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Thin-film-formation study of high-T_c superconductors by resistive evaporation

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Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O thin films were prepared with use of a conventional vacuum system for the evaporation of the constituents. This method produces stoichiometric films upon complete evaporation of the constituents. No thickness monitor or any other control system is required. In this study, substrates were kept at room temperature during the evaporation process. The bismuth-based thin films are shown to lose bismuth during heat treatment unless the Cu constituent is evaporated last and fully oxidized at 400 °C subsequently. Y-Ba-Cu-O films prepared by using a pulverized mixture of Y, BaF_2, and Cu constituents show an improved quality over films obtained from YF_3, BaF_2, and Cu starting materials. This improvement is attributed to fluorine reduction in the starting-material mixture.

INTRODUCTION

Since most microelectronic applications utilize thin films in many electronic devices, much scientific effort and technological interest have been invested in high-T_c thin-film superconductors. These materials have electrical and optical properties which span the range from an insulating dielectric to a superconductor and can be epitaxially grown as thin films on different substrates. The physical transport properties of these ceramics are dominated by weak links at the grain boundaries due to their short coherence lengths. However, because of their brittleness, it is very difficult to fabricate wires, tapes, etc., having the required ductility. It therefore appears that mechanical-integrity problems associated with bulk forms of this kind of superconductor must be resolved before they can be used in commercial applications.

Thin-film forms have near-term potential for applications in many electronic devices such as SQUID (superconducting quantum interference devices) optoelectronic and infrared detectors. Furthermore, being tetragonal or orthorhombic layer compounds, they are extremely anisotropic so that for exhibiting basic physical properties well-oriented thin films are desired.[1] By now it is well recognized that the quality of a film on a given substrate depends not only on the heat-treatment schedule but also very much on the method of preparation. Different methods yield different qualities: For instance, sputtering technique[2] may yield films having microwave-quality surface for applications in microwave devices while films obtained by deposition methods[3] are typically of granular structure after heat treatment, and thus are used in light-detector devices, etc. Accordingly, different applications require different preparation methods. However, when a number of different techniques such as laser ablation, ion beam depositon, coevaporation, etc., yield films of about the same quality suitable for a certain need, then setup cost and system simplicity must be considered as major factors in the entire production process.

In this work a detailed study of preparation techniques utilizing a simple and inexpensive evaporation setup for the fabrication of Bi-based and Y-based cuprate high-T_c superconducting thin films is presented.

EXPERIMENTAL

Y-Ba-Cu-O and Bi-Sr-Ca-Cu-O thin-film superconductors have been fabricated in a simple conventional oil pumped vacuum system[4] with base pressure better than 10^{-5} Torr. The setup was equipped with resistively heated tungsten boat sources mounted on electrical high-power feedthroughs. No control of any kind has been applied to measure thickness or stoichiometry of the films during the evaporation process. The distance between the substrate and the evaporation sources, after a few calibration attempts, was selected to be 6 cm, for which the starting materials were weighed to yield films of desired thickness and stoichiometry upon complete evaporation of the materials in the boats.

A methanol ultrasonic cleaner bath has been used for final substrate cleaning and dry N_2 was used to remove any residual particles before mounting the substrate into the vacuum system. The system was then pumped out and the substrates were baked out to 400 °C for a few minutes to outgas the surface. During the evaporation the substrates were kept at room temperature, which was monitored by an iron-constantan thermocouple attached to the substrate surface. However in some experiments radiation heat from evaporation sources raised the substrate temperature, which in all cases did not exceed 170 °C. After initially trying a variety of starting materials such as pulverized grounded grains of superconducting $YBa_2Cu_3O_x$ or $Bi_2Sr_2Ca_2Cu_3O_x$ in preliminary experiments, and powdered oxides or carbonates later on, it was soon realized that only compositions of the metal elements such as fluorides can be used for evaporation; these compounds do not interact with the boats. Thus the starting compositions BaF_2, SrF_2, YF_3, and CaF_2 are currently used in the evaporation process as source materials for Ba, Sr, Y, and Ca, respectively.

