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Superconducting thin films of Bi–Pb–Sr–Ca–Cu–O synthesized by the spray-inductively coupled plasma technique

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Superconducting thin films of Bi–Pb–Sr–Ca–Cu–O were synthesized on polycrystalline MgO substrates by injecting atomized aqueous solutions of appropriate nitrates into an inductively coupled r.f. plasma (ICP) under atmospheric pressure (the spray-ICP technique). 1–2 μm thick films composed of c-axis oriented phases ($c = 2.4$ and 3.0 nm) could be synthesized in runs of 15–20 min. The phase compositions of the films were varied from $c = 2.4$ nm phase to $c = 3.0$ nm phase through their mixed phases by increasing the distance of the substrates from the ICP. In some cases the mixed phases contained a small amount of $c = 3.7$ nm phase. Annealing in air (850 °C for 10 min and then 800 °C for 5 h) converted $c = 2.4$ nm phase to $c = 3.0$ nm phase. The best as-deposited film showed T_c (resistance = 0) at 55 K, and after annealing its resistance began to drop around 110 K and reached zero at 75 K.

1. Introduction

Oxides having high superconducting transition temperatures (T_c) such as Y–Ba–Cu–O (~ 95 K), Bi–Sr–Ca–Cu–O (~ 110 K), Tl–Ba–Ca–Cu–O (~ 120 K) have been successively synthesized since Bednorz and Muller first reported the superconductivity above 30 K of Ba–La–Cu–O [1]. Recently, tailoring these high T_c oxides into films has attracted considerable attention because of its versatile applicability, and has been performed by chemical vapour deposition [2], sputtering [3], laser evaporation [4], electron beam evaporation [5], molecular beam epitaxy [6], ECR plasma [7], thermal plasma spraying and flame spraying. The last two methods are appropriate for rapid film formation, because their high-temperature heat sources can increase the reactant concentrations in the reaction field. Heintze and McPherson [8], synthesized Y–Ba–Cu–O films by these two methods, and reported that d.c. arc plasma-sprayed films are less dense than flame (O_2–C_2H_2) sprayed ones. Terashima *et al.* [9] also synthesized dense Y–Ba–Cu–O films at a high deposition rate (0.2 μm min^{-1}) by introducing solid reactants into an argon inductively coupled r.f. plasma (ICP). Thus using an ICP can achieve the rapid film formation of dense films. This is because an ICP has a much higher reaction temperature than a flame and a longer reaction zone than a d.c. arc plasma.

For the synthesis of multi-component oxide films or powders by an ICP process, liquid reactants are more appropriate than solid reactants, because metal compositions can be easily adjusted to desired values when the mother solutions are prepared. Introduction of liquid reactants into an ICP has been referred to as the spray-ICP technique [10]. In this method the mother solutions are atomized into fine droplets of 1–2 μm in size and which are then carried into an ICP. The liquid droplets of this size are considered small enough to decompose completely to their component atoms in the ICP. Therefore, the spray-ICP technique can be regarded as a plasma CVD process and be differentiated from the conventional flame pyrolysis. So far, ultrafine $BaPb_{1-x}Bi_3O_3$ powders [11] and $La_{1.85}Sr_{0.15}CuO_{4-x}$ films [12] were synthesized by this method.

A high T_c phase of the Bi–Pb–Sr–Ca–Cu–O system is a candidate superconductor in practical use because its elements are not so harmful. This oxide system has three superconducting phases having layer structures, i.e. $Bi_2(Sr, Ca)_2CuO_x$ ($c = 2.4$ nm, $T_c \simeq 20$ K), $Bi_2(Sr, Ca)_3Cu_2O_x$ ($c = 3.0$ nm, $T_c \simeq 80$ K) and $Bi_2(Sr, Ca)_4Cu_3O_x$ ($c = 3.7$ nm, $T_c \simeq 110$ K) [13, 14], (designated 2.4 nm phase, 3.0 nm phase and 3.7 nm phase, respectively). To obtain 3.7 nm single phase, a careful thermal treatment is required. Also this system is an interesting object for the spray-ICP technique to deal with, because of its multiplicity of components. The spray-ICP technique, has hitherto not been applied to such a system composed of as many as five component metals.

This study was aimed at the rapid film formation of the Bi–Pb–Sr–Ca–Cu–O superconductors on polycrystalline MgO substrates by the spray-ICP technique. The results of this study will contribute to the synthesis of superconductor films and also to further extension of the spray-ICP technique.

