JOURNAL OF Materials CHEMISTRY

A metal-organic chemical vapor deposition approach to double-sided $Tl_2Ba_2Ca_1Cu_2O_8$ superconducting films on $LaAlO_3$ (100) substrates

Graziella Malandrino,[a] Anna M. Borzì,[a] Ignazio L. Fragalà,*[a] Antonello Andreone,[b] Antonio Cassinese[b] and Giulia Pica[b]

[a]*Dipartimento di Scienze Chimiche, Universita' di Catania, and I.N.S.T.M. UdR di Catania, Viale Andrea Doria 6, I-95125 Catania, Italy. E-mail: lfragala@dipchi.unict.it*
[b]*I.N.F.M. and Dipartimento di Scienze Fisiche, Universita' di Napoli Federico II, Piazzale Tecchio 80, I-80125 Napoli, Italy*

Received 24th June 2002, Accepted 10th September 2002

Double-sided $Tl_2Ba_2CaCu_2O_8$ (Tl-2212) films for device applications have been fabricated through thallium vapor diffusion into BaCaCuOF matrices deposited by a novel metal-organic chemical vapor deposition (MOCVD) process onto 10 × 10 mm^2 $LaAlO_3$ (100) substrates. The present approach uses a multimetal molten single source in a monocomponent hot-wall MOCVD reactor whose geometry allows simultaneous and uniform film growth on both sides of the substrate. Both sides are epitaxially coated by homogeneous and monophasic Tl-2212 films, which, even more importantly, have comparable superconducting and transport properties.

Introduction

High critical temperature T_c superconducting (HTc) materials have stimulated considerable interest in terms of potential applications/benefits, and microelectronic devices are expected to have a major commercial impact.[1] In microwave applications, highly performing and smaller size planar passive devices can be fabricated using HTc materials because of their very low surface resistance.

Among the currently known HT_c superconductors, TlBaCaCuO mixed-oxide systems[2] represent the best candidates due to the remarkably high critical transition temperatures of the $Tl_2Ba_2Ca_2Cu_3O_{10}$ (Tl-2223, T_c = 125 K)[3] and $Tl_2Ba_2CaCu_2O_8$ (Tl-2212, T_c = 110 K) phases.[3] The same phases also show appealing microwave properties.[4,5] Challenging surface resistance R_s and critical current J_c values have also been reported for Tl-2212 thin films on $LaAlO_3$ (100) at 77 K.[6]

Several problems are, however, associated with the reproducible production of Tl-based films due to the intriguing interplay among the various TlBaCaCuO superconducting phases, whose properties considerably vary according to their stoichiometry and structure.[7,8] The synthetic control over the desired phase is, therefore, of paramount importance for both fundamental studies and technological applications. A further problem is due to the toxicity and volatility of thallium, which make high-temperature processing studies quite difficult.

Despite the top-level intrinsic properties, fabrication of Tl-based superconducting materials is often confined to laboratory scale, which is expensive and hardly scalable to manufacturing of large area films, while any perspective applications require scalable and reproducible processes suited for high-quality films. Therefore, the development of low-cost processes represents a crucial step for large-scale applications. To date, efforts to produce single-sided (SS)[9–12] and double-sided (DS)[13–15] thin films of Tl-based superconductors have been largely focused on physical vapor deposition (PVD) techniques.

Metal-organic chemical vapor deposition (MOCVD) has proved a challenging alternative due to the use of simplified apparatus, lower deposition temperatures, capability to coat complex shapes, and adaptability to large scale processing.[16,17] This technique, in addition, is well suited for the simultaneously coating of both sides of substrates, whilst line of sight PVD techniques require sequential deposition steps of each of the two sides.

In this paper, we report on the synthesis of DS Tl-2212 films for passive microwave applications. A combined thallium vapor diffusion and a novel MOCVD approach for the fabrication of BaCaCuOF matrices have been used to grow the DS Tl-2212 superconducting films on 10 × 10 mm^2 $LaAlO_3$ (100) substrates. The morphological and structural characterization of both the BaCaCuOF matrices and the DS Tl-2212 films are discussed. The transport and microwave properties have been studied as well.

Experimental

MOCVD of DS Ba-Ca-Cu matrices

Low-pressure MOCVD depositions were performed under Ar (carrier gas) and O_2 (reaction gas) flows, using a horizontal hot-wall quartz reactor.

Depositions of DS-BaCaCuOF films were carried out at 5 Torr total pressure in a reactor fitted with individual inlet tubes and gas flow controllers for the carrier and the reaction gasses, and a single thermocouple/heater assembly for the volatile multicomponent metal-organic source.