Different techniques, such as scanning electron microscopy (SEM) in the secondary electron (SE) mode, SEM in the CL (cathodoluminescence) mode, energy dispersive x-ray Analysis (EDAX), auger electron spectroscopy (AES), x-ray Diffraction (XRD), and resistivity versus temperature measurements, have been used for samples analysis and characterization. The film surface microstructure and morphology has been characterized by SEM, cathodoluminescence, and EDAX inspections. The chemical composition of the film depth cross section has been investigated by an Auger depth profile method. Electrical properties have been determined using a standard dc four-probe electrical measurement, in which pressing indium and silver paint were used for contacts. Voltage values were averaged for both direct and reverse current direction to eliminate any possible thermal emf effects. We will review the preparation of Bi-Sr-Ca-Cu first and then the Y-Ba-Cu.

RESULTS AND DISCUSSION

A. Bi-Sr-Ca-Cu

At least three different systems have been identified by now in the Bi-based superconducting family with the "structural formulas" $Bi_2Sr_2Ca_{n-1}Cu_nO_x$, where $n=1$, 2, or 3, featuring three different phase transition temperatures: $T_c=20$ K for $n=1$, abbreviated 2:2:0:1; $T_c=85$ K for $n=2$, abbreviated 2:2:1:2; and $T_c=110$ K for $n=3$, abbreviated 2:2:2:3. The 2:2:2:3 phase tends to precipitate in the 2:2:1:2 phase in the form of small unconnected grains[5] and is difficult to isolate, whereas the 2:2:1:2 system can grow a large single phase with a well established crystal structure. Many reports on the bismuthate preparation,[6,7] indicate that excess of Ca and Cu is needed for 2:2:2:3 phase formation from a solid reaction of the 2:2:1:2 oxides constituents. For this reason we decided to first study the preparation of the 110-K phase by using one single boat for evaporation of a well-grounded mixture of Bi, SrF_2, CaF_2, and Cu weighed in the atomic proportion to yield 0.5 μm stoichiometric $Bi_2Sr_2Ca_4Cu_5$ film with the hope of obtaining the right 110-K phase after the postannealing process. It is important to heat the evaporation source very slowly in order to avoid the sudden explosion of the powdered mixture from the boat; a typical heating rate in the vicinity of the melting temperature is about 10°C/min. Excess heating must also be avoided to prevent boiling of the liquid mixture.

The result of this attempt without the postannealing stage is presented in Fig. 1, which shows the AES depth profile of as-deposited film on a $LaGaO_3$ substrate. The film thickness is deduced to be about 3800 Å where the La, which is one of the substrates element, starts to build up in the spectrum. All the elements besides bismuth show a constant level throughout the film thickness indicating a simultaneous and homogeneous evaporation of all the mixture constituents. However, the bismuth element distribution peaks up only in the first few hundred Å, it decays rapidly, and is hardly detected inside the film, indicating that the bismuth evaporates first, which is quite expected in view of its known high vapor pressure (its vapor pressure at 520 °C is 10^{-4} Torr). Since the AES depth profile was obtained using a rastered beam with a 0.1-mm^2 cross section,[8] we always sampled the profile at a few points of the specimen. Note that a tungsten line is built up in the last few layers of the film (Fig. 1). In this case the boat was intentionally heated as high as 3000 °C to check possible maximum source-material contamination due to overheating. In all other cases where the source temperature was kept well below 3000 °C, no tungsten contamination could be detected.

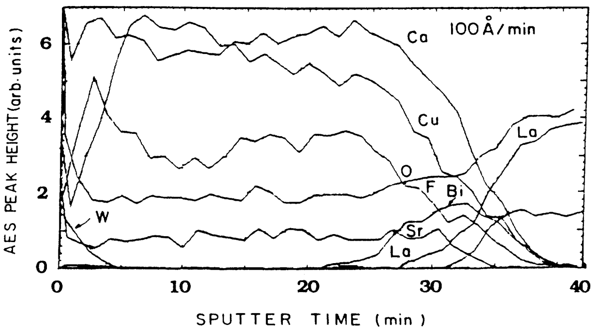

FIG. 1. AES depth profile of as-deposited film aimed to $Bi_2Sr_2Ca_4Cu_5$ on a $LaGaO_3$ substrate, showing a strong inhomogeneity in bismuth distribution. The sputtering rate is 100 Å/min.

