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Formation and properties of copper film on Tl–(Pb, Bi)–Sr–Ca–Cu–O superconductor by electrodeposition from aqueous solution

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A new process of electrodeposition in saturated cupric sulphate aqueous solution was successfully developed for the formation of copper film on a high-T_c, three Cu–O layered Tl–(Bi, Pb)–Sr–Ca–Cu–O superconductor substrate surface for the first time. Scanning electron microscopy and electron micro-probe analysis were used to investigate the morphology of the substrate surface and the composition of the copper–superconductor interface. After the electrodeposition process, no evident changes in the temperature dependence of electrical resistivity were found by four-point probe measurement. The difference of magnetic properties before and after electrodeposition was investigated from magnetization measurements. Almost no degradation of the bulk properties was observed from the susceptibility data. The copper–superconductor contact was confirmed to show Ohmic behaviour by two-point *I–V* characterization at liquid nitrogen boiling temperature.

1. Introduction

The discovery of high-T_c superconductors has given rise to a widespread range of fields for studying copper-based ceramic materials since 1987. After research focusing on $YBa_2Cu_3O_{7-x}$ (T_c at about 92 K) and the rare-earth-free Bi-containing system (with a $T_c = 110$ K phase) [1], lately the higher-T_c (> 120 K) Tl-containing superconductor system was also studied widely. Both the formerly developed high-T_c Y–Ba–Cu–O superconductors and the latterly developed Bi–Sr–Ca–Cu–O superconductors were found to react with water and moisture [2–5]. In addition, degradation and ageing phenomena were also found in the much-higher T_c Tl-Sr–Ca–Cu–O superconductor [6]. A decrease of magnetic susceptibility, zero-transition temperature, resistivity and current density were observed after the degradation reaction with water [2–6].

Obviously, a protective layer on the surface of a ceramic superconductor is needed to prevent the degradation reaction with environmental moisture. Moreover, for the future application of high-T_c superconductors in electronic devices and various transmission lines, the technique of metal film deposition on to superconductors is necessary [7]. Consequently, a wide variety of materials such as metals, polymers, oxides and nitrides have been studied for the purpose of superconductor protection, but metal is the most suitable material from considerations of both protection and electrical contact. Although metal coating could easily be achieved by using a vacuum process such as sputtering, thermal or electron-beam evaporation, it could not fully cover the substrate because of the fatal geometrical weakness of the vacuum deposition process, thus allowing humidity and moisture to interact easily with the superconductor. Moreover, expensive vacuum equipment and the long pumping time greatly increased the cost of metal deposition. For these reasons, it is worthwhile not only to investigate the possibility of a cheaper and faster process of electrodeposition to produce a uniform and fully covering metal thin film on a superconductor substrate surface, but also to study the properties of electrodeposited films.

Previous research on metal electrodeposition on superconductor substrates concentrated on Y–Ba–Cu–O superconductors [8–12]. Silver and mercury were found feasible to deposit on a $Ba_2YCu_3O_7$ sample surface in a neutral aqueous salt solution [9]. In the case of non-aqueous solutions, films of silver, copper, lead and tin can be deposited on $Ba_2YCu_3O_7$ in acetonitrile, and their electrical and magnetic properties and the additive effect in the non-aqueous solution have been well investigated [10–12]. However,

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most copper films deposited from non-aqueous solutions display no Ohmic behaviour and the contacts appear to be semiconducting [12].

For the electrodeposition process in aqueous solution, copper electrodeposition on $Ba_2YCu_3O_7$ was once regarded as impossible due to the competing reaction between copper reduction and water degradation [8–13]. However, after reducing the activity of the aqueous solution and improving the deposition technique in later research, it became feasible to deposit copper on a $YBa_2Cu_3O_x$ substrate and an Ohmic metal contact was observed [14]. Recently, we have found that copper can be deposited on the more stable Bi–Pb–Sr–Ca–Cu–O superconductor from aqueous solution with good adhesion, Ohmic contact and no evident degradation of intrinsic superconductor properties [15]. However, the literature on metal electrodeposition on the much higher-T_c Tl–(Pb, Bi)–Sr–Ca–Cu–O superconductor is fairly limited [15, 16]. So it is worthwhile to investigate the electrodeposition process on the much higher-T_c Tl–(Pb, Bi)–Sr–Ca–Cu–O superconductors for scientific research as well as for practical application.

