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PREPARATION OF $Y_1Ba_2Cu_3Oy$ SUPERCONDUCTING TAPE BY VAPOR DEPOSITION TECHNIQUES

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Abstract

The feasibility of preparing superconducting $Y_1Ba_2Cu_3Oy$ films on metallic substrate was exmined in an attempt to fabricate a tape conductor. Deposition methods employed were sputtering, laser ablation, and plasma flash evaporation. Although zero resistance temperature (Tc) is achieved above 90 K, critical current density values (Jc) obtained so far is still low as compared with those reported in the films grown on single crystal substrates. This may be caused by the misalignment of the crystal structure of the films on metal substrates. A further improvement in Jc for highly-oriented polycrystalling films is being investigated at the present time.

1. INTRODUCTION

With the announcement of superconductivity well tivityabove the boiling point of liquid nitrogen in the YBaCuO[1], BiSrCaCuO[2], TlBaCaCuO[3] systems, the application studies are actively being undertaken at the present time. There are two major applications considered in these high-Tc superconducting materials; applications in the field of electronics and applications to high-power electricity fields. In particular, thin film technologies aiming at the applications to electronic device have made a remarkable progress these days. In addition to device applications, thin film technologies of high-Tc superconductors have many other potential applications, e.g., fabrication technologies of conductors for high field suereconducting magnets. This is because thin film technologies have the following advantages for the fabrication of the tape conductors; an easy method to grow films with a preferred grain orientation and a suitable technique to make flexible tapes with dense films on them. So far, very high critical current densities have been reported in epitaxially grown superconducting thin films prepared on single crystal substrates.[4,5] We have, therefore, started investigating the applicability of thin film technologies to the fabriation of superconducting tape. An effort has been made to make clear whether or not a rather thick film also can exhibit high-Jc values.[6]

In the present study, we report the successful growth of superconducting $Y_1Ba_2Cu_3Oy$ (abbreviated as YBaCuO) films on metallic substrates as well as on (100) MgO single crystal by three different vapor deposition techniques; sputtering, laser

ablation, and high temperature plasma flash evaporation.

2. DEPOSITION OF YBaCuO THIN FILMS BY RF MAGNETRON SPUTTERING

2.1. Preparation of buffer layer

The eventual goal of the present study is to fabricate a high-Tc superconducting tape. For this purpose, it is necessary to deposit superconducting films onto flexible metal substrates. In our study, however, none of the YBaCuO films deposited directly onto the metal substrate exhibited good superconducting properties. Therefore, barious buffer layes have been investigated particularly in terms of the thermal expansion mismatch, the lattice match and the interfacial reactions. The buffer layers examined to date include $BaTiO_3$, MgO, $SrTiO_3$, YSZ, and double layers such as Pt (or Au)/YSZ.[6] Of these materials, Pt(or Au) /YSZ and MgO were proven to be the favorable choice, because these films have a tendency to grow with (100) preferred grain orientation. Preferential orientation of the buffer layer may be desirable for a subsequent growth of superconducting films with a preferred orientation, for this may result in an achievement of high critical current density.

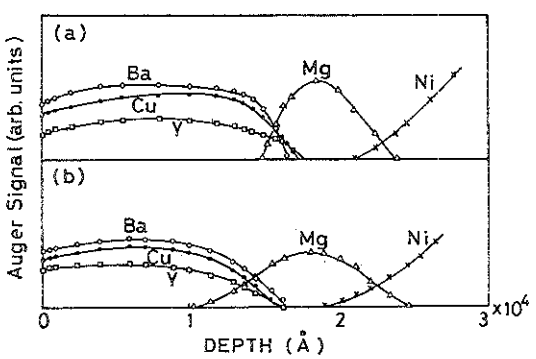

Fig. 1. Auger depth profiles for a 1.5μm superconducting YBaCuO film on Hastelloy-Z with a MgO buffer layer, (a) as grown (b) after annealing at 900℃ for 5 min

Figure 1 shows a sputtered Auger electron spectroscopy(AES) profile of as grown (a) and of films annealed at 900℃ for 5 min (b). As seen in the figure, the Y:Ba:Cu ratio in the film was almost constant. Buffer layers successfully restrained the diffusion of Ni, Fe, Cr into YBaCuO superconducting film (profiles of the elements other than Ni are omitted from this figure). AES, however, clearly revealed strong interdiffusion occurring near the interface of MgO/YBaCuO even though a short period of annealing was performed. It is vital to obtain good superconducting films in an as grown state when metallic substrates are used.