The annealing process greatly affects the bismuth distribution along the cross section of the film. For this study, another film on MgO substrate was prepared in the same way and then annealed as follows: It was inserted into a preheated quartz tube with flowing oxygen bubbled through hot water, where its vapor temperature kept at ~75 °C (so-called wet O_2). The temperature inside the tube was kept at 725 °C for 15 min to allow for defluorination. This stage was followed by 35 min at approximately 840 °C in dry O_2 atmosphere for crystallization, after which the sample was removed from the furnace.

The typical AES depth profile of this annealed sample is given in Fig. 2 showing the striking result that the bismuth concentration is below background throughout

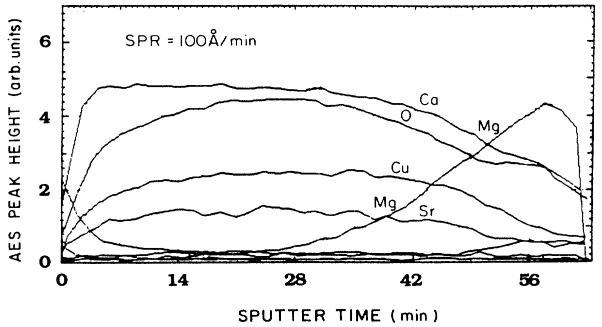

FIG. 2. AES depth profile of an annealed film obtained by deposition of a starting material mixture aimed to $Bi_2Sr_2Ca_4Cu_5$ on a MgO substrate. Note the observed absence of bismuth throughout the film thickness. The sputtering rate is 100 Å/min.

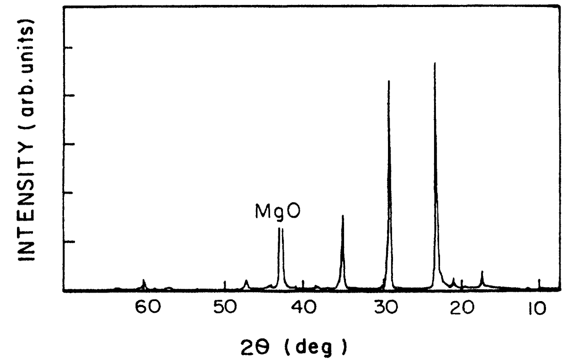

FIG. 3. X-ray diffraction spectra of Cu/(BaF_2,SrF_2, Bi) mixture/MgO aimed to the $Bi_2Sr_2Ca_1C_2O_x$ sample after heat treatment.

all the 4000-Å film thickness. This has been confirmed by XRD analysis carried out on the same specimen, in which the strongest solid bismuth lines (102) and (014) appear below the minimum peak significance. Thus there is no evidence of any possible aggregation of solid bismuth inside the film. By now it is well established that the 2:2:1:2 phase has an ideal composition of 4:4:2:4 which can be described as a packing of 2:2:1:2 layers along the *c* axis shifted with respect to each other,[9] giving rise to stacking faults along with many other disorders and imperfections. This suggests that due to its high vapor pressure, the bismuth can diffuse and evaporate out of the film surface during the heat treatment even after the 2:2:1:2 phase has been partially formed.

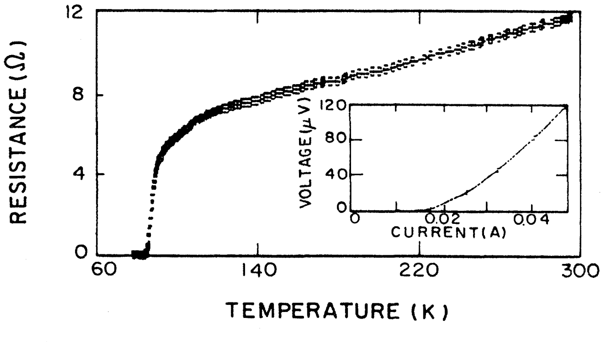

FIG. 4. Resistance-vs-temperature characteristic of $Bi_2Sr_2Ca_1Cu_2O_x$ using a supercurrent density of 0.1 mA/cm^2. Zero resistance was detected at 84 K. Inset: Current-voltage characteristic at 66 K from which the critical current of 1500 Å/cm^2 was calculated.

