Properties of YBCO Films Grown by a Low Gas Pressure Sputtering Method

Toshiyuki Matsui
Hiroshi Kimura
Takeshi Suzuki

1. Introduction

Since high-Tc oxide superconductors whose critical temperature (T_c) exceedes 90K were discovered in 1986, basic research into the fabrication of electronic devices that utilize these materials has been energetically carried out.

Since 1987, in order to develop superconducting three-terminal devices such as transistors, Fuji Electric has established technologies for high-Tc oxide superconductor films and heteroepitaxial growth by reactive sputtering[1]-[3], reactive evaporation[4], and molecular beam epitaxy (MBE) methods, and also has proposed original new-function devices[5].

The superconducting characteristics of high-Tc oxide superconductors heavily depend on their crystallinity, the oxygen concentration in the film, and the composition of metal atoms. The fabrication of $YBa_2Cu_3O_X$ (YBCO) films by a reactive sputtering method generally uses an oxide target composed of Y-Ba-Cu-O (yttrium-barium-copper-oxygen) and a mixed gas of argon (Ar) and oxygen (O_2) for the sputtering gas. When an oxide target is used, negative oxygen ions from the target are driven into the film together with metal atoms. While most of the other particles have kinetic energies of several eV, these negative oxygen ions have kinetic energies of hundred eV because they have been accelerated by the auto-bias. Such high-energy particles change the metal composition and damage the crystallinity when they collide with the film[6].

On the other hand, the arrival on the substrate of particles having a certain degree of kinetic energy (several eV), increases particle migration on the substrate and improves the film crystallinity. Therefore, the selectivity of arrived particles on the substrate is considered important in sputtering methods for oxide materials.

This paper describes the features of Fuji Electric's low gas pressure sputtering method and the YBCO film characteristics obtained by this method.

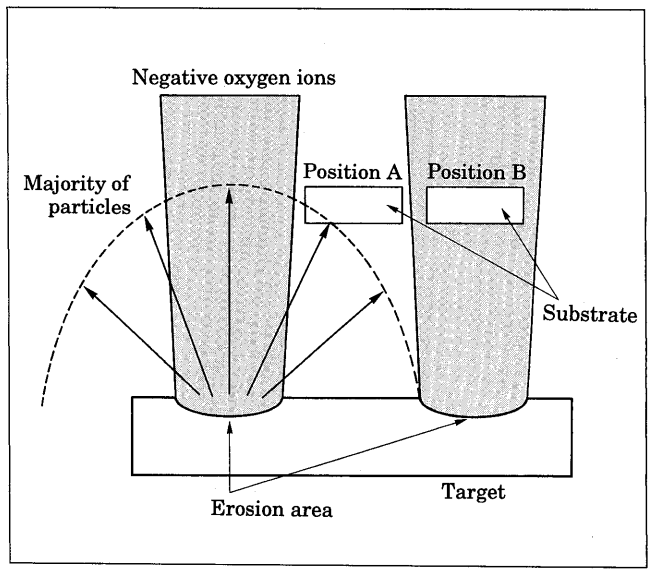
2. Film Fabrication Experiment

Figure 1 shows the arrangement of the target and substrate in the high-frequency magnetron sputtering system used in this experiment. A sintered Y-Ba-Cu-O six inches in diameter was used as the target, and an MgO single crystal with a (100) face and an $SrTiO_3$ single crystal with a (110) face were used as substrates. For the sputtering gas, a mixed gas of Ar and 50% O_2 was used and the substrate temperature was set at 650°C.

The substrate was positioned as in Fig. 1 for the following reason. The negative oxygen ions, accelerated by the auto-bias, are driven out from the erosion area of the target in an approximate vertical direction (as shown by the shaded area of Fig. 1).

On the other hand, the majority of particles have several eV of energy, and are thought to be driven out of the erosion area in a wide distribution of directions. Therefore, as shown in Fig. 1, the selectivity of particles incident upon the substrate is made possible by placing the substrate at the central axis of the target and at the position where the distance between the target and substrate ($D_{t\text{-}s}$) is nearly equal to the mean free path

Fig.1 Positioning of the target and substrate



(Position A).

