ELSEVIER

Ceramics International 28 (2002) 115–121

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Electrochemical synthesis of TBCCO films

L.A. Ekal, P.M. Shirage, D.D. Shivagan, S.B. Kulkarni, N.V. Desai, S.H. Pawar*

School of Energy Studies, Physics Department, Shivaji University, Kolhapur 416 004, India

Received 29 January 2001; received in revised form 15 May 2001; accepted 9 July 2001

Abstract

Tl–Ba–Ca–Cu alloyed films were electrodeposited at a deposition potential of −1.25 V with respect to saturated calomel electrode (SCE). Intercalation of oxygen species into Tl–Ba–Ca–Cu alloyed films were then carried out at room temperature, the first time using the electrochemical technique. The films oxidized for 20, 25 and 28 min from 1 N KOH electrochemical bath show superconducting behaviour with T_c values of the order of 76.5, 103, and 114 K respectively. The room temperature electrochemical technique for oxygenation, reduces the reaction time, avoids annealing at higher temperatures and hence prevents the inhalation of toxic thallous oxide vapours during processing.

Keywords: Electrochemical synthesis; TBCCO films

1. Introduction

Superconductivity above 100 K in the Tl–Ba–Ca–CuO compound was discovered by Sheng and Hermann [1]. The superconductivity above 125 K for the same system was discovered by Parkin et al. [2]. It has been reported that the system exists with both single and double layer Tl–O structures and a multiple Cu–O layer from 1 to 5 [3,4] which gives rise to multiple phases. Of the various phases, the (2223) phase with three Cu–O layer has the highest superconducting transition temperature.

Due to the presence of high T_c superconducting phase in the Tl-based system, it has been at the focus amongst researchers all over the world. However, the Tl-based superconducting compounds have thermally unstable phases, and hence are difficult to prepare as the pure single phase. Various studies were aimed at optimizing the synthesis parameters and fabricating these materials in different forms for various applications. One of the forms for wide application is high quality thin films. Fabrication of high quality films/tapes is, however, a challenging task for research workers. Several kinds of processes are proposed for the thin films/tapes, including powder in a tube method [5], aerosol deposition [6], electrodeposition [7,8], the sol-gel method [9], screen printing and painting, and laser ablation. The majority of the existing thin film techniques require a high processing temperature especially for oxidation. At such a high temperature, Tl gets evaporated due to its high vapor pressure causing damage to the environment. In addition to Tl loss, the heating also transforms the initially formed (2223) phase into the (1223) phase and gives rise to random intergrowths between various layered phases. Thus, lowering the processing temperature is one of the most important problems.

In the present paper, an attempt has been made to replace the high temperature synthesis and the furnace oxidation by an electrochemical route. The electrodeposition allows us to deposit all the ionic constituents of high T_c Tl compound and provides mixing of the as-deposited materials on atomic scale, which permits short reaction times of the order of minutes. The electrochemical route can also be used to intercalate oxygen into alloyed layers of Tl-compound. This method was initiated first time by Wattiuax et al. [10] in 1989. Thus, the method proceeds into two steps: first the deposition of the Tl–Ba–Ca–Cu alloy thin films by the electrodeposition technique and then oxidation of the alloyed films by the same technique. Since the electrochemical route is a room temperature technique, it prevents the inhalation of toxic thallous oxide vapours during processing and one can monitor the oxidation of the Tl–Ba–Ca–Cu alloy layers in a controlled fashion. The technique has been successfully used to intercalate oxygen into

---

* Corresponding author. Fax: +91-231-691-533.
E-mail address: shpawar@pn3.usnl.net.in (S.H. Pawar).

0272-8842/02/$22.00
PII: S0272-8842(01)00066-9

BSCCO (2223) and YBCO thin films [11,12]. The different processing parameters such as deposition potential, current density, deposition period and oxidation period have been studied and reported. These thin films have been tested for their superconducting properties and X- ray diffraction measurements.