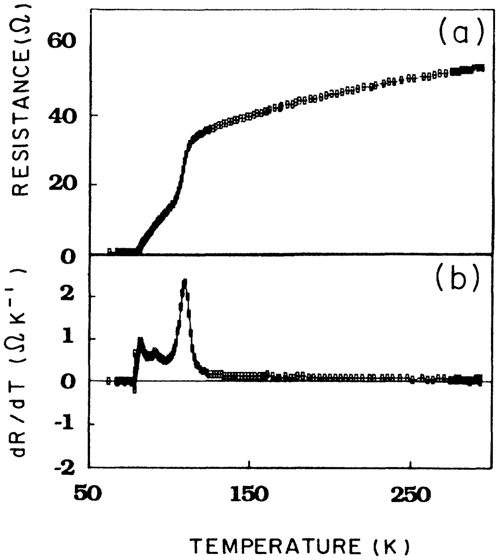

FIG. 5. (a) Resistance-vs-temperature characteristic of a sample prepared from a starting-material mixture aimed to (2:2:4:5) composition. (b) Its derivative plotted on the same temperature scale indicating the different high-T_c phases portions.

In light of this observation and on the basis of previous experience,[10] a technique has been developed, in which films were prepared by sequential evaporation of a BaF_2, SrF_2, and Bi pulverized mixture and Cu in that order from two separate evaporation sources. Samples thus obtained, having copper layers as the top layers, were oxidized first at about 400 °C in air for about 1 h and then defluorinized using "wet O_2" at 725 °C and annealed at 870 °C for about 16 h as described above. The x-ray diffraction plot carried out on this sample is demonstrated in Fig. 3 featuring the well documented lines[6,9] of the 2:2:1:2 phase. *R*-vs-*T* results of a film prepared on a MgO substrate by this method and aimed to the $Bi_2Sr_2Ca_1Ca_2O_x$ phase are shown in Fig. 4. Zero resistance was detected at 84 K, clearly indicating the presence of the 2:2:1:2 phase. The inset shows the *I-V* curve at 66 K from which a critical current of about 1500 A/cm^2 was deduced. It is believed that oxidation of the copper layers on the film surface prior to the annealing process serve to keep the bismuth inside the film and helps in absorbing oxygen into the system for the next heating steps.

An attempt to grow the 2:2:2:3 phase has been carried out using the same method to evaporate nominal 2:2:2:4.5 composition on a MgO substrate and using the same heat treatment. *R* vs *T* results shown in Fig. 5(a) clearly indicate that some portion of the higher-T_c phase is already developed, as can be deduced from the 20% resistance step near 115 K, and as suggested in the derivative curve plotted on the same temperature scale in Fig. 5(b). By recent development of CL measurements along with EDAX technique, we were able to use this method for identifying the various phases in this sample,[11] which clearly confirms this observation.

B. Y-Ba-Cu

Initially, sequential evaporation of the appropriate amounts of YF_3, Cu, and BaF_2 from three different evaporation sources were used for $YBa_2Cu_3O_x$ thin-film preparation; the details have been published elsewhere.[8] In subsequent experiments we have evaporated a well-grounded pulverized mixture of the same starting materials from one single source.[4] Evaporation by this method, followed by the same heat treatments, typically yields films of similar microstructure and morphology, although this method yields somewhat larger grains, yet zero resistance is reached below 50 K.

The use of fluorides in the starting compositions gives rise to possible fluorine complexes. As yet its effect on the superconducting properties is a subject of much controversy. Some groups report on T_c enhancement due to fluorine doping in $YBa_2Cu_3O_{7-x}$ (e.g., Ref. 12), while others notice no affect on the transport properties (e.g., Ref. 13). The same situation holds for the magnetic properties. Recently, LaGraff *et al.*[14] have shown that fluorine ions preferentially occupy the normally vacant O(5) sites along the *a* direction in $YBa_2Cu_3O_{7-x}$ when properly annealed in NF_3 gas atmosphere. They have observed enhancement in the diamagnetism and critical current density in the fluorinated material, while no effect has been detected on T_c. Yet clarification is needed as to the role of the fluorine, since it may also be ascribed to possible fluorine accumulation in the grain boundaries.