2.2. Changes in superconducting properties by the bombardment of high energetic particles on film surfaces

When high Tc superconducting films are prepared by sputtering, we often observe a marked loss of film or compositional change directly above the target. Resputtering due to oxygen anion bombardment of the substrate is thought to be responsible for these phenomena.[7] One of the effective approaches to circumventing this negative-ion problem is an rf magnetron sputtering in an off-axis geometry, in which the direct substrate bombardment by energetic particles is avoided.[8,9] We have reported a successful growth of YBaCuO thin films on Hastelloy X tape(11 cm in length) with a MgO buffer layer by placing the substrate in the region outside the negative ion impact area above the target.[10]

The target substrate arrangement is shown in Fig. 2. A Hastelloy tape substrate ($3\times280\times0.1mm^3$) with a (200) preferentially oriented MgO buffer layer was placed along the circumference of the target, approximately 3cm above the target. The substrate was resistively heated and its temperature was regulated using a

Chromel-Alumel thermocouple spotwelded onto the back side of the tape. Typical sputtering conditions were as follows: sputtering target used; $Y_1Ba_2Cu_3O_y$, sputtering pressure (Ar-50%O_2); 70 mTorr, substrate temperature; 600℃, film thickness; 1-2μm. After deposition, the system was back-filled with oxyen to an atmospheric pressure. The film temperature was decreased down to 500℃, held at that temperature for 1 h and finally slowly decreased to room temperature.

In the present study, film compositions were determined by energy dispersive X-ray microanalysis (EDAX) using $Y_1Ba_2Cu_3O_y$ single crystal as the standard. Measurement of the temperature dependence of the resistance and transport critical current for tape samples were performed using a standard four-probe method.

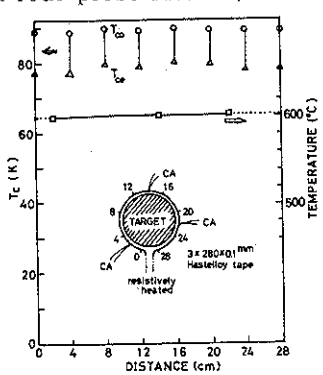

Fig. 2. Critical transition temperature and substrate temperature vs. substrate position. Arrangement of the target and tape substrate is also shown

Figure 2 shows the critical onset (Tco) and zero resistance (Tce) temperature of the film with regard to the specimen position measured. Uniformity of the specimen temperature (Ts) during the deposition was also shown. All the YBaCuO films cut out along the tape length have Tce higher than 77.4K. X-ray diffraction analyses revealed that YBaCuO films obtained are highly orinented with the c-axis perpendicular to the substrate. The highest critical current density, however, was only 200 A/cm² at zero films.

2.3. Film preparation by three-target co-sputtering [11,12]

A schematic view of the cathode and the substrate is shown in Fig. 3. The targets used were a sintered Y_2O_3, $BaCuO_2$, and CuO. Films were prepared by simultaneous co-sputtering and their composition was adjusted to achieve a correct stoichiometry by regulating the power supplied to each target. The substrates of both a Hastelloy-X tape precoated with a MgO buffer layer and a (100) MgO single crystal were mounted on a heated substrate holder. Typical sputtering conditions were as follows: sputtering pressure; (Ar-50%O_2) ; 2 mTorr, substrate holder temperature; 600-700℃, film thickness; 0.7-1.5μm. After deposition, the system was back-filled with oxygen to a nearly atmospheric pressure. The temperature was decreased down to 500 ℃, held at that temperature for 1 h and finally slowly cooled to room temperature.

The substrate was placed outside the region of head-on negative ion flux from each target; the region is indicated as a shaded area in Fig. 3. This geometrical arrangement prevented the detrimental negative oxygen ion bombardment of the growing films.