2. Experimental procedure

Mother solutions were prepared by dissolving nitrates of bismuth, lead, strontium, calcium and copper (guaranteed grade) with molar ratios of 2:0:2:2:3,

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2:0.2:2:2:3, 2:0.3:2:2:3 and 2:0.5:2:2:3 in distilled water (total metal concentration, 1.0 M). They were ultrasonically atomized (droplet size, 1–2 μm), and were introduced (approximately 10 ml h^{-1}) via a narrow-tipped quartz nozzle (diameter 1.5 mm) into an argon-ICP with an argon carrier gas (1.3 l min^{-1}).

The apparatus used for the film formation is illustrated in Fig. 1. The torch was composed of three coaxial quartz tubes with the nozzle at the centre. The argon-ICP (40 mm diameter by 160 mm long) was generated with a three-turn work coil (inner diameter 55 mm, copper pipe 6 mm o.d.) and an r.f. oscillator (frequency 6 MHz, maximum power 15 kW, normally run at 6 kW), and was stabilized with an argon-sheath gas (30 l min^{-1}). No plasma gas was used in this study.

Polycrystalline MgO plates (5–20 mm wide by 1 mm thick) were used as substrates. They were placed on a rotating ceramic stage, and its distance from the ICP was adjusted with a motor-driven mechanism. The distance, x, from the centre of the work coil to the substrate was recorded at each run [15]. The substrates were located in the tail flame of the ICP. Induced electric noise and strong emission from the ICP did not permit measurements of substrate temperatures. The parameter, x, was therefore used as an indication of substrate temperature. The stage was enclosed with a water-cooled glass tube (700 mm long, 140 mm i.d.). Annealing was performed in air for 10 min at 850 °C and then for 5 h at 800 °C.

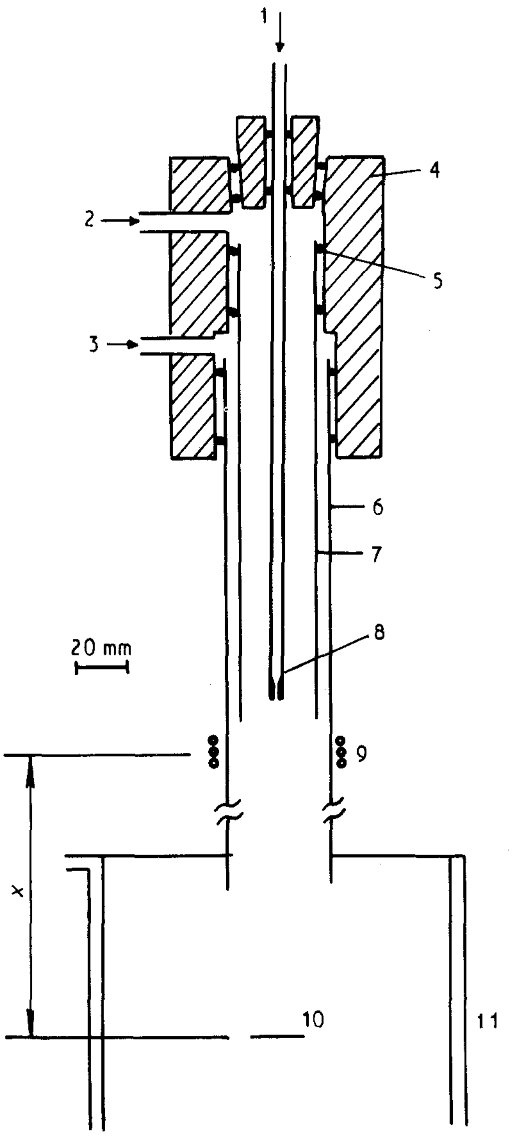

Figure 1 ICP torch: 1, carrier gas; 2, plasma gas; 3, sheath gas; 4, cylinder block; 5, O-ring; 6, outer quartz tube; 7, inner quartz tube; 8, nozzle; 9, work coil; 10, substrate; 11, water-cooled tube; x is the distance from the centre of the work coil to the substrate.

The films were characterized by X-ray diffraction (CuK_α radiation with a nickel filter and a diffractometer with a single crystal graphite monochromator, XRD) and scanning electron microscopy (SEM). The metal compositions of the as-deposited films were analysed by ICP spectroscopy. Resistances of the films were measured by d.c. four-probe method.

3. Results and discussion

An appropriate x for the film formation ranged from 450–600 mm. Above x = 600 mm, fine particles were deposited. Below 450 mm, the substrates were heated at such a high temperature that the evaporation of elements occurred, resulting in no film formation or the deposition of brown non-conductive materials. Phases of the films depended on x. This dependence is subsequently described by taking the case of the 2:0:2:2:3 mother solution. A XRD pattern of the film formed at x = 480 mm is illustrated in Fig. 2, indicating that the film is of c-axis oriented 2.4 nm phase. As shown in Fig. 3, the films formed at x = 530 mm are composed of 2.4, 3.0 and 3.7 nm (very minor) phases of c-axis orientation. Also Fig. 4 indicates that the film formed at x = 580 mm is predominantly of c-axis oriented 3.0 nm phase. Thus the phase changed from 2.4 nm phase to 3.0 nm phase as x increased. This tendency was maintained when the other solutions were used. As a rule, the relation between phase and x was: 2.4 nm phase at x = 450–500 mm, mixtures of 2.4, 3.0 and 3.7 nm (minor or discernible) phase at x = 500–570 mm, and 3.0 nm phase at x = 570–600 mm. Each phase revealed its c-axis orientation.