2. Experimental

Electrodeposition set up consists of a conventional three electrode system with saturated calomel electrode (SCE) as a reference electrode, Ag foil as working electrode, and the graphite plate as the counter electrode. The deposition bath was prepared using reagent grade nitrates of thallium, barium, calcium, and copper dissolved in dimethyl sulphoxide. The concentrations were 33, 60, 40 and 66 mM respectively. These concentrations were decided by optimizing the rates of deposition for individual constituents to get a Tl–Ba–Ca–Cu deposit in the required 2:2:2:3 stoichiometric amount. The deposition rate of each element under a constant potential at steady state condition can be represented by

$$\frac{d[M^{\circ}]}{dt} = k_m[M^{n+}] \tag{1}$$

where, k_m is the potential-dependent rate constant and $[M^{n+}]$ is the solution concentration of the metal ion.

The Tl-based alloy was electrodeposited onto mirror polished silver substrate using a scanning potentiostat / galvanostat (EG & G model 362) under potentiostatic conditions. An Omnigraphic X-Y recorder (model 2000) was used for recording the voltamogram and hence the electrodeposition potential. Electrodeposition was carried out at an ambient temperature.

Oxidation of the film so obtained was carried out using the same electrodeposition cell at room temperature. The Tl–Ba–Ca–Cu alloy thin film was used as a working electrode and 1 N KOH solution as an electrolyte. The oxidation was carried out for different lengths of time.

Microstructure of as-deposited and oxidized Tl–Ba–Ca–Cu alloy films was observed using a close circuit television (CCTV) attachment to a Metzer optical microscope (450×) in reflection mode. SEM was recorded with CAMECA SU-30 scanning electron microscope.

X-ray diffraction data were obtained on a microcomputer-controlled Phillips PW-3710 diffractometer using CuK_α radiation. A standard four-probe technique was used to measure resistance of the films as a function of temperature. Electrical contacts to the sample were made with a conducting silver paint. The sample was cooled using an APD close cycle refrigerator (model HC-2D).

3. Results and discussion

3.1. Processing conditions

Electrodeposition is an electrochemical process that allows deposition on a conducting substrates from a solution containing the ions of interest, here Tl^+, Ba^{2+}, Ca^{2+}, Cu^{2+}. These four ions can be co-deposited on the surface of the substrate when the potential is negative enough. Cathodic polarization curve shown in Fig. 1 determines the deposition potential for the Tl–Ba–Ca–Cu alloy deposition. The deposition was performed at a constant potential of −1.25 V with respect to SCE at the Ag cathode substrate electrode. For a given bath composition, the rate of deposition depends on current density which is found to be the function of time (Fig. 2). Thickness measurement, as it directly influences the surface of the film, was carried out and thickness of the film for a deposition period of 15 min was of the order of 2.5–3 μm. The rate of deposition, the slope of the plot of the thickness versus deposition period, was about 0.25 μm/min.

The Tl–Ba–Ca–Cu alloy film alongwith SCE and counter electrode (graphite) was dipped into 1N KOH solution to intercalate oxygen. The anodic polarization curve for oxidation of Tl–Ba–Ca–Cu alloy film is shown in Fig. 3. Above 700 mV (with respect to SCE), oxygen evolution occurs according to the reaction,

$$4OH^- \rightarrow 2H_2O + O_2 \uparrow +4e^- \tag{2}$$

The electrochemical oxidation was carried out for 15, 20, 25 and 28 min. This is similar to the electrochemical

