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GRANULAR YBaCuO FILMS PREPARED BY METALORGANIC CHEMICAL AEROSOL DEPOSITION TECHNOLOGY

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ABSTRACT

Fine-grain thin superconducting films can be prepared by metalorganic Chemical Aerosol Deposition Technology (CADT). In this paper, we present the preparation and properties of $YBa_2Cu_3O_{7-x}$ films on the different substrates, Si and $SrTiO_3$ (100). It is shown that the zero-resistance temperature ($T_{c,0}$) of the films on $SrTiO_3$ substrates is about 90 K, and the critical current density (J_c) at 77 K is above 10^4 A/cm^2. In addition, these films exhibit significant grain-boundary weak link behaviour, which is very promising for applications in electronic devices.

KEYWORDS

Aerosol depostion; metalorganic; ceramic superconducting thin film; weak link; annealing.

INTRODUCTION

Chemical Aerosol Deposition Technology (CADT) (Lambeck et al., 1986) has some advantages for preparing high T_c ceramic films. It is a simple non-vacuum method and can be used to produce large-area homogeneous (in composition and thickness) films having a high quality. During the last twenty years CADT was developed to produce thin films of metals, metal oxides and sulphides (Popma and Kamminga, 1977, Blandenet et al., 1981). After the discovery of a new class of high T_c superconductors it has been successfully used to prepare high T_c superconducting films using nitrate (Gupta et al., 1988, Golden et al., 1990) or metalorganic (Tang et al., 1990) precursors. In contrast to the vacuum-deposition techniques, the CADT is able to obtain a finely granular morphology with stoichiometric grains. In fact, aerosol process (spray pyrolysis) has aroused great interest in the fabrication of fine single-crystal powders, because by this way the size of the powders is uniform and can be controlled in the range from submicron to a few micron order (Kodas et al., 1989, Tohge et al., 1988, Setaka et al., 1988). With respect to the film studies, our interest lies in some unusual properties which are due to the weakly coupled fine grains. Recently, based on the results of our investigation, a network of grain-boundary weak links has been reported (Driessen et al., 1990). This property is very promising for applications in electronic devices, such as SQUIDs and ultra-fast light detectors (Tang et al., 1990), etc.

In previous studies, we reported that the $YBa_2Cu_3O_{7-x}$ films were prepared by metalorganic precursors $Y(TMHD)_3$, $Ba(TMHD)_2$ and $Cu(TMHD)_2$, where TMHD was the chelating ligand 2,2,6,6-tetramethyl-3,5-heptanedione. The results showed that a single phase of YBaCuO orthorhombic structure could be obtained. We chose these metalorganic salts because they were highly volatile and could be dissolved in several organic solvents (Driessen et al., 1989). In this paper, we report on the deposition characteristics of CADT with the same precursors. The superconducting properties of $YBa_2Cu_3O_{7-x}$ films on $SrTiO_3$ substrates are described and emphasis is laid on the formation of fine grains during the annealing process.

EXPERIMENTAL PROCEDURE

Fig.1 shows the schematic diagram of a non-vacuum CADT apparatus which is placed in a dust-free cabinet. A solution of a mixture of β-diketonates of Y, Ba and Cu in the organic solvent n-butylacetate ($C_6H_{12}O_5$) was nebulized by an ultrasonic nebulizer (3 MHz). The aerosol droplets in the range of 1-3 μm were formed. A carrier gas, consisting of 20% O_2 in N_2 at a flow rate of 3 l/min, was used to spray the aerosol onto a heated substrate at 450°C. The concentrations of the Y-, Ba- and Cu-compounds in the solution were 3.1, 32 and

7.0 mM, respectively. This ratio differed from the stoichiometric ratio because of different volatility of the compounds. It turned out that the metalorganics and the solvent had to be free of water, even of crystalwater. Incorporation of water or OH-groups in the solution drastically changed the solubility and volatility. The concentration of aerosol droplets in the carrier gas was about 0.4 ml/l. The deposition rate was 7 nm/min. Two kinds of substrates, 2" Si wafer and $SrTiO_3$ (100) single crystal, were used in this work. No specific pre-treatment was done on the $SrTiO_3$ substrates, but a 250 nm ZrO_2 buffer layer was evaporated on the Si substrates in order to avoid Si diffusion into the films during annealing. Although the quality of the film on both substrates was quite different with respect to T_c and J_c, the film morphology and grain size were similar. Therefore, in the present work we restrict ourselves to the studies of the grain formation on Si substrates.

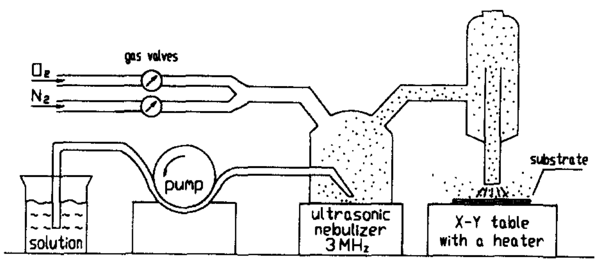

Fig. 1. Schematic diagram of the CADT apparatus.