Naked eye observation clarified that the film surface suddenly became smooth at a certain time after the initiation of film formation. The addition of lead did not largely affect this smoothing process. ICP spectroscopy certified that the metal concentrations of the

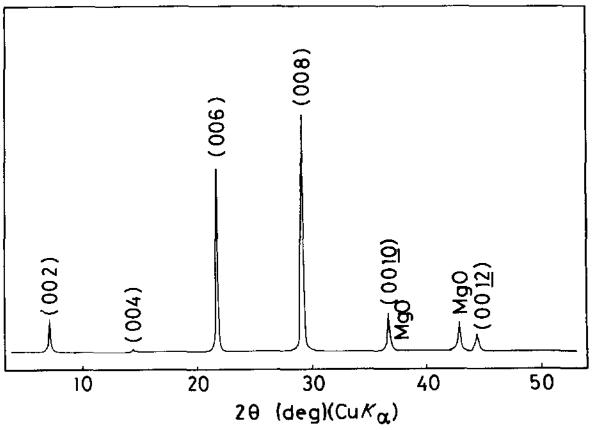

Figure 2 XRD of as-deposited film formed at x = 480 mm. Indices are given in terms of the 2.4 nm phase.

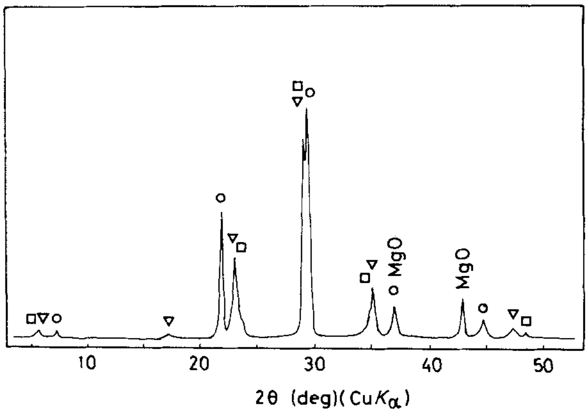

Figure 3 XRD of as-deposited film formed at $x = 530$ mm. (○) 2.4 nm phase, (▽) 3.0 nm phase, (□) 3.7 nm phase.

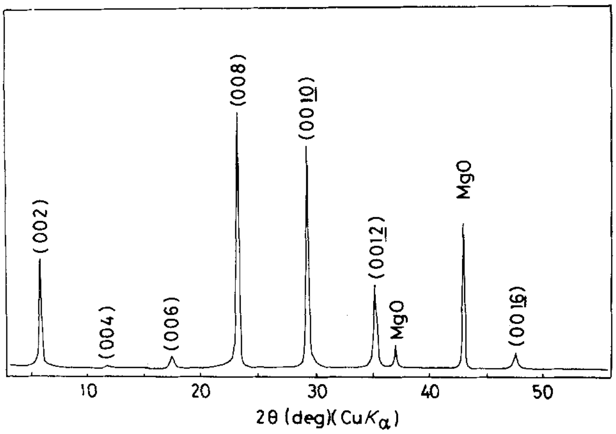

Figure 4 XRD of as-deposited film formed at $x = 580$ mm. Indices are given in terms of the 3.0 nm phase.

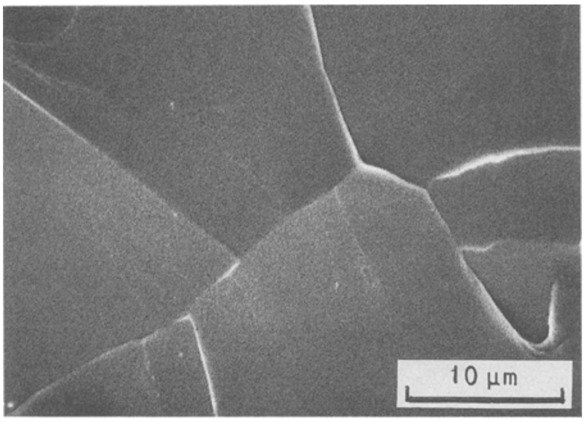

Figure 5 SEM of as-deposited film formed at $x = 580$ mm.

as-deposited film did not largely vary from those of the mother solutions.