The multi-metal metal-organic single source was a mixture of high-purity powders of $Ba(hfa)_2$·tetraglyme, $Ca(hfa)_2$·tetraglyme, and $Cu(tmhd)_2$ (Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, tetraglyme = 2,5,8,11,14-pentaoxatetradecane, Htmhd = 2,2,6,6-tetramethyl-3,5-heptanedione) in an appropriate ratio to yield the desired film stoichiometry. The barium and calcium precursors were synthesized as previously reported,[18] while the $Cu(tmhd)_2$ was purchased from Aldrich and sublimed before use. Films were deposited on single-crystal 10 × 10 mm^2 $LaAlO_3$ (100) substrates which were maintained at 500 °C. In these operational conditions deposition rates were ~5 $\mu m\ h^{-1}$. The substrate was positioned in the center of a 25 mm diameter reactor using a special stainless steel substrate holder.

DOI: 10.1039/b206039f

Thallium vapor diffusion

The precursor BaCaCuOF matrices were processed in a thallous oxide vapor atmosphere. The thallium vapor diffusion step was carried out in a covered crucible inside an atmospheric pressure reactor using a suitable oxide mixture containing Tl_2O_3. A gas flow of 180–210 sccm was maintained during the processing of the films.

Note that great care must be taken to manipulate the thallium-containing mixtures and all the experiments were carried out under well-ventilated hoods. The annealing reactor has to be gas-proof, so that the unique outlet gas flow may be bubbled in a series of three traps containing NaI solution (10% in H_2O) to convert any Tl exhaust to insoluble yellow TlI. The third trap solution has to be colorless. The entire system, reactor and traps, was allocated inside a totally filtered hood.

Characterization

Scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analysis were carried out using a Cambridge Stereoscan 360 electron microscope, interfaced with a Link solid state detector.

θ-2θ X-Ray diffraction (XRD) patterns were recorded on a Bruker-AXS D5005 θ-θ X-ray diffractometer using Cu-Kα radiation operating at 40 kV/ 30 mA. X-Ray rocking curves and pole figures were recorded on a Bruker-AXS D5005Tex θ-2θ X-ray diffractometer using Cu-Kα radiation operating at 40 kV/ 30 mA.

A surface profilometer was used to determine the film thickness as well as the cross-sectional area of the bridge. The films were typically 5–6 μm thick. Transport and superconducting properties of Tl films were investigated using an inductive, non destructive, method, which measures, depending on the temperature and on the driving current, the third harmonic component voltage across a small sensor coil mounted very close to the film surface. The surface impedance R_s was measured at a frequency of 87 GHz using a cylindrical OFHC copper cavity. The transmitted power P is measured as a function of the stepwise swept frequency f of the input signal and detected with a diode voltage. The loaded quality factor Q_L of the cavity is then converted into the surface resistance value. A detailed description of the experimental set up, including a discussion of the accuracy and limits of the technique, is contained in ref. 19.

Results and discussion

MOCVD fabrication of DS BaCaCuOF matrices

The quality of any MOCVD process crucially depends on the apparatus as well as on prerequisites of adopted precursors.[20] Thus, reproducible results are always associated with a careful control of operational deposition parameters and, even more importantly, with the use of highly pure precursors with clean decomposition pathways and constant mass-transport properties.

The present MOCVD process relies upon a novel approach based on the use of a single source multimetal mixture in a monocomponent hot-wall reactor whose geometry allows uniform coating of both sides of the 10 × 10 mm^2 $LaAlO_3$ (100) substrate. The multicomponent precursor consists of a homogeneous mixture of $Ba(hfa)_2$·tetraglyme, $Ca(hfa)_2$·tetraglyme and $Cu(tmhd)_2$ in the appropriate stoichiometric ratio. The $Ca(hfa)_2$·tetraglyme precursor likely acts, upon melting, as a solvent for the other species and gives a homogenous mixture of all the three precursors. Each single precursor possesses high vapor pressure and good thermal stability even considerably beyond the melting point. These prerequisites warrant constant mass transport rates (also under atmospheric pressure) from liquid sources. The multimetal mixture precursor has improved characteristics/advantages over the separate management of singular sources, with different operational parameters. Note that the stoichiometric ratios among the three $Ba(hfa)_2$·tetraglyme, $Cu(tmhd)_2$ and $Ca(hfa)_2$·tetraglyme precursors remain almost constant both in the liquid source and in the transported vapor phase (despite the different precursor vapor pressures), since the mass of subliming species represent less than the 10% of the total mass of the liquid source.