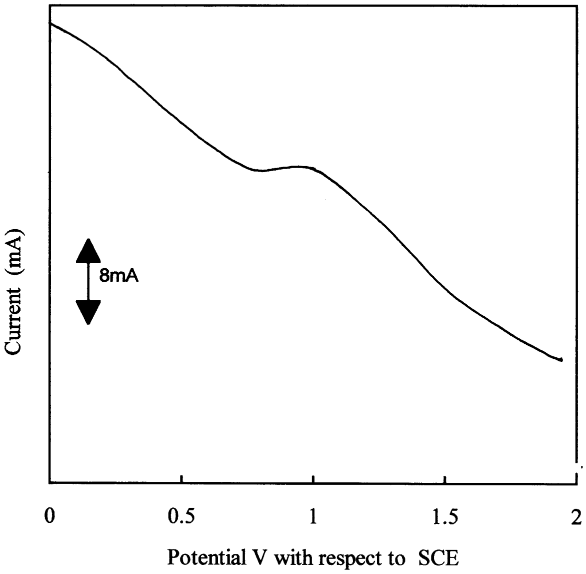

Fig. 1. Cathodic polarization curve for the Tl–Ba–Ca–Cu alloy deposition.

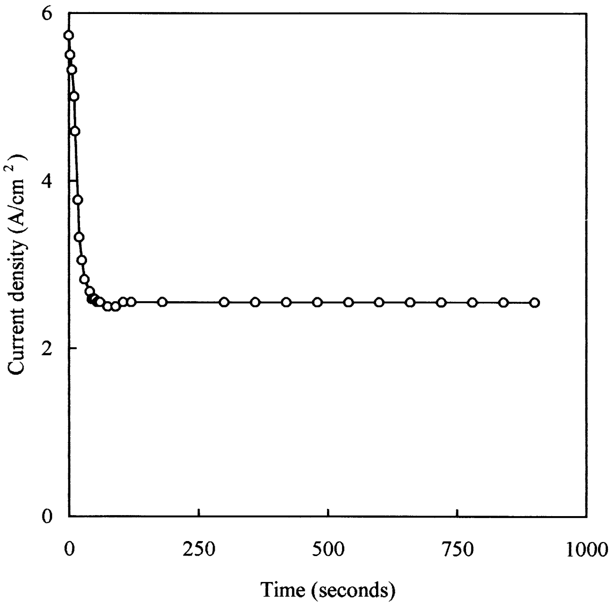

Fig. 2. Variation of current density with deposition period during the Tl–Ba–Ca–Cu alloy deposition at −1.25 V with respect to the SCE electrode.

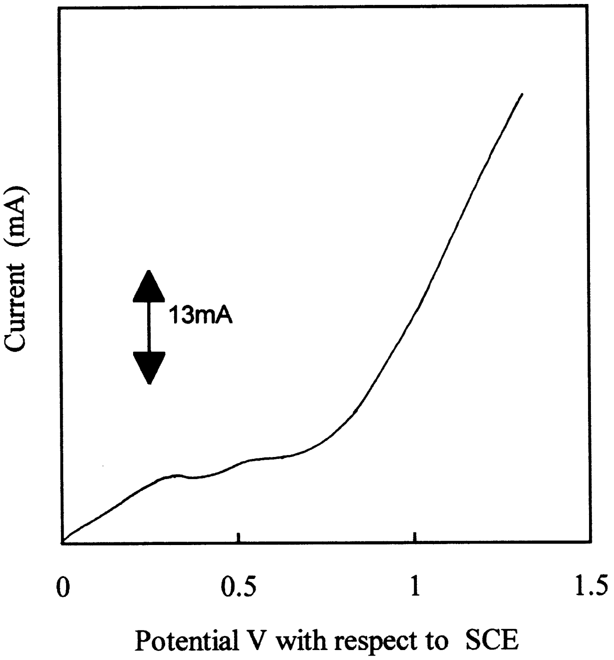

Fig. 3. Anodic polarization curve for oxidation of Tl–Ba–Ca–Cu alloy film.

oxidation of La_2CuO_4 [13,14], converting it from its insulating phase to the superconducting phase.

SEM micrographs of as-deposited and electrochemically oxidized Tl–Ba–Ca–CuO films are as shown in Fig. 4. The films obtained by the electrochemical route were smooth, uniform and dense. The oxidized Tl–Ba–Ca–CuO films showed compact intergrain spacings and improved grain dimensions.