The structure of the film synthesized from the 2:0.5:2:2:3 solution at $x = 580$ mm is shown in Fig. 5. The film has the smooth surface. SEM for the fracture surface indicated that the film thickness was 1–2 μm.

The phases of the films were varied by annealing. XRD patterns of the films before and after annealing are shown in Figs 6 and 7. Single 2.4 nm phase is

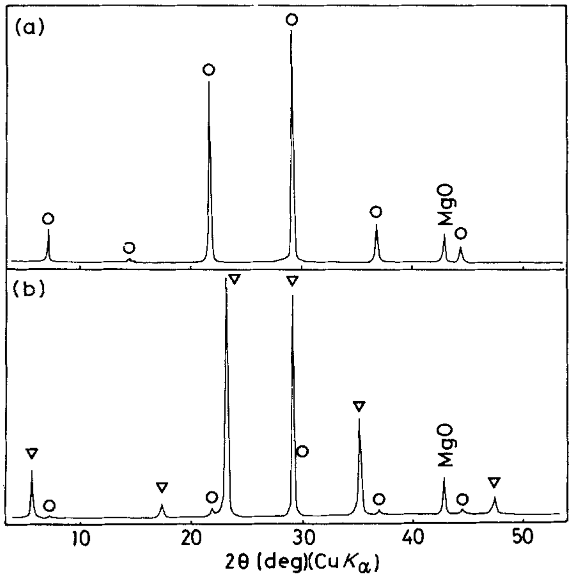

Figure 6 (a) XRD of as-deposited film formed at $x = 480$ mm; (b) XRD of heat-treated film. (○) 2.4 nm phase, (▽) 3.0 nm phase.

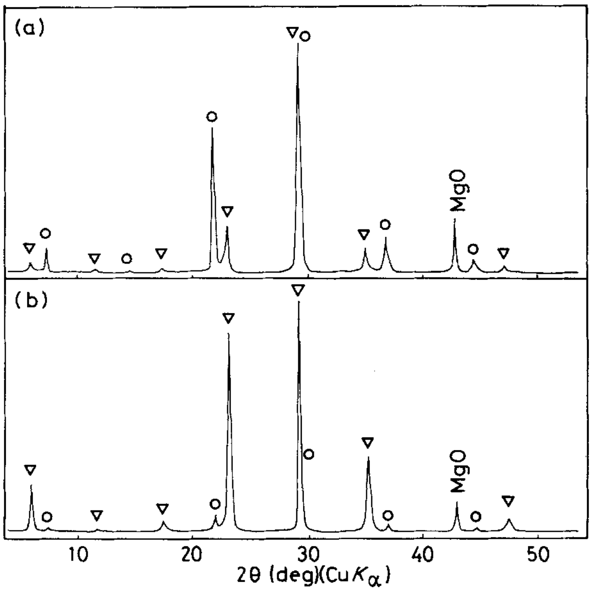

Figure 7 (a) XRD of as-deposited film formed at $x = 550$ mm; (b) XRD of heat-treated film. (○) 2.4 nm phase, (▽) 3.0 nm phase.

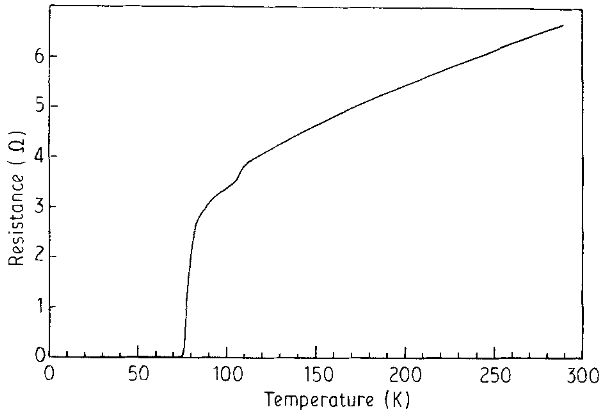

Figure 8 Resistance versus temperature curve of annealed film.

converted to 3.0 nm phase. Also, a mixed phase of 2.4 and 3.0 nm is changed to almost solely 3.0 nm phase. As a result, the annealing resulted in the conversion of 2.4 nm phase to 3.0 nm phase. In other words, the films were predominantly only 3.0 nm phase after annealing.

The best as-deposited film (2:0.3:2:2:3) showed T_c (resistance = 0) at 55 K. Annealing improved its T_c. As demonstrated in Fig. 8, the resistance versus temperature curve of the annealed film (2:0.3:2:2:3) has a small step around 110 K, and reaches zero at 75 K. The small step corresponds to the T_c of the 3.7 nm phase, although XRD could not detect its presence.

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