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Superconducting Oxide Thin Films Prepared by Sol-Gel Technique Using Metal Alkoxides

Takashi MONDE,*† Hiromitsu KOZUKA, and Sumio SAKKA
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611

Superconducting oxide thin films of the $YBa_2Cu_3O_x$ system have been prepared on zirconia (YSZ) substrates by sol-gel technique using metal alkoxide solution. Yttrium butoxide, barium methoxide and copper methoxide in a given atomic ratio were dissolved in a triethanolamine-methanol solution. Coating of the resultant solution, heating at 800 °C in air and annealing in an oxygen atmosphere resulted in superconducting oxide thin films. The onset of superconductivity was seen at 98 K and the resistance rapidly decreased with decreasing temperature, reaching substantially zero at 56 K.

The formation of coating film of the superconducting $YBa_2Cu_3O_x$ system has been attempted on the basis of plasma spray deposition,[1] sputtering,[2] screen printing,[3] and decomposition of acid salt.[4] Dip coating and similar coating methods using simple alkoxides as starting solution should be one of the useful methods for preparing thin superconducting oxide films. So far, however, no successful attempt has been reported, probably due to the insoluble characteristics of copper alkoxides in alcohols and other conventional solvents which are generally used for sol-gel preparation of glasses and ceramics. Finding that copper alkoxides can be dissolved in a triethanolamine-alcohol solution, the present authors have succeeded in preparing thin coating films of superconducting $YBa_2Cu_3O_x$ system by using metal alkoxide solution.

Yttrium n-butoxide, $Y(O\text{-}nC_4H_9)_3$, barium methoxide, $Ba(OCH_3)_2$, and copper methoxide, $Cu(OCH_3)_2$ were used as starting metal alkoxides. $Y(O\text{-}nC_4H_9)_3$ was provided by Hokko Chemical Industry Co. Ltd. $Ba(OCH_3)_2$ was prepared as methanol solution by putting pieces of Ba metal into methanol. The copper methoxide was synthesized by the reaction of lithium methoxide with copper chloride.[5] In order to prepare a metal alkoxide solution with the composition of Y:Ba:Cu=1:1.97:3.01 in atomic ratio, 0.866 g Ba metal was put in 100 ml methanol under the reflux in N_2 to make barium methoxide in methanol. Separately 7.26 ml of solution of 0.44 mol/l $Y(O\text{-}nC_4H_9)_3$ in xylene was added to the mixture

† On leave of absence from Central Research Laboratory, NEOS Co., Ltd., Shiga 520-32.

of 38 ml methanol and 5 ml triethanolamine and the resultant solution was added to the barium methoxide - methanol solution. 1.199 g $Cu(OCH_3)_2$ was added to the resultant solution under stirring to obtain the dark blue starting solution.

Coating was carried out by placing about 0.2 ml of the mixed metal alkoxide solution in 4 drops on the substrate in an ambient air atmosphere. Zirconia (YSZ) rectangular plates of 21 mm x 21 mm x 0.5 mm in size were served as substrates. After being dried on hot plate, the coated substrate was heated at 800 °C for 5 min. This coating procedure consisting of application of the solution and heating at 800 °C was repeated 5 to 10 times to make the film thickness sufficient for the film to show superconductivity after the annealing. The coating film was annealed in an oxygen atmosphere at 800 °C for 60 - 80 hours and cooled slowly in the furnace to room temperature.

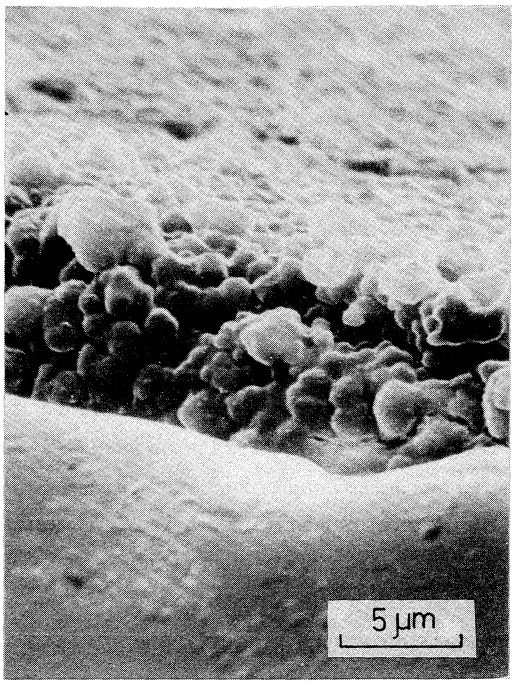

Fig. 1. SEM pictures of the thin coating film which was made by 8 time repetition of coating procedure and after annealing at 800 °C for 60 h in an oxygen atmosphere.

Electric resistance of the film was measured by the four probe method in the temperature range from 300 K to 55 K. Silver organic paste was applied as electrodes.

X-Ray diffraction was made on the coating film with an X-ray apparatus equipped with an attachment for thin film X-ray diffraction. Scanning electron microscopy was employed for examining the microstructure of the film.

Figure 1 shows SEM pictures of the fractured cross-section of thin coating film which was made by 8 time repetition of coating procedure after annealing at 800 °C for 60 hours in an oxygen atmosphere. The picture indicates that the film is composed of layers consisting of grains of about 1 - 2 μm in size. It is also seen from Fig. 1 that the thickness of the film is about 7 μm.