The effects of electrodeposition on the intrinsic bulk properties of superconductors such as electrical resistivity and magnetic susceptibility are of critical importance [8–12]. Especially for such a process developed in aqueous solution, water degradation was regarded as the most important factor in the negative effect of electrodeposition on substrate properties in such an environment [12]. To investigate the feasibility of the electrodeposition process, magnetic and electrical properties must be examined both before and after deposition. Moreover, it is necessary to investigate the interface contact property for the consideration of future practical applications. Ohmic contact is the desired result for metal deposition, otherwise it is difficult to apply the electrodeposited metal–superconductor composite in electronics and power transmission lines.

2. Experimental procedure

2.1. Preparation of superconductor samples

The superconductor electrodes were synthesized by a solid-state reaction. Appropriate amounts of $CaCO_3$, $SrCO_3$ and CuO high-purity reagent powders ($\geqslant 99.9\%$) were well mixed with a cation ratio of Sr:Ca:Cu = 1.6:2.4:3 and then calcined at 920 °C for 10 h in order to obtain a precursor powder whose formula is $Sr_{1.6}Ca_{2.4}Cu_3O_y$ according to previous research [15, 16]. Next Tl_2O_3, PbO and Bi_2O_3 were added to the precursor mixture according to the nominal composition $(Tl_{0.64}Bi_{0.16}Pb_{0.2})Sr_{1.6}Ca_{2.4}Cu_3O_y$. The calcined powders were reground and pressed into disc-shaped pellets. Then the palletized Tl-containing samples were sealed by 99.99% pure gold foil in 0.5 mm thickness before sintering. The final heat treatment was carried out in a tube furnace which was previously heated to 900–940 °C with flowing oxygen. After sintering at 920 °C in O_2 atmosphere for three successive periods of 10 h, the samples were cooled down to room temperature with a cooling rate of 2 °C min^{-1}.

2.2. Characterization of samples

The crystal structure of the as-sintered superconductor sample was confirmed by a Philips APD 1700 X-ray diffractometer with CuK_α radiation. A.c. (16 Hz) temperature-dependent electrical resistivity measurement was carried out using a standard four-point probe with a silver–epoxy contact. Low-field temperature-dependent magnetization data were obtained using a commercial superconducting quantum interference device (SQUID) magnetometer (Quantum) from 120 to 5 K with 10 Oe applied field.

2.3. Electrodeposition process

Copper electrodeposition on Tl–(Bi, Pb)–Sr–Ca–Cu–O samples was performed in a modified saturated copper sulphate bath according to previous research [13, 14]. Before electrodeposition, the electrode surfaces were ground by SiC grinding paper to prevent possible contamination during sample storage. Electrodes of about 0.5 cm^2 contact area were patterned with epoxy in a four-point resistance or fixed-area configuration. The electrodeposition was carried out at 25 °C and lasted for about 20 min with magnetic stirrer agitation and temperature control. An HP 6286A d.c. power supply with a microammeter was used to supply an accurate deposition current. The dip power-on technique was used to accelerate the deposition rate and reduce the rate of possible water degradation which is due to direct contact with water [12, 13]. After electrodeposition, the electrodes were thoroughly rinsed immediately in acetone and dried in air.

