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# RHENIUM DOPED Tl-BASED SUPERCONDUCTORS PREPARED ON $CeO_2$ BUFFERED SAPPHIRE

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High-$T_C$ superconducting thin films based on thallium were prepared by a two step method combining RF magnetron sputtering and ex-situ thallination. We studied the influence of rhenium on the properties of the precursor and final superconducting films. Precursors of the $Re_{0.25}Ba_2Ca_2Cu_3O_x$ composition with a thickness of 300 nm were deposited on top of a $CeO_2$ buffered R-plane sapphire. Thallination was performed at 830–870°C. Rhenium avoids air contamination of the target used for sputtering we observed that it has no influence on the superconducting properties. X-ray analysis showed that the prepared films were $Tl_2Ba_2CaCu_2O_x$ phase with the c-axis growth orientation. The films had a zero resistance below 100 K.

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## 1 Introduction

Thin films of Tl-based high-temperature superconducting (Tl-HTS) phases have applications in a number of practical devices, especially in the field of devices for microwave communication [1]. Sapphire which has a low dielectric function and is very chemically inert is a good substrate for electronic applications. However, its hexagonal structure impose to cut it according to $(1\bar{1}02)$ plane to have a reasonable mismatch with cuprate basal plane ($\varepsilon = (a_{\text{film}} - a_{\text{subst.}})/a_{\text{subst.}} = 17\%$). The dielectric losses depend on the crystal direction and this makes the design of microwave devices complex [2]. The preparation of the Tl-Ba-Ca-Cu-O directly on the sapphire substrate should be processed below 800°C to avoid Al to diffuse into the film while the thallination temperature is generally larger than this temperature. This problem can be solved by the use of an appropriate buffer layer. A good candidate is a $CeO_2$ buffer layer with mismatch only $\varepsilon$ = 0.5 %. Only 20 nm of $CeO_2$ is sufficient to prevent Al diffusion from sapphire substrate toward the cuprate and thus high-quality HTS films can be processed on $CeO_2$ buffered R-plane sapphire [1].

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Rhenium substitution produces a chemical stabilization of the precursor against barium carbonation under ambient air [3]. Experiments with the Tl-based superconductors showed that Re doping reduces air contamination of the $Tl_2Ba_2CaCu_2O_x$ (Tl-2212), which is similar to what has been observed for the Hg-1212 and Hg-1223 phases [4]. In the case of mercury based superconductors rhenium doping increase flux pinning leading to an increased $B_{\rm irr}$ [5] and stabilize the superconducting phase [6].

In this paper we present the preparation of Tl-HTS thin films by RF magnetron sputtering and ex-situ thallination. Superconducting (Tl,Re)-Ba-Ca-Cu-O thin films were synthesized on top of $CeO_2$ buffered R-sapphire substrate. Rhenium doping was used for the stabilization of the target used for sputtering. We have studied the influence of rhenium on the electrical and structural properties of the prepared films.

## 2 Experimental

A two step method was used to prepare the Tl-HTS films. First, amorphous precursor films, 300 nm thick, with a nominal composition of $Re_{0.25}Ba_2Ca_2Cu_3O_x$, were deposited by RF magnetron sputtering from a single target of the same stoichiometry. The sputtering films were prepared at room temperature in Ar atmosphere at the pressure of 20 Pa. The deposition rate was 0.3 nm /s for a magnetron power of about 80 W.

The thallination of the precursor films was performed in a one zone configuration where both source of thallium and precursor film were kept at same temperature. The thallination temperature was of 830 – 850°C and took 30 minutes in oxygen atmosphere. The sample was introduced in the furnace at the annealing temperature. The precursor film was wrapped in a silver foil together with the source of thallium and placed into an alumina crucible. The film was in face contact with the thallium source. The thallium source was composed of an unreacted pellet with $Tl_2Ba_2Ca_2Cu_3O_{10}$ composition. The source of thallium was prepared by mixing $Tl_2O_3$, $BaCuO_2$ and $Ca_2CuO_3$ in stoichiometric ratio. The precursor powders were prepared by solid state reaction from carbonates ($BaCO_3$ and $CaCO_3$) and copper oxide at 920°C / 48 h in air.