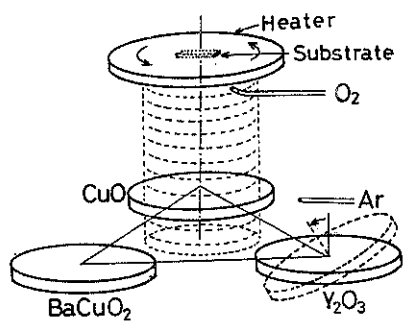

Fig. 3. Schematic view of three-target rf magnetron sputtering system

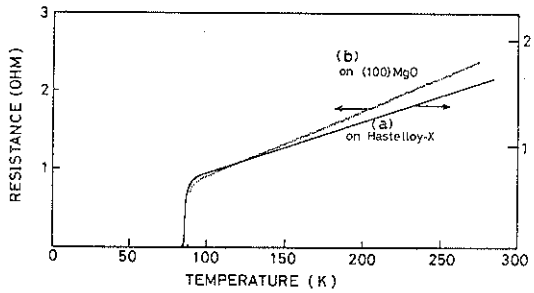

Fig. 4. Resistance vs. temperature curve of YBaCuO thin film on (a) Hastelloy-X with a MgO buffer and (b) on (100) MgO

Figure 4 shows the resistance as a function of temprature for the best films obtained so far on Hastelloy-X(a) and on (100) MgO(b). A complete zero resistance state was reached at 84 K and 88K in a film grown on Hastelloy-X and (100) MgO, respectively. In particular, the resistivity behavior of the film on (100)MgO is more metallic and an extraporated normal state resistance intercepts close to zero. We measured current density values, Jc, of the specimen at 77.4 K with the criterion of 1 μV/cm. No special patterning of the films was conducted for the Jc measurements. The magnetic field dependence of Jc is given in Fig. 5.[13]

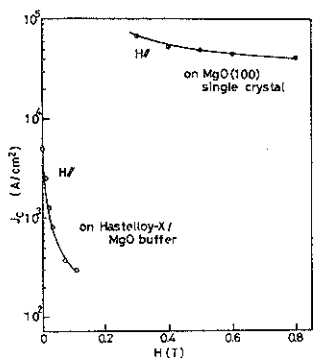

Fig. 5. Critical current density vs. mag-enetic field for a YlBaCuO film grown on a Hastelloy tape and on (100) MgO

The sample was mounted with the a-b plane parallel to the field direction. The Jc in the YBaCuO films on (100)MgO was as high as 7.0×10^4 A/cm^2 at 0.3 T and 77.4K (the specimen was deteriorated at 0.3T probably due to a sharp rise in temperature during the Jc measurement and no Jc data are given at magnetic fields lower than 0.3 T). On the other hand, the highest Jc obtained for the films on Hastelloy-X is 5.0×10^3 A/cm^2 at zero field and 77.4 K. It should be noted that Jc off drastically with increasing H. As compared with the films on (100)MgO, poorer Jc values in the films on Hastelloy-X may be due to the misalignment of the crystal structure of the films.

3. DEPOSITION OF YBaCuO THIN FILMS BY LASER ABLATION TECHNIQUE

The experimental apparatus is shown in Fig. 6. The laser used was a Q-switched YAG(wave length; 532 nm, pulse width; 6ns) and a KrF excimer laser (248nm, 30ns). In order to incorporate the necessary oxygen in the growing film, we attempted to activate the oxygen gas using rf (13.56MHz) or microwave (2.45 GHz) discharge. Typical deposition conditions in a YAG laser ablation were as follows: composition of the target used, $Y_1Ba_2Cu_3Oy$: substrate temperature, 600-750℃ : oxygen pressure, 1×10^{-2} -8×10^{-1} Torr : film thickness, 0.8-1.5μm. The deposition rate was in the range of 6 to 12 A/s in the present study. The post-deposition annealing was the same as in the sputtering already described.