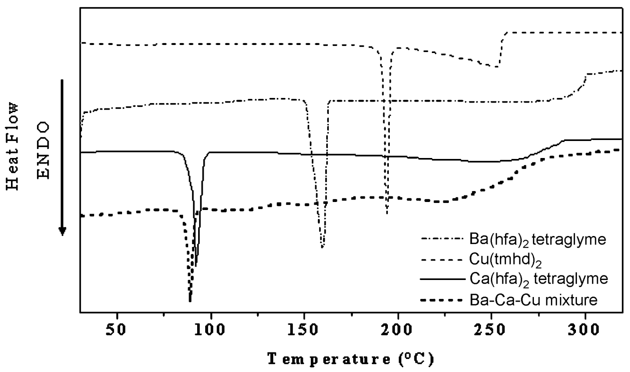

Fig. 1 Differential Scanning Calorimetry (DSC) curve of the 3 : 1 : 0.5 source mixture compared with data of individual precursors, $Ba(hfa)_2$tetraglyme, $Ca(hfa)_2$tetraglyme, $Cu(tmhd)_2$.

In Fig. 1 the differential scanning calorimetry (DSC) curve of a 2 : 1 : 2 (Ba, Ca and Cu precursors, respectively) mixture is compared with those of each individual precursor. The DSC scans of the single Ba, Ca and Cu precursors, show evidence of the endothermic peaks due to melting (94.9 °C for $Ca(hfa)_2$·tetraglyme, 153.6 °C for $Ba(hfa)_2$·tetraglyme, and 196.3 °C for $Cu(tmhd)_2$) and to evaporation from melts in the 250–280 °C, 260–290 °C, and 210–260 °C temperature ranges, respectively. In the DSC scan of the multicomponent precursor, the lower temperature peak (89.9 °C) represents melting of the $Ca(hfa)_2$-tetraglyme component, while the endothermic broad peak in the 110–160 °C temperature range is likely associated with $Ba(hfa)_2$·tetraglyme and $Cu(tmhd)_2$ dissolution. The highest temperature (190–270°C) endothermic process is associated with evaporation of the melt mixture. Note, in this context, that the endothermic peaks expected for the $Ba(hfa)_2$·tetraglyme and $Cu(tmhd)_2$ melting, at 153.6 °C and 196.3 °C respectively, are not observed. Optical polarized light microscopy observations upon heating, and reduced pressure sublimation data of the three component source totally agree with these conclusions. Melting of the $Ca(hfa)_2$tetraglyme is, in fact, observed at 89–93 °C, in agreement with DSC data, while well structured $Ba(hfa)_2$tetraglyme and $Cu(tmhd)_2$ crystals can be observed in the 95–110 °C interval. Dissolution of Ba and Cu crystals begin at 110 °C to be completed at 160 °C.

Sublimation experiments of the multicomponent molten precursor system at 120–140 °C (10^{-2} Torr) have not shown evidence of ligand exchange, since no green emerald $Cu(hfa)_2$ crystals have been observed in the sublimed and/or molten materials. Note that the $Cu(tmhd)_2$ crystals are purple.

Various stoichiometric mixtures and parameter conditions were tested to fix the best suited stoichiometry to grow the 2 : 1 : 2 (Ba-Ca-Cu) matrices (Table 1) and the best ratio was found to be 3 : 1 : 0.5 for the three precursors. The as-deposited matrices have poor crystalline structures. Thus, low intensity peaks can be detected in glancing incidence diffraction (GID) experiments. They can be indexed as reflections associated with BaF_2[21] and CuO[22] phases (Fig. 2a). No crystalline phases

Table 1 MOCVD deposition conditions of the DS-BaCaCuOF matrices

$T_{precursor}$	$T_{substrate}$	Time	F_{Ar}	F_{O_2}	P_{tot}
140 °C	500 °C	60 min	240 sccm	100 sccm	5 Torr