The preparation of superconducting layers by this way was a two-step process. After deposition, an annealing treatment in oxygen was required to form the superconducting phase. In our case the following heat treatments were used: (1) Warming up from 250°C to the maximum annealing temperature at a rate of 20°C/min under a flow of N_2 gas. With this relatively slow rate, cracks in the film could be avoided. (2) Retaining the annealing temperature for 20 minutes, still under the flow of N_2 gas. (3) Finally cooling down to 300°C slowly at a rate of 0.5°C/min under a flow of O_2 gas.

A continuous-flow cryostat with a temperature controller was used to measure the electrical properties. Resistivity versus temperature (R-T) curves were measured by the conventional four-probe technique. The critical current densities (J_c) and current-voltage (I-V) characteristics were obtained with a microbridge, of typical dimensions 10 × 10 μm^2, which was made by ion-beam milling. The film morphology and the grain size were observed by a dual-stage scanning electron microscope (SEM).

RESULTS AND DISCUSSION

Film morphology.

As-sprayed films are dense and show small surface roughness. The Y, Ba and Cu elements in the film are present partially as carbonates which are partly in amorphous state. The

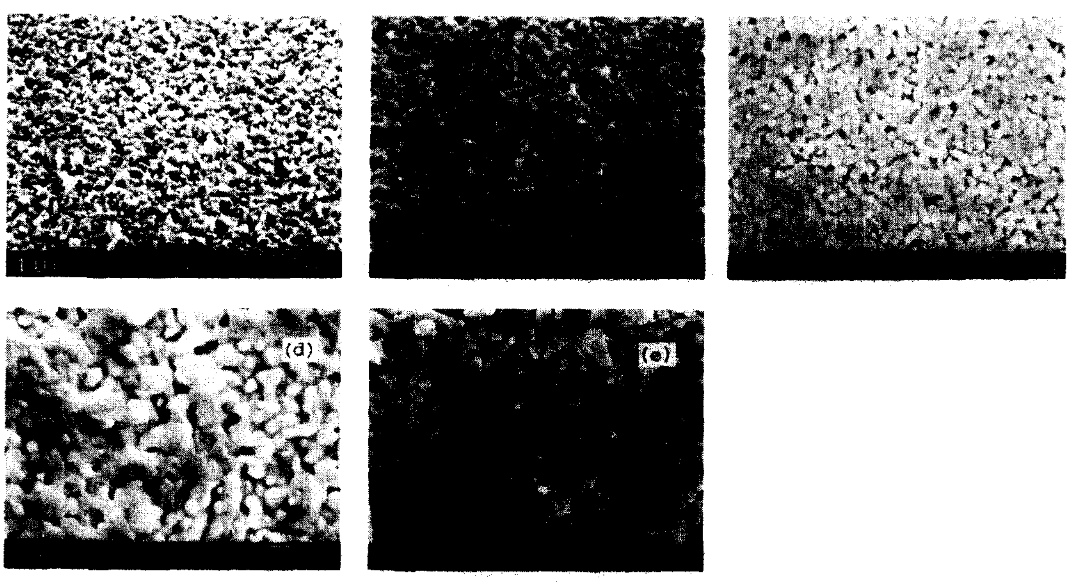

Fig. 2. SEM photographs of the film surface for different annealing temperatures on Si substrates, (a) 650°C, (b) 700°C, (c) 750°C, (d) 800°C and (e) 900°C.

formation of the fine superconducting grains due to annealing are shown in the SEM photographs in Figs.2(a)-(e). The R-T curves as a function of annealing temperature for the same samples are given in Fig.3. Up to 650°C annealing no obvious changes of film morphology are observed; the corresponding R-T curve presents strongly semiconducting behaviour. Above 700°C annealing the layer starts to recrystalize and the compounds convert to the superconducting phase. The average grain size increases singificantly with the increase of annealing temperature. The dimensions of grain size after annealing at 700, 750 and 800°C are 50-100, 100-200 and 250-300 nm, respectively. By annealing at 750°C the resistance does not show obvious increase as the temperature decreases during measurement. And above this annealing temperature the R-T curve exhibits metallic behaviour. In our case the optimal annealing temperature is about 800°C on both Si and $SrTiO_3$ substrates. The R-T curve after annealing at 800°C is also shown in Fig.3. When a further higher annealing temperature is applied, for example 900°C, the crystalline phase after annealing is a nonsuperconducting phase. The resistance of the film then is higher than 20 MΩ at room temperature. Comparing the morphology in Figs.2(d) and (e), some differences can be seen. In Fig.2(e), (1) a lot of large grains with clear boundaries are formed; (2) some small spherical grains are present on the top of the film surface; (3) the film looks more porous. X-ray diffraction patterns show that no diffraction peaks of the superconducting phase can be found. A reason for our optimal annealing temperature is that probably this temperature is just high enough to allow the formation of the orthorhombic structure with stoichiometric oxygen concentration, and low enough to avoid other phase transitions or excessive diffusion from the substrate to the films. Because of the large variety of processing parameters contributing to the formation of these fine grains, the exact control of supercon ducting grain size has not been realized yet.