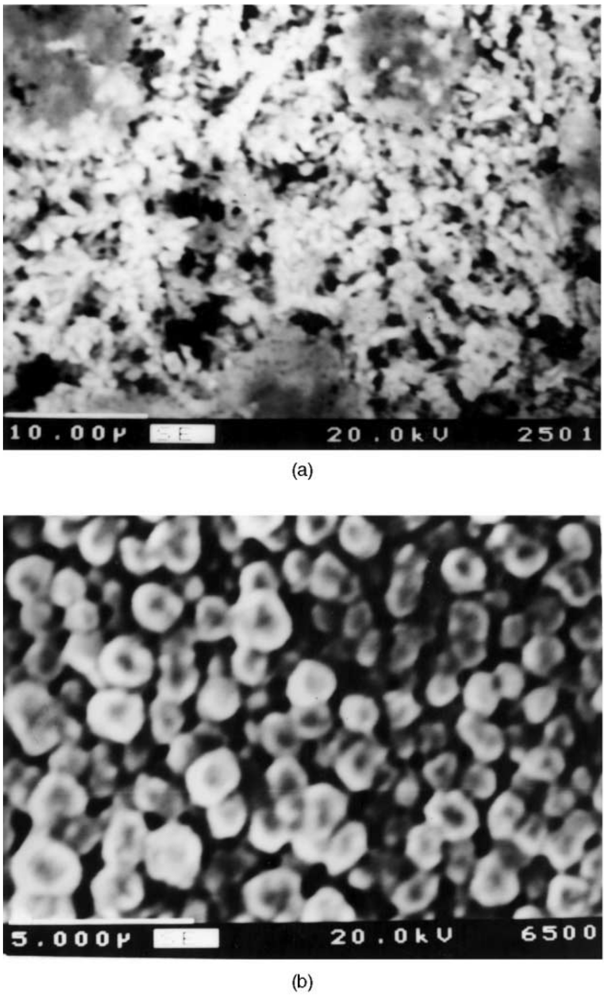

Fig. 4. SEM micrographs of (a) as-deposited and (b) electrochemically oxidized Tl–Ba–Ca–CuO films.

3.2. Structural properties

The X-ray diffraction patterns of the superconducting Tl–Ba–Ca–CuO thin film oxidized for 20, 25 and 28 min are shown in Fig. 5. Despite the bath composition adjusted for the Tl-(2223) phase, the X-ray analysis shows the presence of (2212) phase alongwith the (2223) phase. The fraction of (2212) phase is observed to decrease with the increase of oxidation period. The films oxidized for 20 min. contained a large amount of (2212) phase which was reduced to 80 and 40% for 25 and 28 min oxidation period, respectively. If we further increase the oxidation period, the amount of the (2212) phase increases highly.

The major diffraction peaks were indexed with tetragonal indices. The lattice parameters a and c were calculated from the observed d spacings of the diffraction lines using the formula

$$\frac{1}{d^2}=\frac{h^2+k^2}{a^2}+\frac{1^2}{c^2} \qquad (3)$$

and the calculated values are listed in Table 1.

