Fabrication and Photochemical Modification of High T_c Superconducting Thin Films

高温超伝導薄膜の製作と光化学修飾

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Since December 1986, we have been engaged in high T_c oxide superconductor research with emphasis on the synthesis and processing of thin and thick films of cuprate superconductor as well as on the accumulation of some basic data related with the film preparation. This paper reports some of our recent results of film deposition and photochemical processing of the films. 50Hz ac sputtering has been primarily used for preparing a variety of high T_c films by use of its simple and easily modifiable system. A plasma controlled sputtering is applied to the currently interested layer-by-layer deposition of oxide films as a possible approach to new higher T_c materials. Annealing of films under a laser or a UV light irradiation worked effectively to control the oxygen stoichiometry and induced reversible changes in T_c and crystal parameters of the films.

KEY WORDS: 50Hz ac sputtering, Plasma controlled sputtering, Laser annealing, UV light irradiation

1. FILM FABRICATION PROCESSES

50Hz ac sputtering method.

A simple sputtering apparatus using a pair of targets and 50 Hz ac neon sign transformer was devised and verified to be quite useful for the preparation of high T_c superconducting thin films.¹⁾ The original system of 50Hz ac sputtering is schematically represented in Fig.1.

Fig.1. Schematic diagram of the 50Hz ac sputtering apparatus.

The characteristics of this method include (1) Easily operable simple and inexpensive instrumentation, (2) Exchangeable home-made two targets system, and (3) Possible external modulation of the system. We have successfully prepared high T_c superconducting thin films of La-Sr-Cu-O₂, Yb-Ba-Cu-O₃ and Nd-Ce-Cu-O₄ systems. Bi-Sr-Ca-Cu-O superconducting thin films were prepared on MgO(100) single crystal with polished face. Sputtering was carried out at substrate temperature of 80~720°C and in an atmosphere of Ar and O₂ with total pressure 8×10^{-2} Torr during the deposition. The ratio of the chemical composition of as-deposited films were determined as Bi_{1.8}Sr₂Ca_{1.8}Cu_{2.9}O_x by inductively coupled plasma atomic emission spectroscopy. The film was annealed at 830°C~860°C for 1~5 hours by various methods. Figure 2 shows the X-ray diffraction pattern of the film set on Bi-Pb-Sr-Ca-Cu-O bulk annealed in PbO vapor at 850°C for 1 hour. The films showed a c-axis-preferred orientation to the substrate.

Figure 3 shows the critical temperature for onset, mid point and zero resistivity were 119K, 112K and 92K, respectively.

Fig.2. X-ray diffraction pattern of the film set on Bi-Pb-Sr-Ca-Cu-O bulk annealed in PbO vapor at 850°C for 1 hour.

Fig.3. Temperature dependence of resistivity for the film set on Bi-Pb-Sr-Ca-Cu-O bulk annealed in PbO vapor at 850°C for 1 hour.

On the other hand, as-grown superconducting thin films of Bi-Sr-Ca-Cu-O have been prepared on MgO(100) at 620~720°C by interval sputtering method. We observed c-axis orientation in as-grown films, and These films showed zero resistivity between 65K and 79K, as shown in Fig.4. The superconducting properties of the films were affected by in-situ. annealing time and deposition thickness per 1 cycle during film growth. The best film showed zero resistivity at 79K.

Fig.4. Temperature dependence of resistivity for the as-grown Bi-Sr-Ca-Cu-O film prepared by interval sputtering method.

Plasma controlled sputtering method.

A currently interest in Bi-Sr-Ca-Cu-O film research is focused on the synthesis of artificially designed multilayered structures, since the T_c of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ ($n=1,2,3$) system increases from 20K to 110K with the increase of n , i.e. the number of CuO_2 layers in the unit cell. We employed a plasma controlled sputtering method for the compositional modulation and multilayered film synthesis of Bi-Sr-Ca-Cu-O system.⁵⁾

Figure 5 shows plasma controlled sputtering system has two magnetic coils, one of which placed under and the other to control the distribution of the magnetic field above a target. The radius of discharge plasma formed on the target is changed by changing the magnetic field.