2.4. Analysis of film properties

Optical microscopy (OM) and scanning electron microscopy (SEM) were used for the observation of the surface morphology of samples before and after electrodeposition. Cross-section interface analysis was performed by electron probe micro-analysis (EPMA) for specific element line-scan profile and element position mapping observation. The Cu-deposited samples were connected by an EMB ultrasonic bonding machine with gold wire of 0.025 mm diameter from the copper pad pattern to TO-5 packages and then sealed for I–V measurement. An HP 4145B semiconductor parameter analyser was adapted to take I–V curve measurements at the nitrogen boiling point 77 K.

3. Results and discussion

The sintered Tl–(Bi, Pb)–Sr–Ca–Cu–O samples were identified by X-ray diffraction (XRD) patterns as mostly 120 K high-T_c (Tl, Pb)$Sr_2Ca_2Cu_3O_y$ superconductor phase (1223 phase, three Cu–O layers) with a little impurity. From XRD data, when Ca/Sr changed to a high ratio of 2.4/1.6 with the modified stoichiometric compositions of $(Tl_{0.64}Bi_{0.16}Pb_{0.2})Sr_{1.6}Ca_{2.4}Cu_3O_y$, a nearly single phase of 1223 phase superconductor can be obtained with 3 h of heat treatment [15, 16]. The surface morphology was of a high purity, as shown for sintered samples in Fig. 1a. Plate-like rectangular grains are observed to be well distributed on the surface and contribute to the surface roughness of the samples.

Electrodeposition of copper metal on Tl–(Pb, Bi)–Sr–Ca–Cu–O substrate was achieved in a modified saturated copper sulphate bath. Rosamailia and Miller [9] stated that the cuprate superconductor substrate reactivity and water activity can be reduced in concentrated aqueous solution. Thus saturated copper sulphate solution was first adopted for the copper electrodeposition to reduce the rate of possible reaction between superconductor and solution. In addition, from a study of the electrochemical behaviour of several metal ion solutions at the Y–Ba–Cu–O electrode, Rosamilia and Miller [9, 10] inferred that a metal with a more negative standard potential must compete with reduction of the substrate. Only partial reduction of copper species is indicated with no clear indication of a metal film [9]. As a result, electroplating possibilities in aqueous media are limited by the narrow range of potentials accessible to a cuprate cathode [10]. However, if we can deposit a layer of metal on the superconductor at the moment when the substrate comes into contact with the solution, it is easier for later metal to deposit on the formerly deposited metal and grow. Thus the substrate was connected to a power supply before plating in order to begin deposition at the same time as the substrate made contact with the solution.

