

Use of SrTiO₃ as a substrate for YBa₂Cu₃O_{7-x} electrodeposition

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YBa₂Cu₃O_{7-x} thick films (~40 μm) have been prepared by electrodeposition using reduced SrTiO_{3-x} as a substrate. The process consists of three main steps. The first step is the reduction of a SrTiO₃ single-crystal at high temperature. This generates a conducting substrate, which can be used as a cathode in a three-electrode electrochemical cell. The second step is the co-electrodeposition of Y³⁺, Ba²⁺, and Cu²⁺. This produces a precursor film with a mixture of the elements on the atomic scale. The final step is the oxidation of the precursor film at high temperature. This produces the desired superconducting phase and re-oxidizes the SrTiO_{3-x}. Thus, we have successfully electrodeposited a superconducting film on an insulating substrate (E. Morán, M. Á. Alario-Franco and M. S. Martín-González, *Spanish Patent* P9802655, 1998).

Introduction

The SrTiO₃ perovskite is one of the most common substrates used for HTSC films because of their structural similarity. At room temperature its lattice parameters are similar to the lattice parameters for many superconducting phases, such as YBa₂Cu₃O_{7-x}. In addition, electrodeposition is one of the most simple, inexpensive and fast ways to deposit metals onto *conducting substrates*. This process also has the advantage of being widely used in industry for such processes as galvanization. However, electrodeposition directly onto SrTiO₃ is not possible due to its insulating behaviour. Hence, in order to obtain HTSC films on this substrate by electrodeposition, it is necessary to first make it conducting.

Previously, electrodeposition on insulating substrates has been achieved by depositing a metallic buffer layer, such as silver,¹⁻⁴ onto the insulator using different deposition procedures. Obviously, in these cases, the electrodeposition is carried out on the metal and not onto the substrate surface. Moreover, the use of this buffer layer adds more steps to the process and would raise the cost of the eventual devices.

The *new process* proposed in this work begins with the reduction of the substrate SrTiO₃ at high temperature in an evacuated quartz ampoule employing zirconium metal as a getter. The reduced substrate is then conducting due to the presence of titanium in two different oxidation states (iv and iii).⁵ Secondly, the simultaneous co-electrodeposition of Y, Ba, and Cu is performed. In this electrochemical reduction, a precursor film composed of a mixture of the elements with the stoichiometry of the desired superconductor is obtained. Finally, the precursor film is annealed in air or oxygen to obtain the superconducting phase. Simultaneously, the substrate is re-oxidized. The result is, then, an insulator-superconductor interface obtained by electrodeposition, an inexpensive method. This is of key interest in the fabrication of potential devices.⁶ Here we report the electrodeposition of YBa₂Cu₃O_{7-x} thick films on SrTiO₃ without using a buffer layer.

Experimental

The three steps necessary for obtaining superconducting thick films on SrTiO₃ are: substrate pre-treatment, electrodeposition of the cations, and thermal oxidation. In the first step, SrTiO₃ (100) single crystals (Crystal-GmbH) of 5 × 5 × 1 mm were reduced with Zr metal in an evacuated sealed quartz ampoule at ≈1320 K for 3 days. The reduced crystals were black and conducting, and consequently could be used as substrates for electrodeposition. A single crystal was fixed in the electrolytic bath by means of a home made crystal holder in which a silver wire was pressed against the crystal to establish a good electrical contact.^{7,8}

The second step was the electrodeposition of the precursor film. A typical electrolytic bath consisted of a solution of nitrate salts in dimethyl sulfoxide. The concentrations were 20 mM Y³⁺, 36 mM Ba²⁺ and 44 mM Cu²⁺. This bath was similar to those used for the electrodeposition on a silver substrate.^{3,9} A VersaStat potentiostat/galvanostat Model 253 fitted with a PC computer interface was used for controlling the process. The three-electrode cell consisted of a Ag/AgCl reference electrode, a platinum counter electrode, and a reduced SrTiO₃ single-crystal working electrode. The temperature was held constant at 25 °C by means of a thermostatic bath (Clifton NE4-DCE PLUS). The electrodeposited precursor films were heated at 900 °C for 24 hours in air and post-annealed in O₂ at 450 °C for 24 hours.