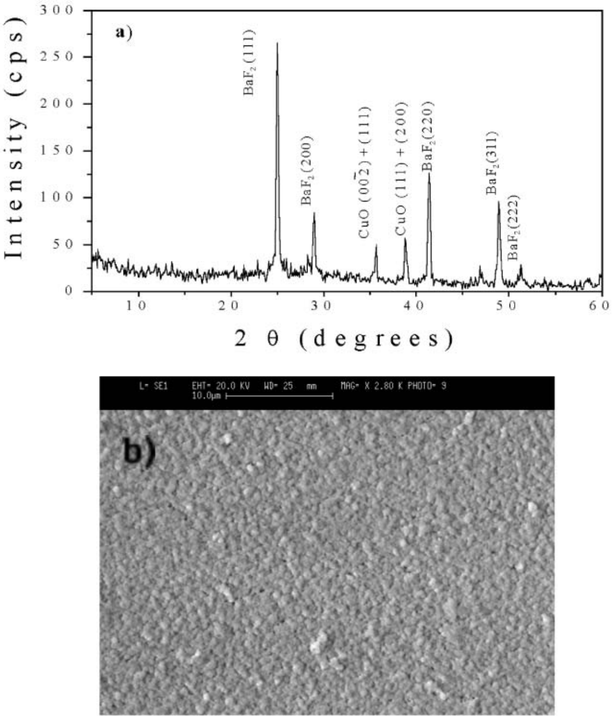

Fig. 2 XRD pattern a) and SEM image b) of one side of a DS BaCaCuOF matrix.

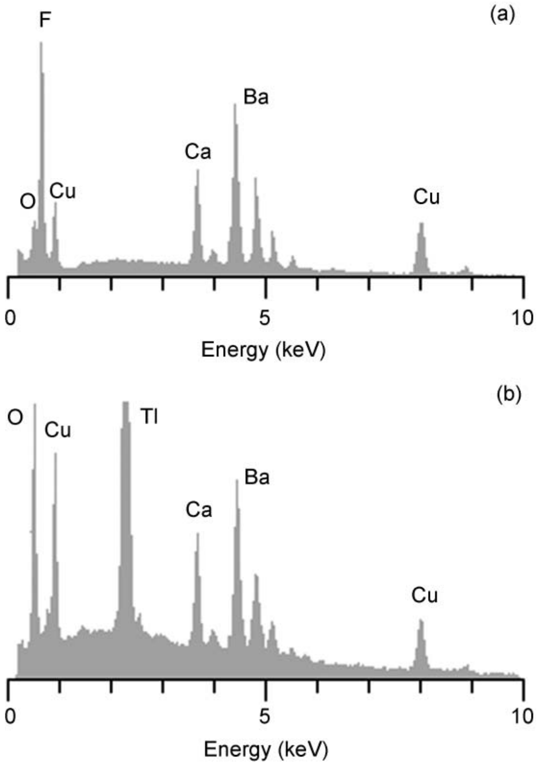

Fig. 3 EDX spectra of one side of a) the DS BaCaCuOF matrix and b) the DS $Tl_2Ba_2CaCu_2O_8$ film.

containing Ca are evident. The formation of fluoride phases is not surprising since it always accompanies decomposition of the present classes of fluorinated precursors.[18] EDX analyses of matrix films show some minor compositional inhomogeneity over the whole area (10 × 10 mm^2) with $2 \pm 0.2 : 1 \pm 0.1 : 2 \pm 0.2$ Ba : Ca : Cu stoichiometries, with the Ca K_α and K_β peaks at 3.690 and 4.010 keV, the Ba L lines spread in the 4.400–5.800 keV range, and the Cu K_α and K_β peaks at 8.040 and 8.900 keV, respectively (Fig. 3a). Identical compositions are found in corresponding points of the two $LaAlO_3$ sides. In addition, the windowless EDX detector allowed the detection of the O and F K_α peaks at 0.520 and 0.670 keV, respectively. Nevertheless, the EDX quantitative analyses of these light elements may be likely affected by a large error and, therefore, the comprehensive quantitative analysis of the BaCaCuOF matrices has been carried out by wavelength dispersive X-ray analyses (WDX). An average $Ba_{2.1}Ca_{1.0}Cu_{1.9}F_{6.2}$ stoichiometry has been found on both sides of the films. The film thickness is about 6 ± 0.2 µm on both sides. The SEM plane view image (Fig. 2b) points to homogeneous films with 1 µm grains.

The advances/advantages of the present synthetic strategy to simultaneously coating both sides of the $LaAlO_3$ substrates can be contrasted with limitation of PVD techniques. The intrinsic line of sight nature of the latter methodologies requires sequential depositions, thus often resulting in contamination/alteration of the first deposited side.

Finally, it is of interest to compare the present horizontal hot-wall MOCVD approach with the vertical hot-wall MOCVD apparatus proposed by Ito *et al.*[23] for the preparation of DS-YBaCuO thin films. This earlier procedure has an 80 °C temperature differential along a 10 mm substrate and requires a pulling up procedure to balance the thermal inhomogeneities. By contrast, the present approach allows uniform temperatures in a static substrate, and, therefore, an easier scaling to larger area films.