Figure 2 shows the X-ray diffraction patterns of the film which was made by 10 time repetition of coating procedure before and after annealing at 800 °C for 80 hours in oxygen. Single phase of $YBa_2Cu_3O_x$ is seen either of the patterns before and after annealing. However, it should be pointed out that splitting of the peak near about $2\theta = 46^{\circ}$ is observed in the pattern after annealing but not

before annealing, indicating that the $YBa_2Cu_3O_x$ phase transforms from semiconducting tetragonal phase into superconducting orthorhombic phase by the annealing.[6)]

Figure 3 shows the temperature change of the electrical resistance of the coating films before (a) and after (b) annealing at 800 °C for 80 hours in an oxygen atmosphere. The repetition of coating procedure is 10 times (a) and 5 times (b) respectively.

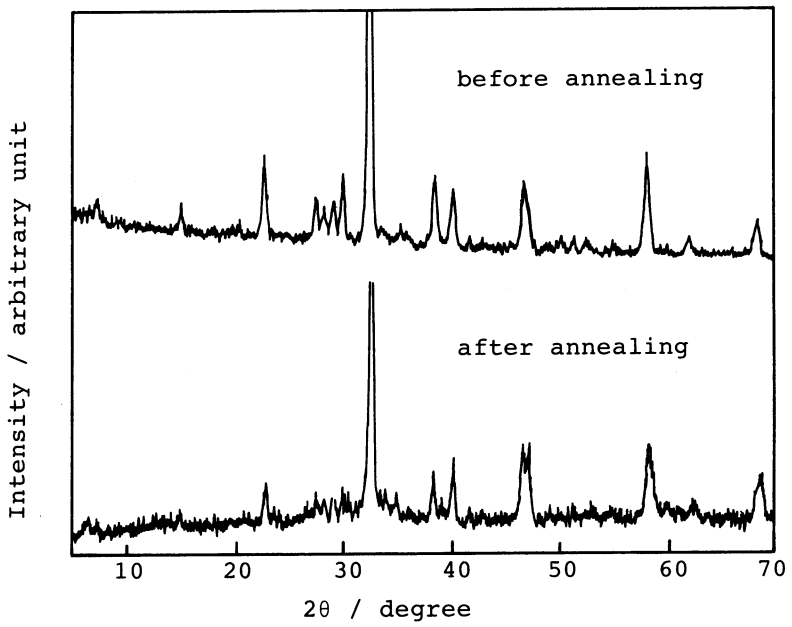

Fig. 2. X-Ray diffraction patterns of the thin coating film before and after annealing at 800 °C for 60 h in an oxygen atmosphere.

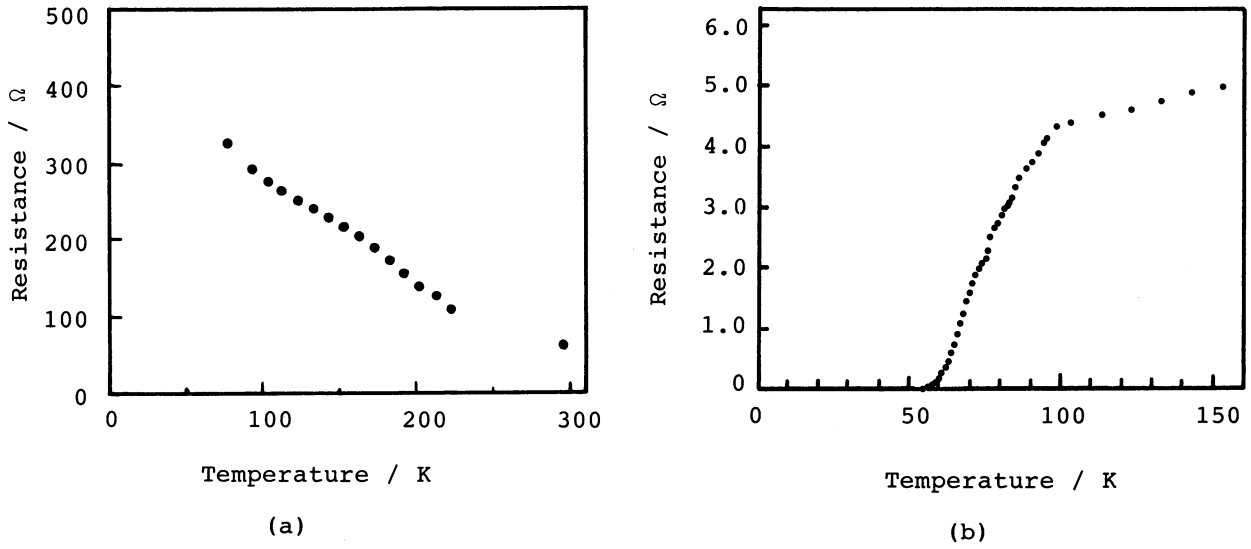

Fig. 3. The dependence of electric resistance of the thin coating film on temperature. (a) 10 time repetition of coating procedure and before annealing. (b) 5 time repetition and after annealing at 800 °C for 80 h in an oxygen atmosphere.

It is seen that the temperature dependence of the resistance is semiconducting before annealing, whereas the film after annealing is superconductive. The onset of the superconduction of the annealed sample is 98 K and the resistance becomes zero at about 56 K. The transition from metallic conduction to superconduction is not so sharp. These indicate that the annealing in oxygen is important[4] for the occurrence of superconductivity in the present films.

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