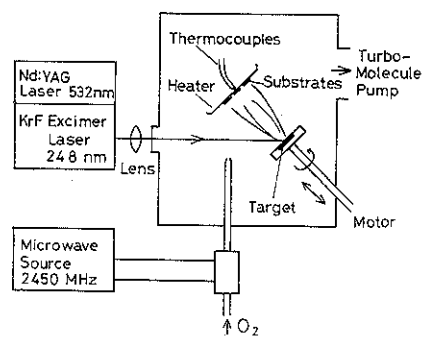

Fig. 6. Laser ablation apparatus

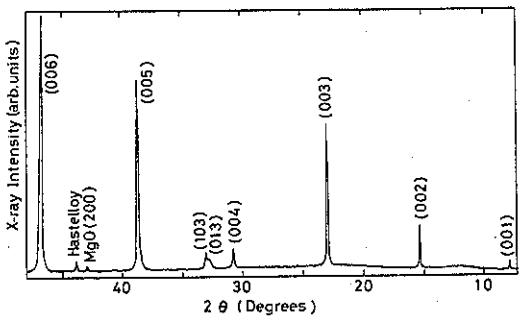

Fig. 7. Typical X-ray diffraction pattern for superconducting YBaCuO films prepared on Hastelloy-X with a MgO buffer

Figure 7 [14] shows a typical X-ray diffraction pattern of YBaCuO thin films deposited on Hastelloy-X with an amorphous MgO buffer layer. The film is highly oriented with the c-axis perpendicular to the substrate. It should be noted, however, that a week peak from the (103) plane consistently appears. The highest zero resistance temperature obtained so far is 86.0 K in its as grown state, and the critical current density is 8.6 $\times 10^3$ A/cm^2 at zero field and 77.4 K. We have started deposition experiments using a KrF excimer laser. So far a successful growth of YBaCuO films with a Tc above 90 K and Uc of above 4.0 $\times 10^4$ A/cm^2 at 77.4 K was achieved on a Hastelloy tape. Details are to be reported soon.

4. PREPARATION OF YBaCuO FILMS BY A THERMAL PLASMA FLASH EVAPORATION

The rf plasma deposition technigue offers distinct advantages over many of the deposition techniques; high deposition rate, relatively easy way to control the film stoichiometry, etc. These characteristics make this deposition method very attractive particularly for the fabrication of the superconducting tapes. This method has been previously used to grow YBaCuO films by Terashima et al. [15] We have modified their plasma technique, and obtained superconductive films under the deposition pressure of as low as 20 Torr.

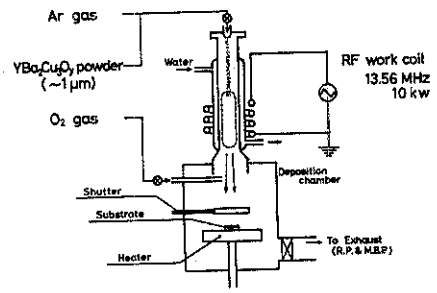

Fig. 8. Schematic of the plasma flash evaporation apparatus

Figure 8 shows a schematic of the experimental setup. A fine power (~1μm in dia.) of YBaCuO is fed into the Ar or Ar/O^2 plasma using argon as the carrier gas. The plasma is sustained at 20 to 30 Torr by the 13.56 MHz rf generator operated at 10 KW. Single crystalline MgO(100) substrates were mounted on a heated substrate holder located at a distance of about 20 cm from the torch exit nozzle. Oxygen is supplied through gas inlets incorporated near the torch exit. Additional oxygen can be introduced close to the substrate holder. Emission spectroscopy measurements during deposition revealed that rf plasmas generate high concentrations of atomic oxygen. After traveling through the plasma region, the starting powders are evaporated and the ionized vapor is deposited onto the substrate. Typical deposition conditions are summarized in Table 1.

Table 1. Typical deposition conditions

Rf Power	10KW, 13.56MHz
Gas Flow Ar/O2	~11.0/4.01/min
Pressure	20~30 Torr
Substrate	MgO(100)S.C.
Temperature	700~800℃
Deposition Time	20~30 min

The "as-deposited" films were shiny black and highly c axis oriented normal to the substrate. The highest zero resistance temperature was 91.0 K and a critical current density was 1.2×10^4A/cm^2 at 77.4 K and zero field.[16]

5. SUMMARY

$Y_1Ba_2Cu_3O_y$ superconducting films were successfully grown on a flexible metallic substrate with various buffer layers as well as on (100) MgO single crystal substrates by vapor deposition techniques. Although the zero resistance temperature obtained was above 90K, the critical current density was still insufficient particularly for the film grown on metallic substrates. The possibility of further improvements in Jc by optimizing the deposition conditions and improving the crystallinity is being investigated at the present time.

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