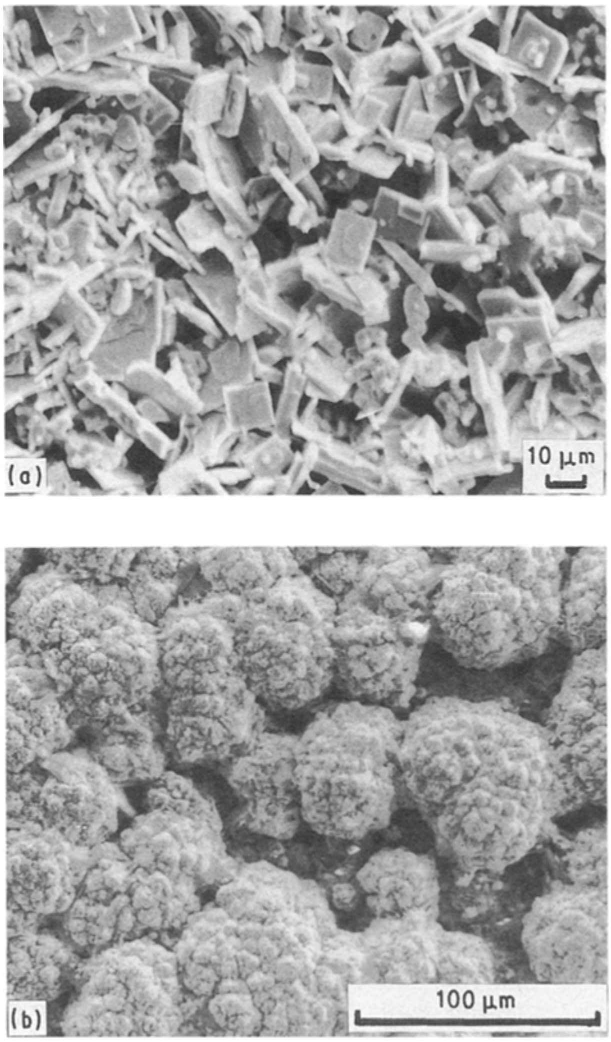

Figure 1 SEM photographs of Tl–(Bi, Pb)–Sr–Ca–Cu–O sample surface morphology (a) as sintered, (b) after electrodeposition.

After the success of electrodeposition of copper on Y–Ba–Ca–O and (Bi, Pb)–Sr–Ca–Cu–O substrates by this dip power-on method [13, 14], we applied the same idea to the Tl–(Pb, Bi)–Sr–Ca–Cu–O sample. With the modified method and solution, copper can fully cover the Tl-(Pb, Bi)–Sr–Ca–Cu–O sample within 20 min. The surface morphology of the substrate after electrodeposition is shown in Fig. 1b. Original rectangular superconductor grains can no longer be seen. The substrate surface is fully covered by dense round-like copper grains. Accordingly it is still possible to electroplate copper on cuprate superconductors directly from aqueous solution, not only on Y–Ba–Cu–O or (Bi, Pb)–Sr–Ca–Cu–O samples but also on Tl–(Pb, Bi)–Sr–Ca–Cu–O samples, a process which was once regarded as impossible with traditional plating techniques by Rosamilia and Miller [9–11].

An electron micrograph of a cross-section of the copper–superconductor interface is shown in Fig. 2a. It is clear that the film on the superconductor displays considerable evenness and uniformity within 10 µm of film thickness. After 120 min of electrodeposition, the thickness of copper film is about 70 µm. Copper film did adhere to the superconductor substrate according to its surface morphology. No crack or inclusion was found at the interface. Compared with the result from non-aqueous solution [10–12], a more compact Cu-deposited structure was found. After mechanical polishing, the copper film still strongly stuck to the superconductor. No evident degradation layer was found at the copper–superconductor interface.

The line scan of copper element by EPMA indicates the relative composition of copper in the copper film and cuprate superconductor as shown in Fig. 2b. A flat-topped curve showing a sharp transition of the copper scan profile locates the precise position of the interface. Uniform compositions of copper in both film and substrate are observed and the content of copper in the film (in the middle of the micrograph) is higher than that in the superconductor (on the right of the micrograph). From the interface scan observation, no other evident layer formed by the reaction of superconductor with solution at the interface was found, as can be identified by an intermediate stage in the copper element line scan profile between copper film and superconductor. Moreover, Cu atom mapping demonstrates the relative distribution of Cu atoms as shown in Fig. 2c. The relative amount of copper in the metal film is much larger than in the superconductor with no transition layer. A definite interface was observed, whose curve is identical to previous cross-section surface morphology observation as shown in Fig. 2a. The above investigations reveal the possibility of direct contact of electrodeposited copper metal on a superconductor without any