Thallium vapor diffusion of DS matrices

BaCaCuOF matrices have been cleanly converted into pure TlBaCaCuO superconducting films adopting the thallium vapor diffusion from a suitable thallium source, an intimately mixed powder containing Tl_2O_3, BaO, CaO and CuO, using the crucible geometry. Tl_2O, which is actually the thallium source in the diffusion process, is produced upon heating the source:

$$Tl_2O_3 \leftrightarrow Tl_2O\uparrow + O_2$$

The use of this oxide mixture, instead of pure Tl_2O_3, is required to correctly tune the Tl_2O vapor pressure to the best suitable value for the Tl-2212 superconducting phase.

In this context, the overall reaction to the Tl-2212 phase could be likely indicated as:

$$2\ BaF_2 + CaF_2 + 2\ CuO + 4\ Tl_2O + O_2 = \\ Tl_2Ba_2Ca_1Cu_2O_8 + 6\ TlF\uparrow$$

Note that, this procedure requires a fine tuning of the Tl_2O vapor pressure over both sides of the processed matrices to cleanly convert fluoride phases and to drive the transformation into the desired Tl-2212 superconducting pure phase.

Several experiments have been made to produce the most suitable Tl_2O uniform partial pressure over the entire sample. This is crucial to have synthetic control over a desired phase, and becomes even more difficult in the case of DS films. The BaCaCuOF matrices have been exposed to Tl_2O vapors in alumina crucibles with optimized geometry for 10 × 10 mm^2 substrates and tightly covered with a thin gold foil. The geometry of the crucible assembly has proven crucial to maintain uniform Tl_2O pressures over both sides of the matrices and, hence, to form homogeneous DS Tl-2212 films. DS matrices placed on the bottom of the boat produced DS films with different phases on the two sides, namely the Tl-2212 phase formed on the top and the Tl-1212 phase on the bottom side. This is evidence of a varying Tl_2O vapor pressure along the vertical of the boat. Identical Tl_2O vapor pressures, hence identical Tl-2212 phases, have been obtained on both sides upon suspending, over a finally grounded oxide mixture, the 10 × 10 mm^2 matrices horizontally and equally spaced between

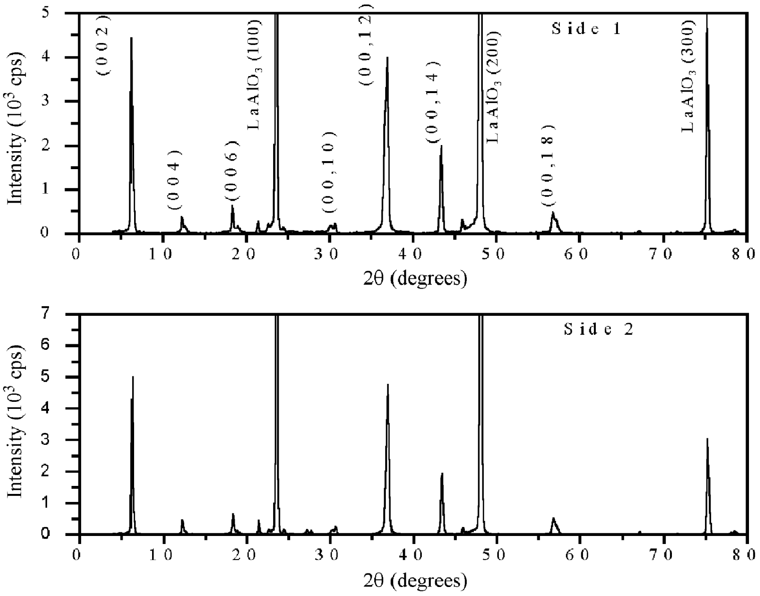

Fig. 4 XRD patterns of the two sides of a DS $Tl_2Ba_2CaCu_2O_8$ film.

the bottom of the boat and the gold covering foil. This geometry yielded best results, in terms of identical Tl-2212 phase formation on both sides as well as minimal failures.

In terms of best operational annealing parameters, monophasic DS Tl-2212 films have been obtained adopting: i) 800–820 °C annealing temperature, ii) 30–40 min annealing time, iii) 0.7–1 atm oxygen partial pressure, and finally iv) an oxide mixture $Tl_2O_3:BaO:CaO:CuO$ in 1 : 1 : 2 : 3 ratio. The resultant films exhibit XRD patterns (Fig. 4) indicative of a well-crystallized c-axis oriented Tl-2212 phase. The (00,12) rocking curve with a full width half maximum (FWHM) of 0.9° points to highly aligned crystallites. The (107) pole figure of a 5 μm thick DS-Tl-2212 film on $LaAlO_3$ is reported in Fig. 5. In the polar plot, the radial dimension, χ, refers to the angle between the normal to the film surface and the plane of the X-ray beam. The azimuth, φ, corresponds to the rotation of the substrate about the surface normal. The peaks at $\chi = 47.8°$ are the (107) reflections from $<001>$ oriented Tl-2212 films. There are four peaks at 90° intervals as expected for this tetragonal material.

