Superconducting Tl- and Hg-based cuprate thin films

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Abstract

We have prepared and studied both Tl- and Hg-based high critical temperature superconducting (HTS) thin films. The standard two-step fabrication procedure was used. Ba-Ca-Cu-(O,F) precursor film was prepared from fluorides BaF_2, CaF_2 and metallic Cu at room temperature. After ex-situ thallination or mercuration of the precursor film at high temperature 750 - 860 °C the superconducting Tl- and Hg-based cuprate thin films were obtained. The zero resistivity critical temperature above 100 K was reached for both types of HTS. The estimated transport critical current densities were 10^4 A/cm^2 at 77 K for Tl- and 10^4 A/cm^2 at 100 K for Hg-based cuprate thin films. The stability of the films properties during more than 1 year will be presented.

1. Introduction

The Tl- and Hg-based cuprate thin films are promising candidates for high critical current density, high frequency, high performance applications and also microwave passive devices operating at the temperature above 77 K. The microwave surface resistance R_S of the HTS thin films at 77 K and 10 GHz (~ 0.1 - 0.5 mΩ) is a few times lower than that of copper (~0.9 mΩ). The $HgBa_2CaCu_2O_{6+\delta}$ (Hg-1212) thin film provides such low R_S ~ 0.3 mΩ even at temperature 120 K [1]. On the base of Hg-1212 thin film deposited on bicrystal $SrTiO_3$ substrate, dc SQUID was prepared operating up to 111 K [2]. Thallium based HTS thin films as band pass filter for Mobile Communication System was used [3].
In this letter we refer about the Tl- and Hg-based HTS thin films prepared from fluorine containing precursor Ba-Ca-Cu-(O,F). The preparation, structural characterization and some thin film structures were investigated.

2. Experimental

The Tl- nad Hg-based thin films were fabricated using two-step process. At first the precursor film was prepared by sequential evaporation of BaF_2, Cu and CaF_2 to produce 0.2 μm thick precursor film with the 2:2:3 cation ratio on various substrates (single crystal MgO, $LaAlO_3$, $SrTiO_3$ or Al_2O_3 buffered by CeO_2). During the precursor deposition, the substrate was kept at room temperature, followed by an ex-situ vacuum annealing step at the temperature 720 °C, in dry oxygen at partial pressure of 10^{-2} Pa. The oxygen partial pressure was gradually increased to the atmospheric one, without changing the temperature of the substrate, to remove substantial part of fluorine from the BaF_2 and CaF_2 containing precursor film. We prefer this type of fluorine reduction invented by our group, because this process avoids that more complicated one linked with using a wet oxygen. Such precursor films show increased chemical resistance to atmospheric surroundings [4]. In the second step precursor films were thallinated at 850 °C for 30 min. in an oxygen flow being placed in a close contact with the crude Tl-Ba-Ca-Cu-O pellet used as a source of thallous (Tl_2O) oxide [4]. The similar procedure was used for mercuration of the same precursor films placed between two HgPbSrBaCaCuO pellets sealed in a quartz tube and annealed at 800 °C for 60 min. [5]. The more stable Re doped HgBaCaCuO pellets as a Hg-source were also used [6].
Many structural investigations we have employed. The material phases and film crystallographic orientation were investigated using the X-ray diffraction (XRD) (Θ - 2Θ scan, ω-curves and grazing incidence method). Both, energy dispersive X-ray (EDX) and wave dispersive X-ray (WDS) electron microanalyses were performed to study chemical compositions of the films. Scanning electron microscopy (SEM) was used to determine film surface morphology. The normal state and

superconducting properties of thin films were measured by a four-probe method and by microwave cavity technique.