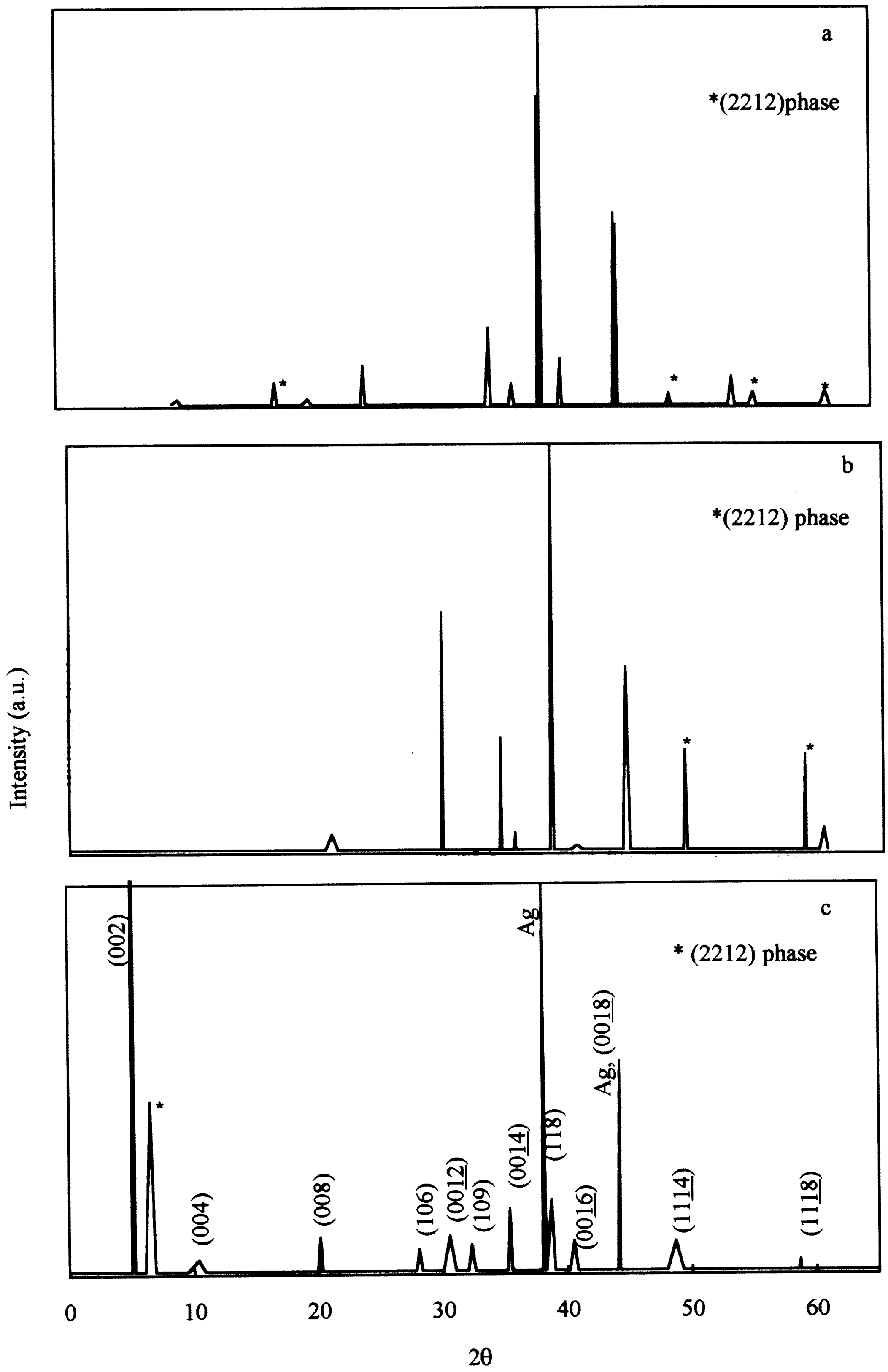

Fig. 5. X- ray diffraction patterns of the Tl–Ba–Ca–Cu–O films oxidized for 20, 25 and 28 min.