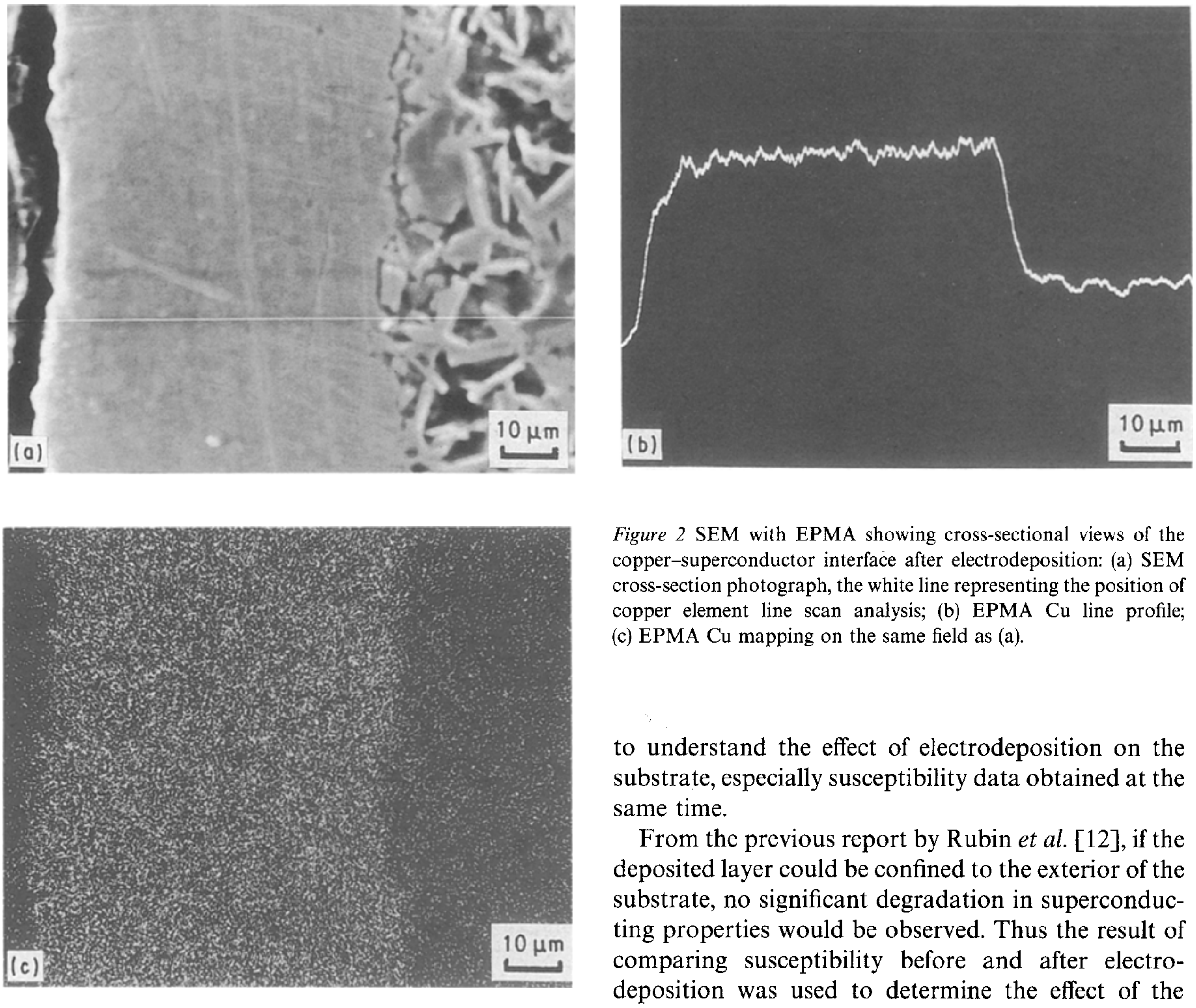

Figure 2 SEM with EPMA showing cross-sectional views of the copper–superconductor interface after electrodeposition: (a) SEM cross-section photograph, the white line representing the position of copper element line scan analysis; (b) EPMA Cu line profile; (c) EPMA Cu mapping on the same field as (a).

measurable reaction layer forming between them during the process of electrodeposition.

