (b).

Table 1 shows a relationship between $R_P$.$CO_2$ and $T_{c(onset)}$. The narrow window in $R_P$.$CO_2$ for finite $T_{c(onset)}$ reveals the concentration of CO₂ group is another key for realizing superconductivity in the Ba-Cu-O films. In some of RHEED patterns of the superconducting 2c films, streaks, which corresponded with a real space periodicity twice as long as that of the simple infinite layer structure were observed. These results suggest that ordering of Cu vacancies or incorporated CO₂ group may promote the superconductivity. The highest $T_{c(onset)}$ and $T_{c(0)}$ in this study were 60 and 47 K, respectively. Figure 4 (a) shows valence band spectra of insulating SrCuO₂, metallic Sr₀.₉CuO₂ films and the superconducting 2c Ba-Cu-O films measured by in-situ XPS. For the Ba-Cu-O film, finite spectral weight at Fermi level was clearly observed. In-situ UPS measurement of the 2c films also showed a high density of states at Fermi level. Within our knowledge, these are the first observation of photoelectron Fermi level of 2c Ba-Cu-O films. Among the spectra, prominent features around binding energy of 1 ~2 eV, which has Cu 3d character, of the 2c phase film was most close to Fermi level. Considering that the rise of density of states and the peak shift originate in a decrease of Fermi level by hole-doping, these results are evidences of the...
easiness of hole-doping in the 2c phase. Figure 4 (b) showed XPS valence band spectra of the superconducting Ba-Cu-O, YBCO, Bi$_2$Ba$_2$CaCu$_2$O$_y$ [Bi-2212] and Tl$_2$Ba$_2$CaCu$_2$O$_y$ [Tl-2212] [7]. In low energy region, spectral intensity of the Ba-Cu-O was stronger than that of Bi- and Tl system. A shape of the spectra of the Ba-Cu-O was quite similar to YBCO. Taking into consideration that the spectral weight of YBCO in a low binding region is mainly due to heavily doped Cu-O chain, these results suggest that Cu ions in the Cu-depleted layer in the Ba-Cu-O should be highly oxidized. This structure should play as a charge reservoir which should result in high hole concentration in another half of CuO$_2$ planes as well as superconductivity in the Ba-Cu-O films.

4. Conclusions

Ba-Cu-O films with structures related to the infinite layer cuprates have been grown on SrTiO$_3$ (001) planes by pulsed laser deposition. All of the films showed tetragonal symmetry and cube-on-cube epitaxial relationship. An introduction of CO$_2$ into the growth atmosphere results in a growth of the conductive “2c” phase, which has c-axis parameter twice as long as that of the simple infinite layer BaCuO$_2$. Simultaneous control of the CO$_2$ pressure and target composition resulted in a remarkable decrease of resistivity in normal state ($< 1\Omega \text{cm}$) as well as superconductivity. The highest $T_c$ (onset) of 60 K and $T_c$ ($\rho=0$) in 47 K are obtained so far. In in-situ photoemission spectra of the superconducting Ba-Cu-O films, finite density of states is observed. The change of photoemission spectra of the 2c phase films and comparison of the spectra with other HTS reveal an easiness of hole-doping into this phase and heavily hole-doped states of the superconducting specimens. The present study shows the Ba-Cu-O structure is a suitable candidate of superconducting block for investigating novel functions by means of superlattice technique.

References

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