3. Results

Superconducting Tl-based cuprate thin films

The structural analyses and electrical measurements revealed that Tl-based films consist wholly from $Tl_2Ba_2CaCu_2O_x$ (Tl-2212) phase regardless of cation ratio 2:2:3 or 2:1:2 in precursor film and substrates [7]. The XRD pattern yields pure c-axis growth orientation of Tl-2212 phase with lattice parameter c = 2.92 nm. The Tl-2212 thin films show superconductivity transition with typical values T_C(onset) ≥ 120 K and T_{C0} ≥ 100 K. In Fig.1 the temperature dependence of resistivity is shown for 16 μm wide

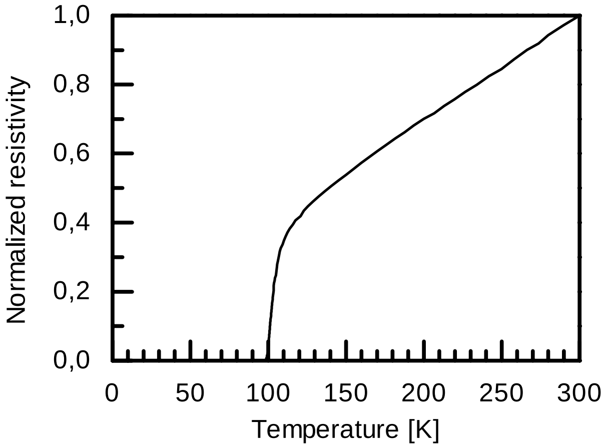

Fig. 1. Normalized resistivity versus temperature of the 16 μm wide microstrip.

microstrip patterned from Tl-2212 thin film. The room temperature resistivity ranged from 1 to 10 mΩcm and decreased approximately linearly down to 130 K with the ratio of $\rho_{300} / \rho_{130} \approx 2$. The critical current density j_C reaches values $1x10^5$ at 4.2 K and $1x10^4$ A/cm^2 at 77 K. The analyzes of temperature dependence of j_C indicate two different mechanisms of critical current limitation. At lower temperature flux-creep mechanism is responsible for limitation of critical current, at temperatures close to T_{C0} (0.8-1.0 T_{C0}) the S-N-S (Superconductor-Normal metal-Superconductor) type of weak links determine the critical current density of the films [8].

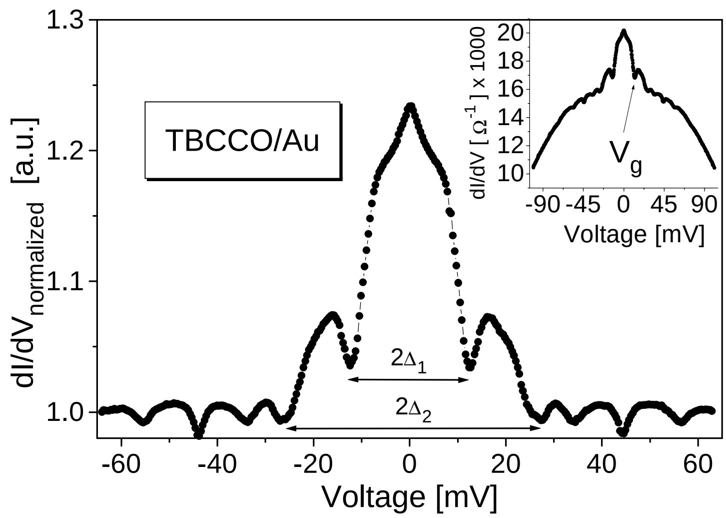

Fig. 2. Normalized differential conductance of $Tl_2Ba_2CaCu_2O_x$/Au junction for lower voltage. The inset shows a decrease of junction differential conductance with increasing voltage.