The Tl-2212 phase films are fluorine free, as confirmed from the EDX and WDX data. The EDX spectrum (Fig. 3b) shows, in addition to the Ba, Ca and Cu peaks, the Tl M lines centered at 2.270 keV. Moreover, Auger electron spectroscopy (AES) depth profiles have shown no fluorine contamination both in the surface and the bulk of present DS films, in accordance to data previously reported for SS films similarly processed.[17b]

SEM micrographs of both sides of present DS Tl-2212 films (Fig. 6) show dense and homogeneous structures consisting of smooth overlapping platelets up to roughly 10 μm diameter.

Transport properties and microwave measurements

Properties of Tl films that are key diagnostics to film quality and applications readiness have also been investigated. J_c and T_c values measured on each side of a typical sample are respectively $J_{c,1}$ (77 K) = 3×10^4 A cm^{-2}, $T_{c,1}$ = 98.5 K and $J_{c,2}$ (77 K) = 7×10^4 A cm^{-2}, $T_{c,2}$ = 100 K, with $\Delta T_c = 1$ in both cases. Note that slight differences in T_cs are usually observed also for films grown by PVD techniques. The plot of the third harmonic component voltage U_{31} as a function of the temperature is reported in Fig. 7. The peak represents the T_c value of a typical double-sided 2212 film. Surface impedance measurements have been performed at 87 GHz employing an end wall cavity method. The surface resistance as a function

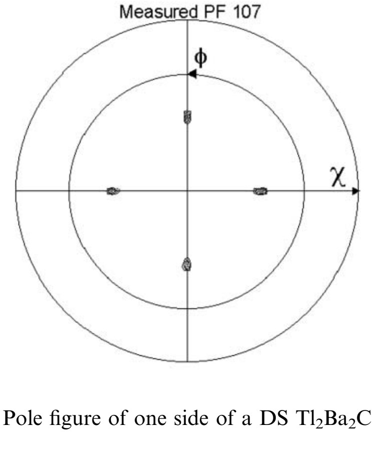

Fig. 5 (107) Pole figure of one side of a DS $Tl_2Ba_2CaCu_2O_8$ film.

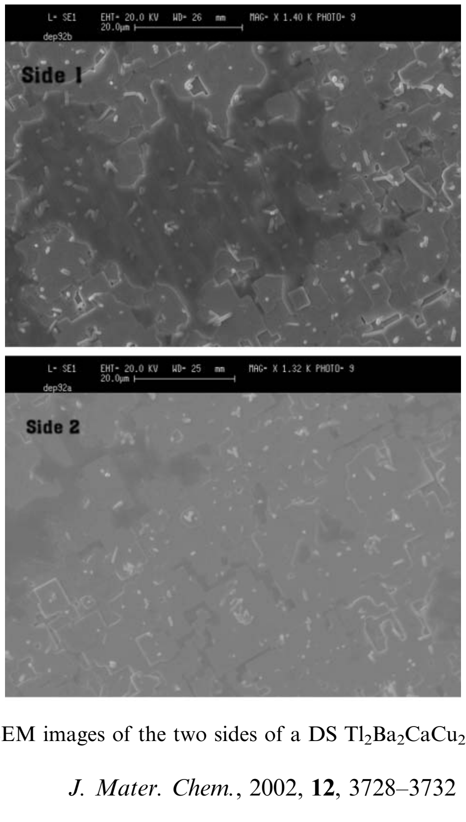

Fig. 6 SEM images of the two sides of a DS $Tl_2Ba_2CaCu_2O_8$ film.

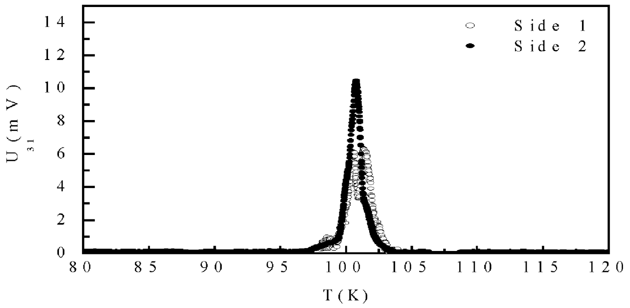

Fig. 7 T_c inductive measurements of a typical DS $Tl_2Ba_2CaCu_2O_8$ film.