The films were characterized by resistance measurements (R-T) using four probe configuration. The phases were analysed by X-ray diffraction (XRD) in back reflection configuration ($\theta$–$2\theta$, $CuK_\alpha$) and composition and microstructure were analysed by scanning electron microscopy – SEM and energy dispersive X-ray analysis - EDX.

## 3 Results and discussion

The composition of our precursor films was confirmed to be $Re_{0.25}Ba_2Ca_2Cu_3O_x$ by EDX analysis. Precursor films were thallinated at 830, 850 and 870°C in oxygen atmosphere. By XRD diffraction we found only (00$l$) reflections of the Tl-2212 phase (Fig. 1) whatever the thalliation temperature was. This indicates a strong c-axis texturation without any reaction with the $CeO_2$ buffer layer. Although the precursor films were Tl-0223, we obtained Tl-2212 phase. Higher phases (Tl-2223 and Tl-1223) are very difficult to synthesize in the open system. Thermodynamics and kinetics studies as well as neutron diffraction experiments have shown that the formation of the unsubstituted Tl-1223 phase implies the double TlO layer phases according to the

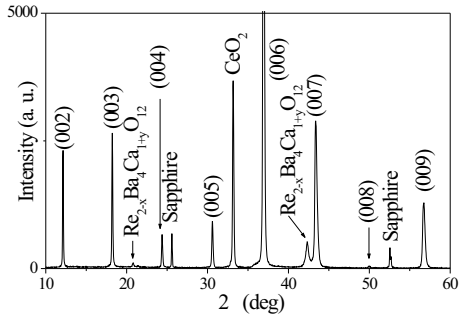


Fig. 1. The XRD pattern of rhenium doped Tl-based superconducting film. The diffractometer was slightly dis-aligned ($0.2^\circ$) to reduce the intensity of the sapphire substrate.

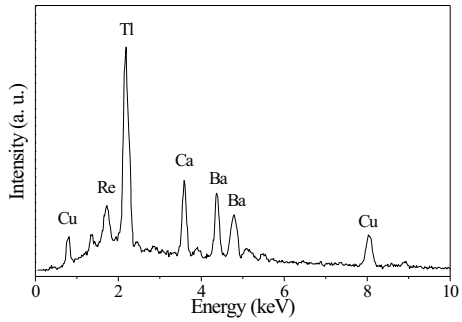


Fig. 2. The EDX spectrum of a Tl-based thin superconducting film.

sequence: precursors → Tl-2201 → Tl-2212 → Tl-2223 → Tl-1223 [7]. Obtained results suggest that much higher synthesis temperature and/or longer time should be used to obtain Tl-2223 phase.

From the positions of Bragg ($00l$) peaks we calculated the c-axis parameter. The average value of the c-axis parameter (c = 2.91 nm) corresponds within our experimental error to typical values given in the literature (c = 2.93 nm) [8]. In all diffractograms we observed two peaks (respectively at $2\theta = 20.80^\circ$ and $42.20^\circ$) that could be assigned to Bragg peaks of a cubic parasitic phase attributed to $Re_{2-x}Ba_4Ca_{1+y}O_{12}$ [9].

A qualitative analysis (EDX) (Fig. 2) confirmed the presence of Tl, Re, Ba, Ca and Cu elements in the films. From a quantitative analysis (EDX) and using ZAF correction we estimated the atomic fraction of Tl, Re, Ba, Ca and Cu elements, it corresponded to the nominal composition $Tl_{2-x}Re_xBa_2CaCu_2O_8$ with Re = 0.25.

The measurements of $R(T)$ confirmed a superconducting transition at low temperature. We studied the influence of the thallination temperature on the critical temperature $T_{C0}$ (zero resistance critical temperature). The thallination temperature of 830°C was sufficient to induce the

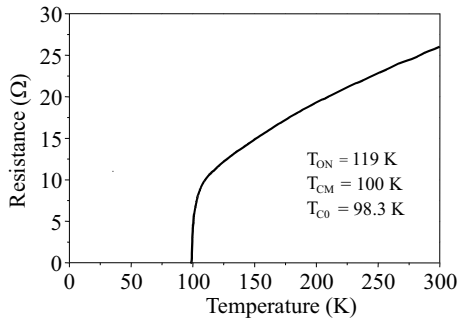


Fig. 3. The R(T) for a sample thallinated at 850°C.