The mean free path λ is given by λ (cm) $\fallingdotseq$ 1.33/P, P: pressure (Pa). Actual settings were P = 0.5 Pa and $D_{t\text{-}s}$ = 28 mm. To Form oxide superconductor films, the usual sputtering methods are high gas pressure sputtering at $\fallingdotseq$ 100 Pa and off-axis sputtering[7] where the substrate is vertical to the target face. With a gas pressure of one tenth to a hundredth lower than these sputtering methods, our method is called low gas pressure sputtering. In the experiment, another substrate was set directly above the erosion area (Position B) and characteristics of the obtained YBCO films were compared.

After the films were formed, the substrate temperature was maintained at 650°C and oxygen was introduced into the chamber until the pressure reached 1 atm. Then the films were cooled to room temperature. The composition of metal atoms was analyzed by induced coupled plasma emission spectroscopy (ICP) and the surface roughness of the YBCO film was measured with an atomic force microscope (AFM). The T_c's of YBCO films were evaluated by resistivity-temperature measurement using the dc four-probe method.

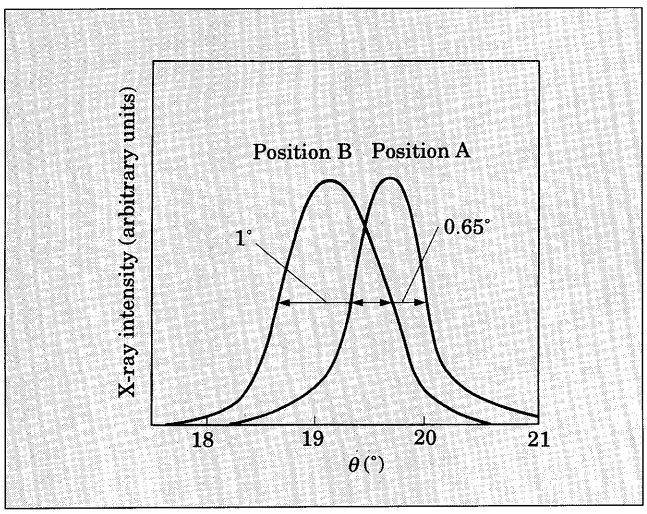
To investigate the oxidation mechanism during YBCO growth, YBCO films were also prepared using pure Ar as the sputtering gas. In this case, films were formed only with pure Ar gas and then cooled in a 1-atm nitrogen or oxygen atmosphere.

3. Results and Discussion

3.1 Low gas pressure sputtering

Figure 2 shows the rocking curves of (005)-peaks on the (001)-oriented YBCO films fabricated at positions A and B. An MgO (100) face was used for the substrate. So that the composition of metal atoms could be maintained at the Y:Ba:Cu ratio of 1:2:3 in each sample, the target composition was compensated. As a result, at position A, the target composition Y:Ba:Cu ratio was 1:2:4 to maintain the above composition of metal atoms. At position B, a ratio of 1:2.6:6 was required for greater compensation of Ba and Cu metals. Full width at half maximum was 0.65° for the film grown at position A, and 1° at position B. Moreover, the growth rate was 13 nm/min at position A in contrast to 9 nm/min at position B.

Fig.2 Rocking curves of (005)-peaks in films obtained at different substrate positions



From the above, it can be seen that position B is bombarded by negative oxygen ions. Ion bombardment of the film causes sputtering of metal atoms and damage to the crystallinity of the film being grown. This damage can be reduced by placing the substrate at position A. The films formed by low gas pressure sputtering (at position A) had T_c $\fallingdotseq$ 80 K, and an average surface roughness (R_a) of 2 nm for the (001)-oriented 120 nm thick film and 1 nm for the (013)-oriented 120nm thick film grown on a $SrTiO_3$ substrate. YBCO films with superior quality were formed at a growth rate several times faster than high gas pressure sputtering or off-axis sputtering.