Structural characterisation of the substrate was accomplished using grazing incidence X-ray diffraction (PHILIPS X'PERT modified for that purpose) and atomic force microscopy (AFM, Autoprobe CP, PARK). Infrared spectroscopy (IR, Midac Prospect-IR) was used to determine the presence of various species in the precursor films. X-Ray diffraction of the precursor and superconducting films was done with a Siemens D-5000 powder diffractometer. Scanning electron microscopy (SEM) was used in conjunction with energy dispersive spectroscopy (EDS) to study the morphology and determine the composition of the films (JEOL-JSM 6400

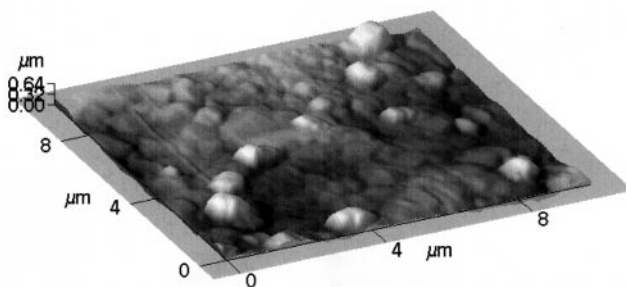


Fig. 1 AFM micrograph of SrTiO_{3-x} after thermal treatment in evacuated quartz ampoules using Zr as a getter.

scanning electron microscope). Superconducting temperatures and the $M(H)$ loops were recorded using a Quantum Design MPMS XL SQUID. The critical current densities in A cm^{-2} were obtained, for a slab plane geometry, using the Bean model.^{10,11}

Results and discussion

1. The substrate

Careful study of the surface of SrTiO_3 reveals that the morphology and the composition depend strongly on the reduction method used.^{5,12} In this work, strontium titanate was reduced upon heating in evacuated quartz ampoules using Zr as a getter. Before the reduction process, the surface was smooth, with very small steps (4 \AA) characteristic of an (100) oriented SrTiO_3 single crystal surface. After the reduction process, however, the surface is rough (Fig. 1). The reflections observed in the grazing incidence X-ray diffraction pattern (Fig. 2) can be attributed to the presence of some polycrystalline SrSiO_3 on the SrTiO_3 surface and to the (200)

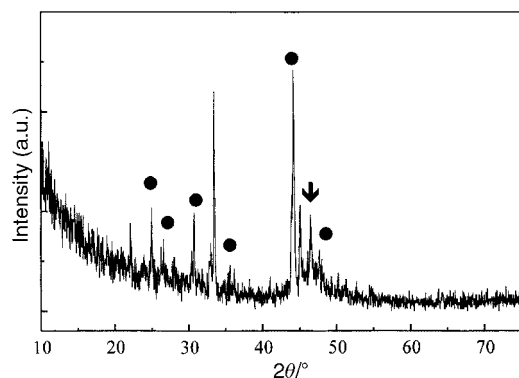


Fig. 2 Grazing incidence X-ray diffraction pattern of the SrTiO_{3-x} crystal of Fig. 1. Identification marks: ● SrSiO_3 and ▼ SrTiO_{3-x} . Not all the reflections were identified.

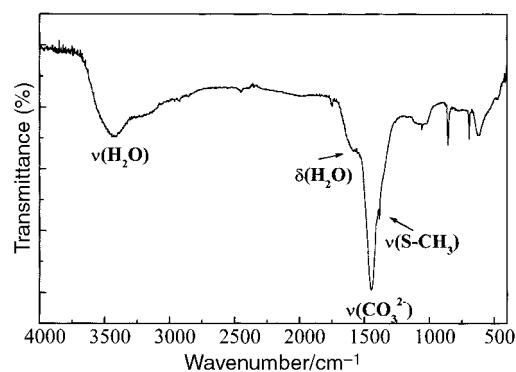


Fig. 3 Infrared spectrum of a Y:Ba:Cu precursor film deposited on reduced strontium titanate taken after leaving the film for two days in air at room temperature.

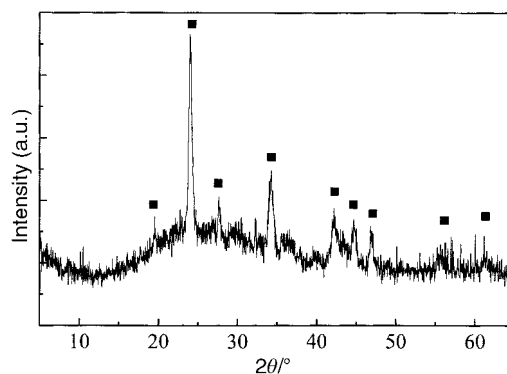


Fig. 4 X-Ray diffraction patterns of a Y:Ba:Cu precursor film deposited on reduced strontium titanate. Identification mark: ■ BaCO_3 .

SrTiO_3 reflection. The presence of Si on the SrTiO_3 surface was confirmed by EDS data. The average particle size is $\approx 0.257 \mu\text{m}$, as determined by AFM. The SrSiO_3 originates in the reaction between SrTiO_3 and SiO_x , which, we believe, comes from the quartz wool used as a separator between Zr and the crystals in the evacuated quartz ampoule. Nevertheless, not all the reflections in the X-ray diffraction pattern could be indexed using the JCPDS database. A more detailed study of the reduced strontium titanate surface (structural and compositional) using photoelectron spectroscopy (PES), low energy electron diffraction (LEED), EDS and transmission electron microscopy (TEM) will be given elsewhere.¹² Nevertheless, the growth of this additional phase on the SrTiO_{3-x} surface does not hinder the electrodeposition of the precursor film.