The temperature dependence of electrical resistivity of the Tl–(Pb, Bi)–Sr–Ca–Cu–O sample was measured before and after electrodeposition using a standard four-probe method. Each pair of current and voltage leads was soldered directly to the superconductor surface before electrodeposition or on the electrodeposited copper pad after electrodeposition. The a.c. temperature-dependent electrical resistivity is given in Fig. 3. Both measurements almost merged in the same curve and were in the range less than 20 mΩ. The result shows that the electrodeposited copper–superconductor composite structure has the same transition temperature as the original substrate at about 113 K, when the resistance drops to zero. It did show that copper metal made direct contact with the superconductor substrate. However, from these data alone we cannot prove that there was entirely no degradation at the interface. Rubin *et al.* [12] stress that four-point resistivity measurements alone may not give an accurate measure of the degree of retention of bulk superconductivity in an aqueous environment. When the degree of retention decreased, it was observed that the bulk susceptibility dropped significantly but there were no changes in the four-point resistivity characteristics at the same time [12]. Accordingly, we must consider other properties in order to understand the effect of electrodeposition on the substrate, especially susceptibility data obtained at the same time.

From the previous report by Rubin *et al.* [12], if the deposited layer could be confined to the exterior of the substrate, no significant degradation in superconducting properties would be observed. Thus the result of comparing susceptibility before and after electrodeposition was used to determine the effect of the plating operation on bulk superconductivity. The temperature-dependent magnetization curve from 130 to 5 K for Tl–(Pb, Bi)–Pb–Sr–Ca–Cu–O samples before and after electrodeposition is shown in Fig. 4. From Fig. 4, copper deposition on highly dense Tl–(Pb, Bi)–Pb–Sr–Ca–Cu–O substrates was achieved with no apparent drop of the a.c. susceptibility. Sharp diamagnetic transitions to the superconducting state occurred at 113 K in measurements on both Cu electroplated samples and as-sintered ones in excellent agreement with the transport data shown in Fig. 3. The magnetization values at 5 K are 0.28 memu g^{-1} for field cooling measurement curve and 4.5 memu g^{-1} for the zero-field cooling measurement curve. The curves measured both before and after electrodeposition almost overlap. From the unchanged average bulk diamagnetic data, the superconductivity was retained after electrodeposition for such specimens.The operation of electrodeposition from aqueous solution thus has no apparent effect on the intrinsic properties of the Tl–(Pb, Bi)–Sr–Ca–Cu–O superconductor.

For practical application of copper electrodeposition to electronic devices, the electrical metal contact property between deposited film and high-T_c superconductor must be understood. Two-point I–V curve measurements were carried out at 77 K as shown in Fig. 5. Linear current–voltage behaviour (Ohmic behaviour) was observed for the copper–superconductor composite structure. From calculation of the slope of