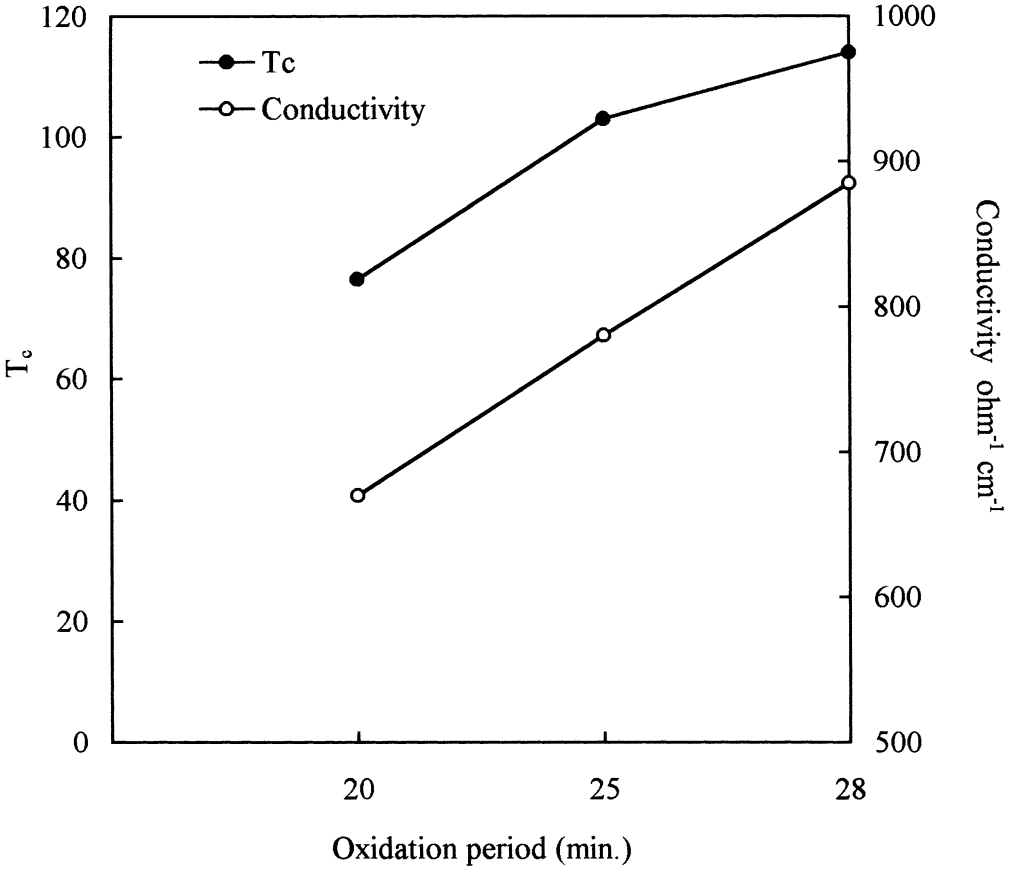

Fig. 6. Variation of room temperature conductivity and T_c with oxidation period.

Table 1
Values of *a* and *c* parameter of the films oxidized for 20, 25 and 28 min

Oxidation period	*a* A°	c A°
20	3.85	36.07
25	3.87	35.86
28	3.89	35.66

3.3. Electrical characterization

Conductivity was measured at room temperature for the Tl–Ba–Ca–CuO thin films oxidized for different periods and the variation of conductivity with oxidation period is shown in Fig. 6. It has been observed that the conductivity depends on the oxygen content of the films. For increasing oxygen content the conductivity increases.

Temperature dependence of the resistance of the Tl–Ba–Ca–CuO films oxidized electrochemically for different periods is shown in Fig. 7. It has been observed that the normal state behaviour for all the films is metallic and the superconducting transition temperature, T_c, increases with the increase of the oxidation period. The maximum $T_c = 114$ K was obtained for the film oxidized for 28 min. The variation in T_c with the oxidation period is shown in the Fig. 6.

The superconducting transition temperature within a given homologous series of cuprate phases varies with the number n of consecutively stacked CuO_2 layers in the infinite-layer unit [15,16]. In each phase, the transition temperature depends on the carrier concentration generally refers to as the amount of excess charge in the conducting CuO_2 sheets. This excess charge in the CuO_2 sheets is governed by the oxygen stoichiometry and can be varied by varying the amount of oxygen [17,18]. Therefore, as we increase the oxidation period of the Tl–Ba–Ca–Cu alloy, there is an increase in the amount of charge carriers in the conducting CuO_2 sheets and the relative intensity of peaks increases with oxidation period and hence the critical transition temperature.