2. Precursor film

After electrodeposition, the presence of a black film on the substrate surface was observed. This precursor film became grey upon contact with air at room temperature. The same behaviour was previously detected for films deposited onto silver substrates.⁹ In order to study in detail the composition of the precursor film, infrared spectroscopy and X-ray diffraction were used.

The presence of water, carbonates and dimethyl sulfonate was detected in the films by infrared spectroscopy (Fig. 3). These results are in agreement with those obtained for YBCO on silver substrates. When the precursor film was studied by X-ray diffraction, BaCO_3 was unequivocally detected (Fig. 4). Some differences were observed in comparison with the silver substrate results. In the latter, the presence of Cu and Cu_2O was detected,⁹ but BaCO_3 was not. However, the presence of BaCO_3 was inferred from the thermogravimetric analysis. It is interesting to point out that in no case was the presence of an yttrium crystalline phase detected in the precursor film.

3. Superconducting film

The X-ray diffraction pattern of the film, heated at 900°C and annealed at 450°C in oxygen, corresponds to a mixture of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with some minor impurities of CuO .⁷ Scanning electron micrographs of representative films are shown in Fig. 5. The study of the morphology reveals the presence of columnar-type growth (Fig. 5(a)) where the average thickness of the superconducting films was $\approx 40 \mu\text{m}$. The average particle size was $\approx 5 \mu\text{m}$, Fig. 5(b). This microstructure indicates the presence of empty spaces between the crystals. The films were well formed, but not continuous. It is worth mentioning that film growth was not epitaxial under these conditions and the observed morphology was similar to that of films obtained on polycrystalline silver substrates.⁹ We conclude that the presence of SrSiO_3 on the SrTiO_3 surface does not prevent the formation of a film by electrodeposition but seems to prevent epitaxial

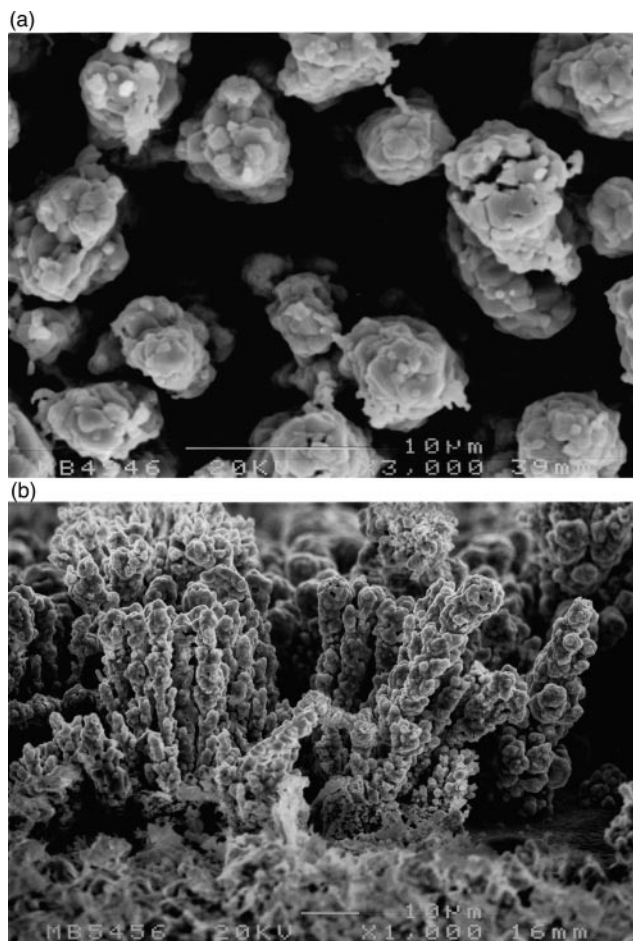


Fig. 5 Scanning electron micrographs of a $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ superconducting film on re-oxidized strontium titanate: (a) is the top view and (b) the lateral view.

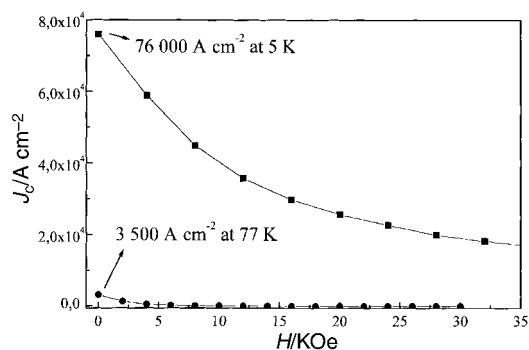


Fig. 6 Current density values for different magnetic fields for $\text{SrTiO}_3/\text{SrSiO}_3/\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films at 77 and 5 K.

growth despite the thickness of the film. Work is in progress to correlate the columnar growth observed in the superconducting YBCO film obtained under these conditions with the specific surface characteristic of the reduced crystals.