3.2 Oxidation during film formation

Recently, Char et al. have reported the results of their investigation of contact resistances between YBCO and various metal oxides. On the basis of these results, a model has been proposed in which a thermal expansion mismatch creates an forms deficiency in the interface. Because the film is oxygen at a substrate temperature greater than 600°C in a decompressed atmosphere, YBCO films formed by reactive evaporation or MBE will grow in a tetragonal structure. The cooling process in an oxygen atmosphere after film formation causes oxygen to be introduced into the Cu-O plane and a phase transition to a superconducting orthorhombic structure. Accompany-ing this crystal structure transition, YBCO lattice constants undergo a quick change. According to the model, when a junction of YBCO and metal oxides is formed at a high temperature greater than 600°C, strain during the cooling process prevents oxygen from being completely introduced into the Cu-O plane, and local oxygen deficiencies are formed. As a result, interfacial resistance adds in series to resistance of the bulk-metal oxide. This is a serious problem in fabricating heterojunctions such as layered Josephson junctions. However, if oxygen can forcibly be introduced into the film during growth to make the film grow in an orthorhombic structure, it is believed that a junction interface having little thermal strain during cooling can be formed. To study oxidation during the growth of YBCO films at the position A, film formation experiments using only with pure Ar were carried out.

Figure 3 (a) shows the X-ray diffraction patterns of a film which used only pure Ar for the sputtering gas and a 1-atm N_2 gas atmosphere for cooling. An MgO (100) face was used. for the substrate. As shown in the figure, diffraction peaks corresponding to the YBCO (00n) plane were observed. The YBCO structure formed