It has been observed that the peak width reduces with oxidation period which is attributed to:

1. flatness of the CuO_2 sheets i.e. the alignment of the atoms in CuO_2 sheets becomes more perfect. (The flat CuO_2 sheets are responsible for an increased critical transition temperature.)

1. perfect alignment of the film with the substrate. (*c* axes are highly oriented with the substrate normal).

The films oxidized for 28 min exhibit a narrow peak and hence a relatively higher critical transition tem-

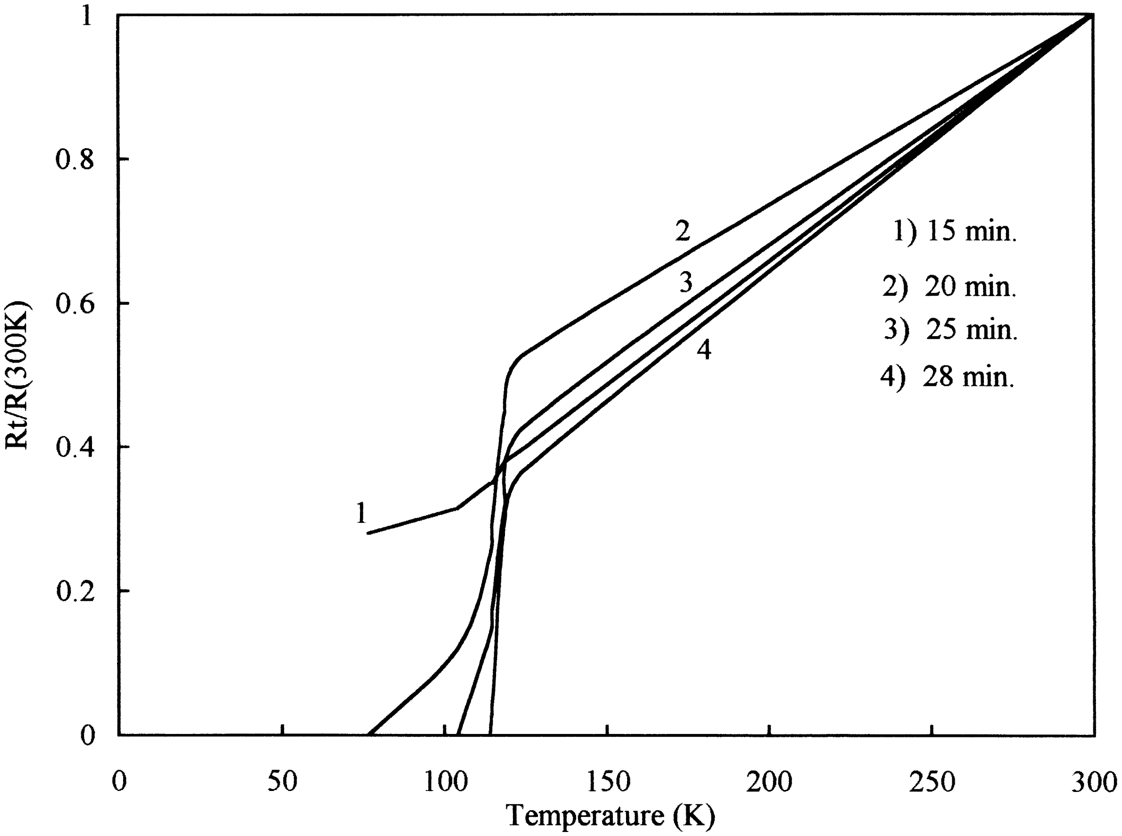

Fig. 7. Temperature dependence of the normalized resistivity of Tl-(2223) thin films oxidized for different periods.

perature. In addition, as we increase oxidation period the *c* axis parameter decreases and T_c increases which is in agreement with results reported earlier [19].

Also, it has been observed that the transition width changes with the oxidation period. The maximum width is found for the film oxidized for 20 min. For this oxidation period there may be small inhomogeneity in the oxygen content, due to which different areas in the film may have different T_c, leading to a wide transition. The minimum transition width for the films oxidized for 28 min clearly indicates homogeneous oxygen ordering which results in maximum T_c.