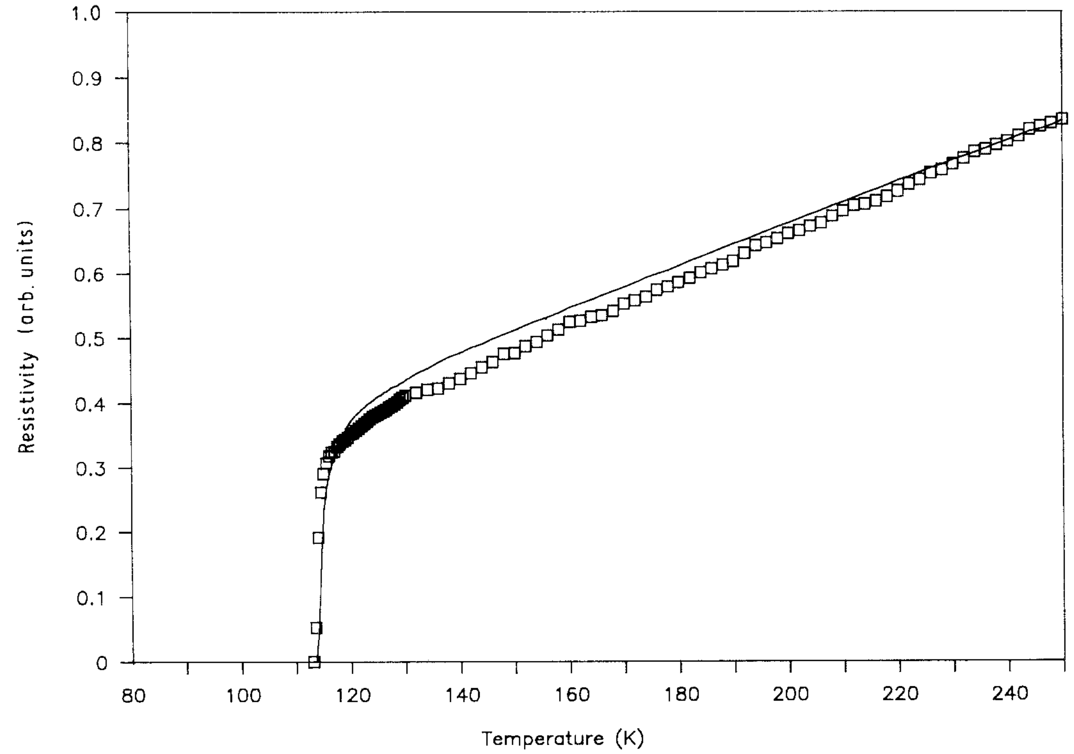

Figure 3. Temperature dependence of the electrical resistivity of Tl–(Bi, Pb)–Sr–Ca–Cu–O sample (□) before and (——) after electrodeposition.

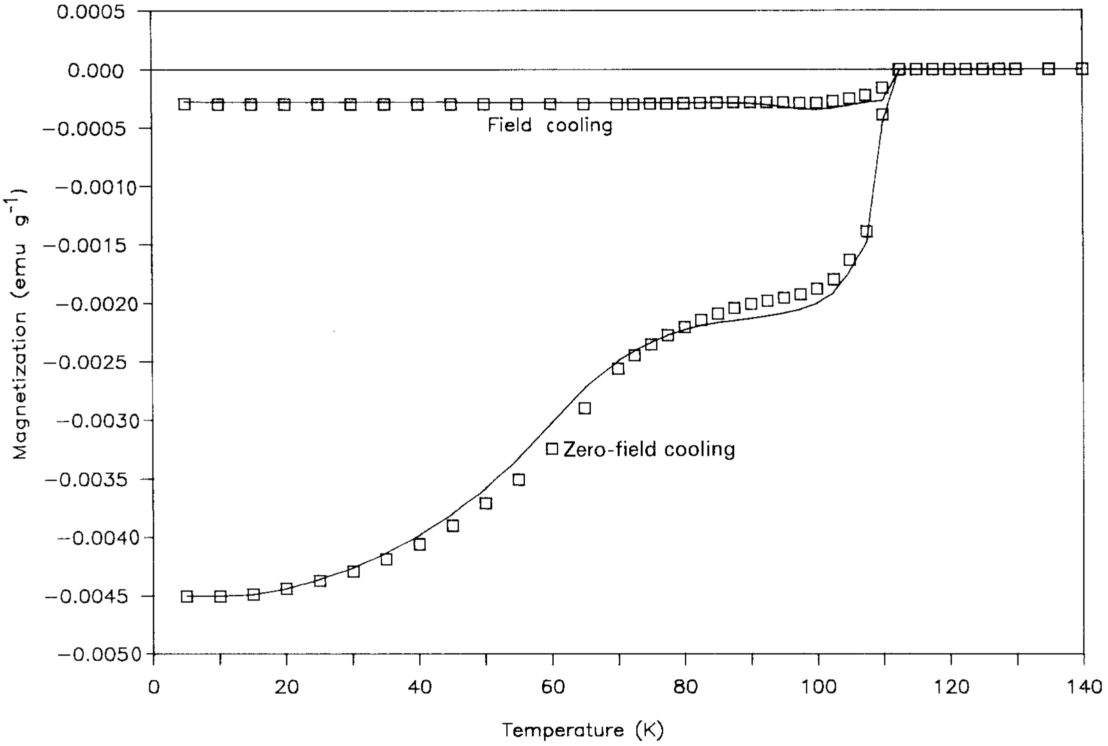

Figure 4 Temperature dependence of magnetization curve from 130 to 5 K for Tl–(Bi, Pb)–Sr–Ca–Cu–O sample (□) before and (——) after electrodeposition.