Fig.5. Schematic diagram of the plasma controlled sputtering apparatus.

Therefore, it is possible to control the sputtering area of the target. Alternating application of two different magnetic fields to the plasma generated above the target which has different compositions along its radius, realizes continuous preparation of multilayered films.

When artificial multilayered films were prepared, the possibility of interdiffusion of each atom at each interface took in to account. However the problems have not been yet reported.

In the preceding study, we have reported the construction of compositional modulated multilayered films from a binary target with $\text{Bi}_{1.6}\text{Sr}_{1.0}\text{O}_x$ and $\text{Ca}_1\text{Cu}_{1.5}\text{O}_{9.6}$. On the other hand, Y-Ba-Cu-O superconducting thin films were prepared by using inner YCuO_x and outer BaCuO_x target.

Figure 6 shows the compositional variation of films deposited at various currents I_c in the compressive magnet coil. The film composition was continuously changed by varying the magnetic field. BaCuO_2 and $\text{Y}_2\text{Cu}_2\text{O}_5$ films were sputtered from Ba-Cu-O and Y-Cu-O targets, respectively, and alternately deposited on MgO substrate.

Figure 7 depicts low-angle X-ray scattering pattern of the film accumulated at substrate temperature of 200°C . The film was designed to be constructed by a BaCuO_2 and $\text{Y}_2\text{Cu}_2\text{O}_5$ layer of thickness of $50\text{\AA}$. Those scattering peaks were assigned to the multilayers of about $102\text{\AA}$ interval, although each layer was amorphous.

Fig.6. The compositional variation of films deposited under magnetic field varied with the coil current I_c while the other coil current I_m fixed 4.0A .

Fig.7. Low-angle X-ray scattering result of the Y-Cu-O/Ba-Cu-O multilayered as-deposited film designed to be $100\text{\AA}$ of periodicity. n indicates the reflection order.

The X-ray diffraction pattern of a multilayered film designed to have $12\text{\AA}$ periodicity showed (003) and (006) peaks of $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ superconducting phase when the film was deposited at a substrate temperature of 500°C as shown in Fig.8. The peak intensities increased with the increase in the substrate temperature. Annealing the film deposited at 450°C made it strongly c-axis oriented $\text{YBa}_2\text{Cu}_3\text{O}_{7-d}$ film in which planar texture-like structure was observed by SEM. The annealed film showed superconductivity with T_{c0} at 49K .

Fig.8. X-ray diffraction patterns of as-grown multilayered films deposited at various substrate temperatures.

2. PHOTOCHEMICAL MODIFICATION OF SUPERCONDUCTING FILMS

Laser annealing.

The property and phase structure of oxide superconductors can be modified by annealing, since they are quite sensitive to the nonstoichiometry which is dependent on temperature and atmosphere. Insulating or semiconducting YBCO films prepared by ac sputtering at substrate temperatures below 400°C could be partially crystallized into the triple layered perovskite structure by the Nd:YAG laser annealing. Subsequent furnace annealing produced the YBCO single phase having a high T_c (~80K). Laser annealing also made it possible to form micropatterning of insulating lines by the rapid melting and quenching of superconducting YBCO films.⁷⁾ We verified the reversible control between the crystalline superconductor formed by the furnace annealing and the amorphous semiconductor formed by the laser annealing.

UV light irradiation effect.

Oxygen activation by a photochemical process was found useful for the control of oxygen content in oxide films at low temperatures (~400°C). The irradiation of low pressure mercury light to YBCO and BSCCO films in O_2 atmosphere using the apparatus shown in Fig.9 increased and decreased, respectively, the T_c 's of the films.⁸⁾

Fig.9. Schematic representation of 50Hz ac sputtering apparatus installed with a UV light irradiation system.

The T_c change in BSCCO shown in Fig.10 accompanied by the variation in the c-lattice parameter. Besides this O_2 /UV system, several other methods for activating oxygen were examined and compared their effects by measuring the T_c and crystal parameter of the films.

Fig.10. Resistivity change in a Bi-Sr-Ca-Cu-O film by the annealing under various conditions.

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