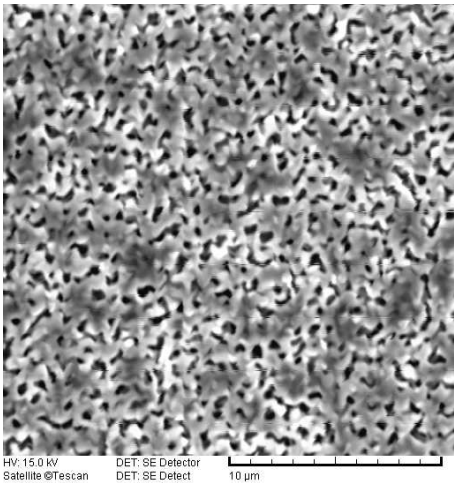


Fig. 4. The SEM image (secondary electrons) of the surface of Re doped Tl-based film.

Tl-2212 phase but without superconducting properties. At 850°C, critical temperatures up to 100 K were observed (Fig. 3) in good agreement with published data [10].

The observed critical temperature $T_{ON}$ (temperature at the onset of the transition) and $T_{CM}$ (the midpoint transition temperature) are typical for Tl-2212 phase. At 870°C the films had the same composition as those synthesized at 850°C, the superconducting properties were also identical. Increasing of the thallination temperature from 850 to 870°C did not influence the quality of the films.

The morphology of the films was studied by scanning electron microscopy (SEM) (Fig. 4).

It can be seen that the prepared films are homogenous with fine grains and only a small amount of impurities. Grains form an interconnected net providing channel for transport of the superconductivity channel. Rhenium containing non-superconducting phase $Re_{2-x}Ba_4Ca_{1+y}O_{12}$

identified by XRD analysis we observed on the surface of the film. This phase did not have influence on the critical temperature ($T_{ON}$, $T_{CO}$) of the sample so we suppose that this phase is not in the jointed grains of the superconducting phase.

## 4 Conclusion

Rhenium doped high-$T_C$ superconducting thin films based on thallium were prepared by a two step method: RF magnetron sputtering and ex-situ thallination in oxygen atmosphere. The use of rhenium ensures the stability of the target used for sputtering and did not have influence on the superconducting properties of the films. The films were made of Tl-2212 phase with a small amount of nonsuperconducting $Re_{2-x}Ba_4Ca_{1+y}O_{12}$ phase. This secondary phase did not depress $T_C$ which suggests its localisation out of grain boundaries. The critical temperatures $T_{C0}$ are up to 100 K. Our results indicate that the nonsuperconducting rhenium phase do not degrade the $T_{C0}$ values in comparison with Tl-Ba-Ca-Cu-O films on the base of fluorine precursors which we prepared before [11]. In the future we want to use these films for the preparation of the thin superconducting films based on mercury.

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### References

[1] A.P. Bramley, J.D. O'Conor, C.R.M. Grovenor: *Supercond. Sci. Technol.* **12** (1999) R57

[2] M. Shirakawa, M. Miura, T. Ohazama, Y. Shingai, A. Saito, M. Mukaida, S. Ohshima: *Physica C* **412–414** (2004) 1277

[3] A. Sin, P. Odier, M. Nunez-Regueiro: *Physica C* **330** (2000) 9

[4] H. Zhao, J.Z. Wu: *J. Appl. Phys.* **96** (2004) 2136

[5] J. Shimoyama, S. Hahakura, R. Kobayashi, K. Kitazawa, K. Yamafuji, K. Kishio: *Physica C* **235–240** (1994) 2795

[6] H. Schwer, R. Molinski, E.M. Kopnin, M. Angst, J. Karpinski: *Physica C* **311** (1999) 49

[7] Th. Hopfinger, M. Lomello-Tafin, J.L. Jorda, Ph. Galez, M. Couach, R.E. Gladyshevskii, J.L. Soubeyroux: *Physica C* **351** (2001) 53

[8] L.G. Johansson et al.: *Physica C* **220** (1994) 295

[9] D. De-Barros: *DSc. Thesis (2004)*, Université Joseph Fourier, Grenoble, France

[10] A. Sundaresan, C. Ström, S. Eriksson, I. Bryntseet.: *Physica C* **388–389** (2003) 473

[11] Š. Chromik M. Jergel, Š. Gaži, V. Štrbík, F. Hanic, C. Falcony, M. Vaško, Š. Beňačka.: *Physica C* **354** (2001) 429