4. Conclusion

In conclusion, we have succeeded first time to oxidize the Tl- based system by using electrochemical potential as a driving force and made the superconducting Tl-(2223) thin films. The electrochemically prepared films show the presence of the (2212) as a secondary phase, the percentage of which is reduced as we increase oxidation period. An increase in the intensity of the major peaks and superconducting transition temperature provides a strong evidence for the electrochemical oxidation. Hence, carrier concentration in the CuO_2 sheets can be increased by inserting more amount of oxygen into the film using electrochemical technique.

Acknowledgements

The authors wish to thank the University Grants Commission, New Delhi (India), for financial support and Dr. A.V. Narlikar, Former Head, Superconductivity Group (National Physical Laboratory), New Delhi, for his constant encouragement.

References

[1] Z.Z. Sheng, A.M. Hermann, Nature (London) 332 (1988) 138.
[2] S.S. Parkin, V.Y. Lee, E.M. Engler, A.I. Nazzal, T.C. Huang, G. Gorman, R. Savoy, R. Beyers, Phys. Rev. Lett. 60 (1998) 2539.
[3] B. Raveau, C. Michel, M. Hervieau, D. Groult, Crystal Chemistry of High-Tc Superconducting Copper Oxides, Springer, Berlin, 1991.
[4] C.C. Toradi, in: T.A. Vanderah (Ed.), Chemistry of Superconducting Materials, Noyes, New Jersey, pp. 485–544.
[5] M. Okada, T. Nabatame, T. Yuasa, K. Aihara, M. Seido, S. Matsuda, Jpn. J. Appl. Phys. 30 (1991) 2747.
[6] H.K. Shing, X. Saxena, O.N. Srivastava, Supercond. Sci. Technol. 8 (1995) 448.
[7] R.N. Bhattacharya, R.D. Blaugher, Physica C 225 (1994) 269.

[8] L.A. Ekal, N.V. Desai, S.H. Pawar, Bull. Mater. Sci. 22 (4) (1999) 775.

[9] W. Jian, D. Yongiuan, Ch. Wenhui, Z. Yiaojun, Supercond. Sci. Technol. 6 (1993) 614.

[10] A. Wattiaux, J.C. Park, J.C. Grenier, M. Pouchard, C.R. Acad. Sci. Paris 310 (II) (1990) 1047.

[11] S.H. Pawar, S.B. Kulkarni, M.J. Ubale, Philos. Mag. Lett. 70 (1994) 327.

[12] L.A. Ekal, N.V. Desai, S.H. Pawar, Proceeding of "K.S. Krishnan Birth Centenary Conference on Condensed Matter Physics", Allahabad, India.

[13] J.C. Grenier, A. Wattiaux, N. Laueyte, J.C. Park, E. Maequestaut, J. Etourneau, M. Pouchard, Physica C 173 (1995) 139.

[14] J.C. Grenier, J.M. Bassat, J.P. Doumerc, J. Etourneau, Z. Fang, L. Founes, S. Petit, J. Mater. Chem. 9 (1999) 25.

[15] H. Yamauchi, T. Tamura, X.J. Wu, S. Adachi, S. Tanaka, Jpn. J. Appl. Phys. 34 (L) (1995) 349.

[16] T. Wada, A. Ichinose, H. Yamauchi, S. Tanaka, J. Ceram. Soc. Jpn. Int. Ed. 99 (1991) 303.

[17] R.G. Buckley, J.L. Tallon, I.W. Brow, M.R. Presland, N.E. Flower, P.W. Gilberd, M. Bowden, M.W. Milestone, Physica C 156 (1988) 629.

[18] Y. Shimakawa, Y. Kubo, T. Manaco, T. Satoh, S. Ijima, T. Ishibashi, H. Igarashi, Physica C 157 (1989) 279.

[19] W.L. Holstein, L.A. Parisi, J. Mater. Res. 11 (1996) 1349.