The superconducting transition temperature (T_c) of the electrodeposited thick films was established from a.c. magnetic susceptibility measurements. The T_c is of the order of 92 K, although the transition is somewhat large.

The J_c values (Fig. 6) were calculated using the Bean model. At 77 K under zero-field cooling the J_c values obtained are $\approx 3500 \text{ A cm}^{-2}$ and at 5 K $\approx 76000 \text{ A cm}^{-2}$ for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ thick films on $\text{SrSiO}_3/\text{SrTiO}_3$ substrates obtained by electrodeposition. Nevertheless, as is the case on silver, the application of an external magnetic field markedly decreases the J_c values. Table 1 summarizes the superconducting parameters from YBCO films obtained by electrodeposition on different substrates. J_c values for YBCO films range from ≈ 50 to 11500 A cm^{-2} for different substrates and different methods of measurement. The results obtained in this work are comparable in value to those observed for MgO/Ag and ZrO_2/Ag substrates (nevertheless, it has to be taken into account that different measurement techniques can give different values of J_c , see Table 1). Moreover, the J_c values obtained are lower than those observed for films grown on silver foil.

Table 1 Comparative of the superconducting properties of the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films *via* electrodeposition onto different substrates

Substrate	Electrodeposition conditions	Superconducting properties			Method used	Ref.
		T_c/K	$J_c/\text{A cm}^{-2}$	$(T/H)/\text{K Oe}^{-1}$		
Ni	Constant potential	74	500	4/0	Four-points	1
MgO/Ag	Constant potential	78	3960	4/0	Four-points	1
ZrO ₂ /Ag	Constant potential	91	4000	4/0	Four-points	1
ZrO ₂ /Ag	Constant potential	91	360	77/0	Four-points	1
MgO/Ag	Pulsed potential	78	5160	4/0	Four-points	2
MgO/Ag	Pulsed potential	78	142	4/500	Four-points	2
Ni strip	Constant potential	74	500	4/0	Four-points	3
Ni wire	Constant potential	74	325	4/0	Four-points	3
MgO/Ag	Constant potential	78	3960	4/0	Four-points	3
MgO/Ag	Pulsed potential	78	5160	4/0	Four-points	3
ZrO ₂ /Ag	Constant potential	91	4000	4/0	Four-points	3
Ag wire	Constant potential	92	500	4/0	Four-points	3
SrTiO ₃ /Ag	Pulsed potential	93	—	—/—	—	4
CaTiO ₃ /Ag	Pulsed potential	93	—	—/—	—	4
ZrO ₂ /Ag	Pulsed potential	93	—	—/—	—	4
Steel	Pulsed potential	90	—	—/—	—	13
Ag	Constant potential	92	500	77/0	Four-points	14
Ag	Constant potential	92	3000	77/0	Four-points	14
Ag	Constant potential	92	462	77/0	Four-points	15
Ag	Constant potential	92	1200	4.2/0	Four-points	15
Ag	Constant potential	92	2908	4.2/0	Four-points	15
Ag	Constant potential	92	51	77/0	Four-points	16
Ag	Cation by cation + annealing	82	6600	77/—	Four-points	17
Ag	Constant potential	92	9500	77/0	Bean	9
Ag	Constant potential	92	11500	77/0	Bean	18
SrTiO ₃	Constant potential	92	3250	77/0	Bean	7
SrTiO ₃	Constant potential	92	3500	77/0	Bean	This work

It is worth mentioning that although there is room to improve the J_c values for YBCO deposited on SrTiO₃ using our method, this is the first time in which a superconductor film has been obtained directly on an insulator substrate by means of electrodeposition. This offers hope for the use of this technique for practical applications in which superconductor–insulator interfaces are needed.

Conclusions

For the first time, superconducting YBa₂Cu₃O_{7-x} thick films have been prepared on insulating SrTiO₃ via the reduction of the substrate, by means of the electrodeposition of a precursor film, and post annealing of the composite material.¹⁹ As revealed by different experimental techniques, when SrTiO₃ is reduced using quartz ampoules, a polycrystalline SrSiO₃ film appears on the strontium titanate surface. However, the presence of this layer does not impede the electrodeposition process. The superconducting properties of the YBa₂Cu₃O_{7-x}/SrSiO₃/SrTiO₃ films obtained under these conditions are $T_c = 92$ K and J_c at 77 K of $\approx 3\,500$ A cm⁻² and at 5 K of $\approx 76\,000$ A cm⁻².

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