In this study the starting materials include solid fluorides which are hard to decompose—hence any residual fluoride left after the heat treatment would presumably accumulate as a halide-stabilized perovskite phase[15] in the grain boundaries of the granular films. This may explain the transition broadening and the chronic tailing observed in our *R*-vs-*T* measurements as shown in Fig. 6, sample A. Therefore further experiments were initiated in which pure yttrium metal replaced YF_3 to reduce the fluorine content in the constituents. A powdered mixture of the appropriate amounts of Y, BaF_2, and Cu was evaporated onto $SrTiO_3$ substrate using a single resistively heated source. Samples thus obtained were heated to 725 °C in wet O_2 atmosphere for 15 min and then annealed at about 860 °C in flowing dry O_2 for 1 h followed by furnace cooling to room temperature. Typical results of resistance as a function of temperature are plotted in Fig. 6 for two different methods of evaporation on $SrTiO_3$ substrates samples: A, prepared by sequential evaporation of YF_3, Cu, and BaF_2[8] and B, prepared by evaporation of a Y, BaF_2, and Cu mixture from one single evaporation source, using the same supercurrent density for both. The thickness of sample A was 2500 Å, yielding an approximate value of 1 mΩ cm for its resistivity at room temperature,[8] whereas the thickness of sample B was deduced to be about 3000 Å from calibration conditions of the distance between the substrate and the evaporation source, thus giving a similar resistivity value at room temperature. However the resistance-versus-temperature behavior of sample B in the normal state is more metalliclike with a sharper transition as compared to that of sample A. Note that its zero resistance value is 20 degrees higher than that of sample A.

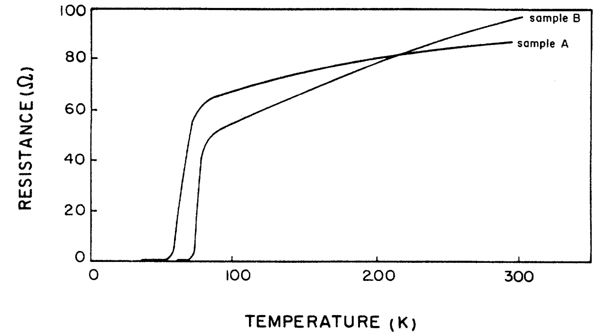

FIG. 6. Resistance-vs-temperature characteristic using a supercurrent density of approximately 2 A/cm^2. Sample A: Film prepared from YF_3, Cu, and BaF_2 utilizing the layer-by-layer method. Sample B: Film obtained by evaporation of a Y, BaF_2, and Cu mixture from a single source. Zero resistance was observed at 50 K and 67 K for A and B films, respectively.

Transport measurements done by Tozer *et al.*[16] show clear evidence for conductivity anisotropy in single-crystal $YBa_2Cu_3O_{7-x}$. They report on semiconducting-like behavior in the *c* direction above T_c having a 14-mΩ cm room-temperature resistivity and a strong metalliclike behavior in the (*a*,*b*) plane having a 0.5-mΩ cm room-temperature resistivity value. The four-point measurement technique probes the conductivity in a plane parallel to the substrate surface. Thus it is inferred that the grains in sample B are more oriented with the *c* axis perpendicular to the film surface than the ones in sample A, and that substantial fractions of film B have the correct $YBa_2Cu_3O_{7-x}$ composition and crystal structure. Relating this to the replacement of YF_3 by Y in the starting constituents, it is believed that the improved quality of this sample is due to fluorine reduction.

SUMMARY

A simple inexpensive conventional vacuum system was shown to be very efficient in superconductor film preparation using a resistively heated evaporation source only. This method produces stoichiometric films, provided that no remanents are left in the sources after evaporation is completed.

Evaporation of the Cu constituent in the last place, in bismuth-based superconductors, followed by its oxidation at 400 °C was found to be very effective in precluding the bismuth constituent escape. Improved quality of $YBa_2Cu_3O_{7-x}$ films was achieved by reducing the fluorine content when Y replaced YF_3 in the constituents.

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