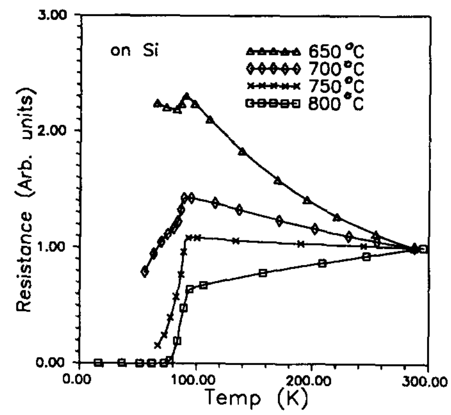

Fig. 3. R-T curves for different annealing temperatures on Si substrates.

Superconductivity.

In Fig.4 we display the R-T curve of a high quality film with thickness 250 nm on a $SrTiO_3$ substrate. As can be seen, the $T_{c,0}$ is 90 K and the transition width is about 3 K. The

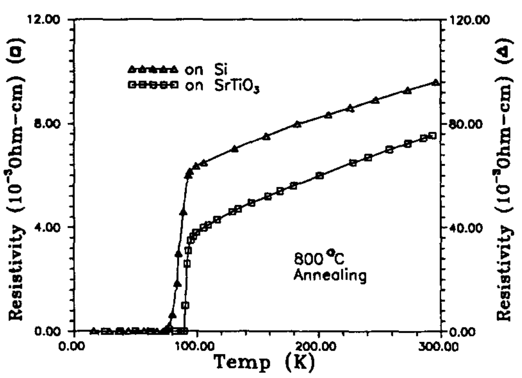

Fig. 4. R-T curves on different substrates. 10 μA currents are used for the measurements.

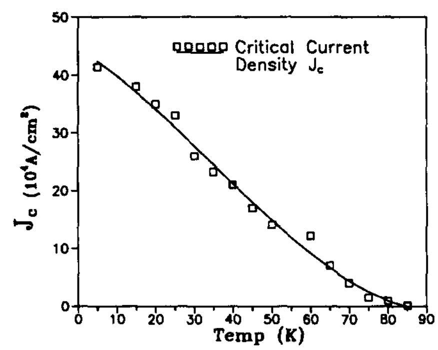

Fig. 5. Critical current density J_c as a function of temperature on a $SrTiO_3$ substrate.

film with thickness 700 nm on a Si substrate however exhibits a low T_c and a broad transition. X-ray diffraction analysis indicates that the best films on both substrates possess an orthorhombic structure with a perpendicular c-axis orientation and only 00*l* diffraction peaks (*l*=2,3,4,5,6 and 7) can be observed. When the composition deviates from the stoichiometric 1:2:3 (Y:Ba:Cu) compound, a second phase is also present in our films and a lower T_c (less than 50 K) can be found (Tang et al., 1990). The temperature dependence of the critical current density J_c on a $SrTiO_3$ substrate is shown in Fig.5. The curve measured on a 10 x 10 μm^2 microbridge indicates that the J_c at 77 K is above 10^4 A/cm^2 and approximate 4×10^5 A/cm^2 at 4 K.

There are two points to be noted. First, the films prepared by CADT have relatively high resistivity at the temperature just above the onset transition. The values of resistivity are about 4×10^{-3} Ω·cm on $SrTiO_3$ substrates and are about 6×10^{-2} Ω·cm on Si substrates. The maximum values of ratio R_{300}/R_{100} on $SrTiO_3$ and Si substrates are about 1.98 and 1.52, respectively, where R_{300} and R_{100} are resistances of the film at temperatures of 300 and 100 K. Second, with respect to the extrapolation of the R-T curves to the zero temperature, the resistivity does not go to zero. These two points can be explained by assuming that the total resistance is caused by the contribution of the superconducting grains and also of the grain boundaries. The boundaries act as barriers of normal metal separating the superconducting grains. Therefore intrinsic weak links are present in these fine grain films. Weak link behaviour in an I-V curve has been observed on a $SrTiO_3$ substrate at 79 K. An oscilloscope photograph is shown in Fig.6. The vertical scale is 0.5 V/div and the horizontal one is 3.5 mA/div. This abrupt voltage jump in the I-V curve provides strong evidence of nonequilibrium superconductivity.

Fig. 6. Weak link behaviour in an I-V curve at 79K. Bias current is supplied by a triangle wave of 20 Hz frequency.

In conclusion, fine-grain $YBa_2Cu_3O_{7-x}$ superconducting films with a perpendicular c-axis orientation have been obtained by CADT. The film quality is strongly dependent on the different substrates and annealing processes. In our case the optimal annealing temperature on both Si and $SrTiO_3$ substrates is about 800°C. These films exhibit significant weak link behaviour. Based on that the films can be applied to electronic devices.

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