Fig.3 X-ray diffraction patterns of YBCO films grown under different pressures

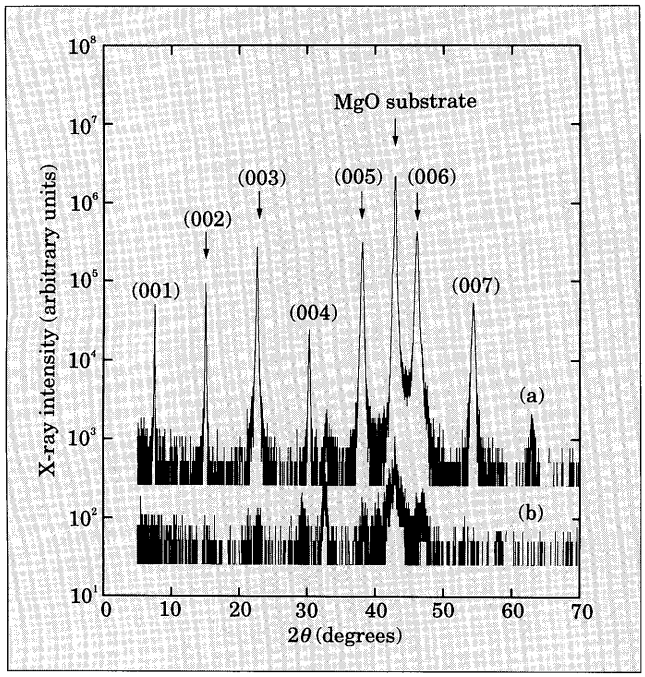


Fig.4 ρ -*T* curve of a YBCO film grown by pure Ar sputtering

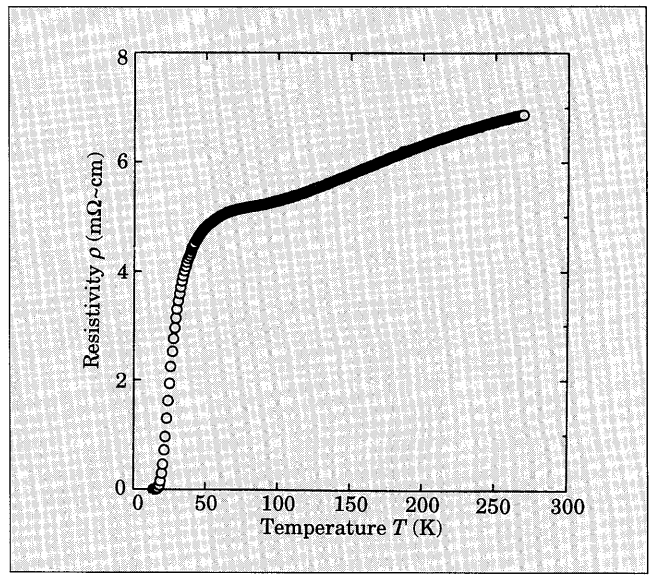
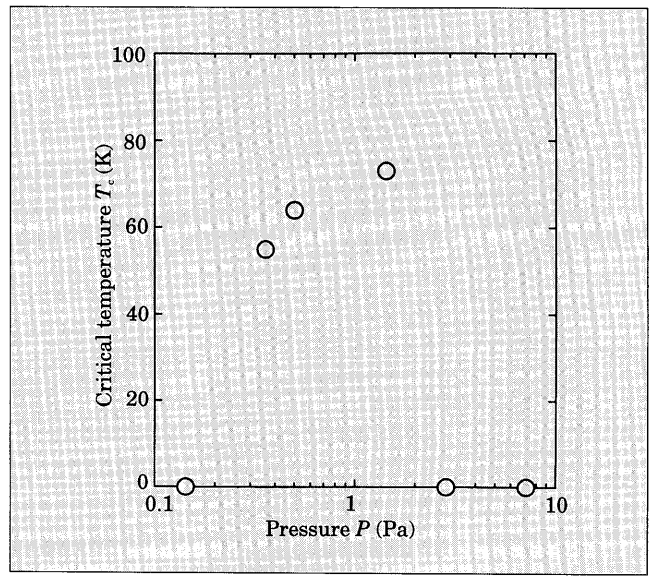


Fig.5 Relation between Ar pressure and T_c



without the artificial introduction of oxygen suggests that oxygen necessary for YBCO formation is supplied from the target to the film. Pressure during the film formation was P = 0.5 Pa.

On the other hand, Figure 3 (b) shows the X-ray diffraction patterns of the film formed at P = 3 Pa, in which peaks seemingly due to impurity layers such as $BaCuO_2$ and Y_2BaCuO_5 are observed near $2\theta \fallingdotseq 30°$ and almost no YBCO structure is formed. Figure 4 shows the temperature dependence of resistivity for the YBCO film shown in Fig. 3 (a). When the metal atom composition of YBCO is 1:2:3, the temperature dependence of resistivity and T_c depend upon the oxygen concentration of the film. That is to say, tetragonal YBCO ($y \fallingdotseq 6.5$) shows activation type conduction ($d\rho/dT > 0$) and $T_c = 0$. By increasing the oxygen concentration in the film ($y > 6.5$), the crystal structure changes to a superconductive phase, orthorhombic structure, and the temperature dependence of resistivity changes to that of a metal ($d\rho/dT < 0$). For the films obtained by introducing 1-atm N_2 after film formation, as shown in Fig. 4, $d\rho/dT < 0$, and $T_c \fallingdotseq 15$ K. This result suggests that the YBCO film grows in an orthorhombic structure. However, there is a possibility that oxygen in the film was discharged outside during cooling, and therefore we cannot report the exact oxygen quantity.

To prevent oxygen discharge during cooling, YBCO films were cooled in a 1-atm oxygen environment. Figure 5 shows the relation between Ar gas pressure and T_c during film formation. $T_c > 0$ was obtained in the range of film formation pressure P = 0.5 to 1.5 Pa. This shows that in low gas pressure sputtering, by setting $D_{t\text{-}s}$ to λ, with the exception of negative ions driven out from the target during film formation, oxygen is supplied to the film in an active state and as a result, the YBCO grows in orthorhombic structure.

On the other hand, in the case of $D_{t\text{-}s} \gg \lambda$, collision with other particles causes scattering and the quantity of oxygen that contributes to oxidation of the film is thought to drop sharply.

4. Conclusion

This paper described the features of low gas pressure sputtering and characteristics of YBCO film fabricated by this method. This film formation is characterized by the selectivity of particles incident upon the substrate attained by placing the substrate on the central axis of the target and setting $D_{t\text{-}s}$ to λ. As a result oxide films with superior surface roughness characteristics and crystallinity are formed at a growth rate of 13 nm/min. Also this film formation shows that active

oxygen discharged from the target contributes to oxidation of the film and that YBCO grows in an orthorhombic structure.

YBCO film fabrication by the low gas pressure sputtering method can be applied not only to the growth of superconducting films but also to oxides such as ferro-electric materials and giant magnetoresistive materials.

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