the current–voltage diagram, the measured total resistance of the copper contact at 77 K is about $7 \times 10^0\,\Omega$ order of magnitude. When the temperature dropped to 77 K, the sample turned to a superconducting state and the resistance dropped to zero; thus the resistance measured by the two-point method includes only the contact resistances between silver paste and copper, silver paste and line for measurement, and copper film and superconductor. The contact resistance between copper film and superconductor substrate must therefore be smaller than $7 \times 10^0\,\Omega$ order of magnitude. This range of contact characteristics is similar to that of copper film deposited on Y–Ba–Cu–O and (Bi, Pb)–Sr–Ca–Cu–O substrates from both aqueous and non-aqueous solution [12, 13].

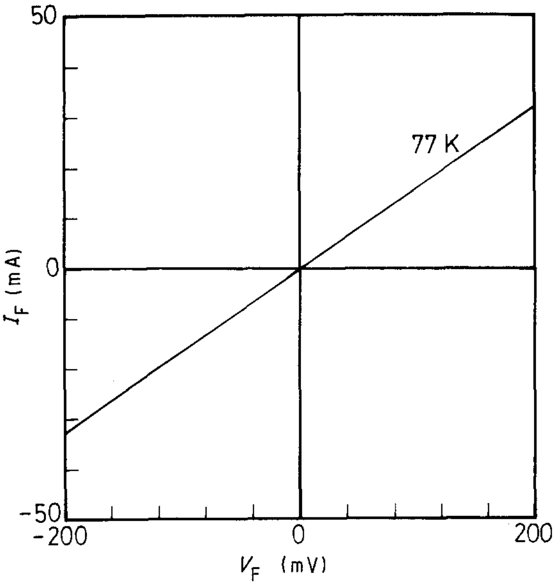

Figure 5 Experimental current–voltage (I–V) characteristic of copper/Tl–(Bi, Pb)–Sr–Ca–Cu–O contact interface at 77 K.

From the linear property of current–voltage characterization, we can infer that there is no apparent corroded layer produced during the electrodeposition process in aqueous solution, otherwise a Schottky barrier or a tunnelling phenomenon (non-linear property) would be found in this case. Combining this property with resistivity measurements, susceptibility data, cross-section observation and adhesion tests, it is clear that the copper film formed on a Tl–(Pb, Bi)–Sr–Ca–Cu–O surface by electrodeposition from aqueous solution does not change its original superconducting properties. Moreover, with good mechanical bonding, full cover and ohmic contact between copper and superconductor, this technique has proved feasible not only in Y-system and Bi-system superconductors but also in the Tl-system superconductor; thus it could be regarded as suitable for metallization processing of superconductor electronic devices in the future.

4. Conclusion

By using the chemical electrodeposition technique and dip power-on method, a copper film has been successfully grown on the surface of high-T_c, nearly single-phased Tl-(Pb, Bi)–Sr–Ca–Cu–O superconductor substrates from aqueous solution. Uniform electrodeposited copper film has shown good adhesion with full cover on the superconductor electrode surface. From resistivity and susceptibility measurements before and after electrodeposition, the nearly unchanged electrical and magnetic properties illustrate that the electrodeposition process has no apparent effect on the intrinsic properties of the superconductor. Moreover, the Ohmic behaviour needed in electronic devices was observed at the copper–superconductor interface. The success of this work may open up new avenues of research and device technology since electrodeposition methods are fast, cheap and simple.

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