of temperature shows a residual term $R_{res} \approx 10$ mΩ for the side 2, while for the side 1 the R_{res} term is about one order of magnitude higher. The former R_{res} value is comparable to the surface resistance values measured on SS Tl-2212 film,[24] and when scaled for the usual quadratic frequency law, it is even better than results reported by Willemsen *et al.* for SS films ($R_{s,min} \sim 50$ μΩ at 3.7 GHz).[6]

On the basis of the presented results, DS Tl-2212 films grown using MOCVD are very promising for the development of passive microwave planar devices for telecommunication applications. C-Band filters based on these films are presently under investigation in terms of device performance and power handling capability.[25]

Conclusions

These results represent, to our knowledge, the first report of the fabrication of DS Tl-2212 films *via* MOCVD.

The proposed method represents a challenging application of a multimetal single source in a monocomponent, simple hot-wall MOCVD reactor for the deposition of DS multicomponent BaCaCuOF matrices. It offers the best promise for a scalable and reproducible deposition technology due to the overall simplification of the MOCVD process. Besides this, it offers prerequisites of good selectivity and reproducibility in the formation of DS Tl-2212 phase films, mostly due to the accurate control of the matrix stoichiometry and of the Tl vapor diffusion process. The electrical transport properties point to good T_c and J_c values on both sides of the Tl-2212 films. Surface resistance data indicate that these films are very promising for passive filter applications, even though the microwave properties still require optimization.

In summary, the proposed approach certainly represents a promising low-cost route to large, high-quality, double-sided superconducting Tl-Ba-Ca-Cu-O films, since both the MOCVD deposition and the annealing appears well suited for fabrication of larger-area films.

Acknowledgements

This work has been supported by I.N.F.M. under Progetto Sud "Filtri Superconduttori" and by MIUR under Progetto Cluster 14 P.E. 2. The authors wish to thank Dr Gunter Müller of the University of Wuppertal for the use of the apparatus for surface resistance measurements. The technical support of A. Maggio and S. Marrazzo is also gratefully acknowledged. G. Pica has been partially supported by Fondo Sociale Europeo.

References

1 (*a*) A. Lauder, K. E. Myers and D. W. Face, *Adv. Mater.*, 1998, **10**, 1249; (*b*) A. P. Jenkins, D. Dew-Hughes, D. J. Edwards, D. Hyland and C. R. M. Grovenor, *IEEE Trans. Applied Supercond.*, 1999, **9**, 2849.

2 A. M. Hermann and J. V. Yakhmi, *Thallium Based High Temperature Superconductors*, Marcel Dekker, Inc., New York, NY, USA, 1994 and reference therein.

3 (*a*) R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, C. G. Hadidiacos, P. J. Heaney, D. R. Veblen, Z. Z. Sheng, A. E. Ali and A. M. Hermann, *Phys. Rev. Lett.*, 1988, **60**, 1657; (*b*) S. S. P. Parkin, V. Y. Lee, E. M. Eugler, A. I. Nazzal, T. C. Huang, G. Gorman, R. Savoy and R. Beyers, *Phys. Rev. Lett.*, 1988, **60**, 2539.

4 S. Huber, M. Manzel, H. Bruchlos, S. Hensen and G. Müller, *Physica C*, 1995, **244**, 337.

5 A. P. Jenkins, A. P. Bramley, D. J. Edwards, D. Dew-Hughes and C. R. M. Grovenor, *J. Supercond.*, 1998, **11**, 5.

6 B. A. Willemsen, K. E. Kihlstrom, T. Dham, D. J. Scalapino, B. Gowe, D. A. Bonn and W. N. Hardy, *Phys. Rev. B Condens. Matter*, 1998, **58**, 6650.

7 A. P. Bramley, J. D. O'Connor and C. R. M. Grovenor, *Supercond. Sci. Technol.*, 1999, **12**, R57.

8 (*a*) M. P. Siegal, E. L. Venturini, B. Morosin and T. L. Aselage, *J Mater. Res.*, 1997, **12**, 2825; (*b*) M. P. Siegal, E. L. Venturini, D. L. Overmyer and P. P. Newcomer, *J. Supercond.*, 1998, **11**, 135.

9 J. Y. Lao, J. H. Wang, D. Z. Wang, S. X. Yang, Y. Tu, J. G. Wen, H. L. Wu, Z. F. Ren, D. T. Verebelyi, M. Paranthaman, T. Aytug, D. K. Christen, R. N. Bhattacharya and R. D. Blaugher, *Supercond. Sci. Technol.*, 2000, **13**, 173.

10 H. Q. Chen, L. G. Johansson, Q. H. Hu, Z. G. Ivanov, D. Erts and E. Stepantsov, *J. Supercond.*, 1998, **11**, 73.

11 W. L. Holstein, A. L. Parisi, C. Wilker and R. Flippen, *Appl. Phys. Lett.*, 1992, **60**, 2014.

12 J. D. O'Connor, A. P. Jenkins, C. R. M. Grovenor, M. J. Goringe and D. Dew-Hughes, *Supercond. Sci. Technol.*, 1998, **11**, 207.

13 (*a*) S. Huber, M. Manzel, H. Bruchlos, F. Thrum, M. Klinger and A. Abramowicz, *Applied Superconductivity 1997. Proceedings of EUCAS 1997, Third European Conference on Applied Superconductivity*, Institute of Physics Publishing, Bristol, UK., 1997, Vol. 1, p. 351; (*b*) H. Schneidewind, M. Manzel, G. Bruchlos and K. Kirsch, *Supercond. Sci. Technol.*, 2001, **14**, 200.

14 (*a*) K. S. Kale, A. P. Jenkins, K. L. Jim, J. D. O'Connor, D. Dew-Hughes, D. J. Edwards, A. P. Bramley, B. J. Glassey, C. R. M. Grovenor, M. J. Goringe and B. Pecz, *High Temperature Superconductors: Synthesis, Processing, and Large-Scale Applications. Proceedings TMS, Miner. Metals & Mater. Soc., Warrendale, PA, USA*, 1996, p 345; (*b*) A. P. Jenkins, K. S. Kale, D. Dew-Hughes, D. J. Edwards, A. P. Bramley and C. R. M. Grovenor, *IEE Colloquium on Superconducting Microwave Circuits*, IEE, London, UK, 1996, p. 3.

15 F. A. Miranda, S. S. Toncich and K. B. Bhasin, *Microwave Opt. Technol. Letters*, 1993, **6**, 752.

16 (*a*) R. J. McNeely, J. A. Belot, T. J. Marks, Y. Wang, V. P. Dravid, M. P. Chudzik and C. R. Kannewurf, *J. Mater. Res.*, 2000, **15**, 1083; (*b*) B. J. Hinds, R. J. McNeely, D. B. Studebaker, T. J. Marks, T. P. Hogan, J. L. Schindler, C. R. Kannewurf, X. F. Zhang and D. J. Miller, *J. Mat. Res*, 1997, **12**, 1214; (*c*) X. F. Zhang, Y. S. Sung, D. J. Miller, B. J. Hinds, R. J. McNeely, D. B. Studebaker and T. J. Marks, *Physica C*, 1997, **274**, 146.

17 (*a*) A. Andreone, A. Cassinese, F. Palomba, G. Pica, M. Salluzzo, G. Malandrino, V. Ancarani and I. L. Fragalà, *Int. J. Mod. Phys.*, 1999, **13**, 1321; (*b*) G. Malandrino, G. G. Condorelli, G. Lanza, I. L. Fragalà, U. Scotti di Uccio and M. Valentino, *J. Alloys Comp.*, 1997, **251**, 332; (*c*) G. Malandrino, G. G. Condorelli, I. L. Fragalà, F. Miletto Granozio, U. Scotti di Uccio and M. Valentino, *Supercond. Sci. Technol.*, 1996, **9**, 570.

18 G. Malandrino, F. Castelli and I. L. Fragalà, *Inorg. Chim. Acta*, 1994, **224**, 203.

19 S. Hensen, G. Mueller, C. T. Rieck and K. Scharnberg, *Phys. Rev. B*, 1997, **56**, 6237.

20 M. L. Hitchman and K. F. Jensen, *Chemical Vapor Deposition: Principles and Applications*, Academic Press, London, 1993.

21 JCPDS No 1-533.

22 JCPDS No 44-706.

23 Y. Ito, Y. Yoshida, M. Iwata, Y. Takai and I. Hirabayashi, *Physica C*, 1997, **288**, 178.

24 G. Pica, A. Andreone, F. Palomba, M. Salluzzo, R. Vaglio, G. Malandrino, V. Ancarani, I. L. Fragalà, A. Cassinese and G. Müller, *Eur. Phys. J. B*, 2000, **18**, 105.

25 A. Cassinese, A. Andreone, E. Di Gennaro, G. Pica, R. Vaglio, G. Malandrino, L. M. S. Perdicaro, I. L. Fragalà and C. Granata, *Supercond. Sci. Technol.*, 2001, **14**, 406.