The $Tl_2Ba_2CaCu_2O_x$/Au sandwich-type heterostructures were prepared to study the interface quality of Tl-based cuprates (S) in contact with a normal metal (N) which is frequently used in cryoelectronic devices. To characterize the superconducting properties of thin films and S/N interface, resistance vs. temperature, current-voltage chracteristics and their derivates were measured. The $Tl_2Ba_2CaCu_2O_x$/Au junctions exhibit a decrease of the junction resistance with temperature indicating a direct metallic S/N contact. Such claim is confirmed by the derivate chracteristic shown in Fig. 2. The differential conductance decreases with increasing voltage but a rapid increase of the differential conductance below V_g (voltage corresponding to an energy gap) is a typical feature in the case of the presence of Andreev reflections at the S/N interface [9].
Our investigations showed that the degradation of $Tl_2Ba_2CaCu_2O_x$/Au interface is negligible and no or very small native oxide barrier on the surface of $Tl_2Ba_2CaCu_2O_x$ film is created. The Tl-based films are more convenient for preparation of direct metallic S/N contacts than YBaCuO films. On the other hand, the $Tl_2Ba_2CaCu_2O_x$ surface morphology is much worse compared with YBaCuO surface morphology. Therefore, it is necessary to improve sufficiently the technology for the preparation of higher quality $Tl_2Ba_2CaCu_2O_x$ thin films.

Superconducting Hg-based cuprate thin films

The structural analyses showed that Hg-based cuprate thin films consist mainly from $Hg_1Ba_2Ca_1Cu_2O_y$ (Hg-1212) phase and partially from $Hg_1Ba_2Ca_2Cu_3O_z$ (Hg-1223) phase. Fig.3 shows the XRD pattern

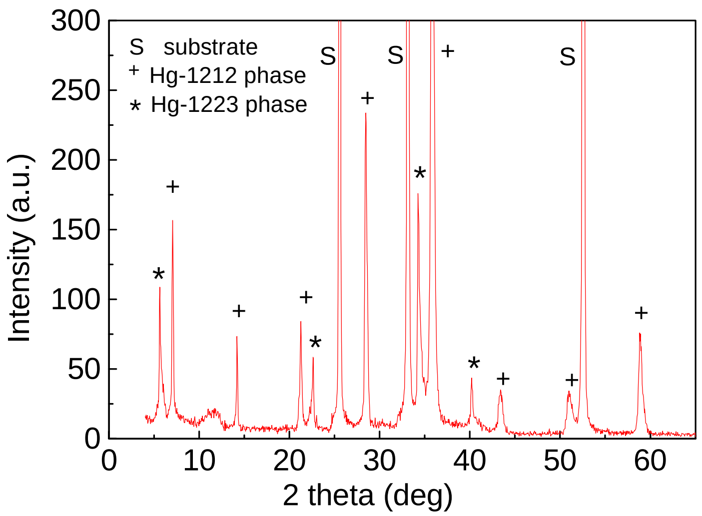

Fig. 3 XRD pattern of the Hg-cuprate film with the highest content of Hg-1223 phase

of our Hg-based cuprate film with the highest content of Hg-1223 phase. The Hg-1223 phase is a superconductor with the highest critical temperature T_C ~ 135-138 K for bulk samples at ambient pressure [10]. In thin films $T_{C0} \approx 130$ K was achieved [11]. From SEM studies and electrical measurements we found that the Hg-based films do not cover the substrate homogeneously. The film parts with Hg-1223 contribution are only of area a few mm^2. The covering of the substrate by Hg-1212 film is much better. The dc transport current properties of the thin films are strongly depended on crystallography and electrical connections of individual Hg-1212 or Hg-1223 grains. Therefore, the T_{C0} values of thin films are lower than for bulk materials. The intergranular connections are more sensitive to degradation processes, which hinder the superconducting current path. We prepared Hg-1212 thin films on $LaAlO_3$ substrates without evident granular morphology of the film and stability of electrical parameters significantly increased. In Fig.4 are shown transition curves for Hg-1212 thin film sample without changes of superconducting transition temperature during 18 months. The highest T_{C0} values about 117 K were observed and critical current density $j_C \approx 1x10^4$ A/cm^2 of Hg-1212 film at 100 K and zero magnetic field was achieved. The estimation of j_C for thin films with increased content of Hg-1223 phase is in progress.

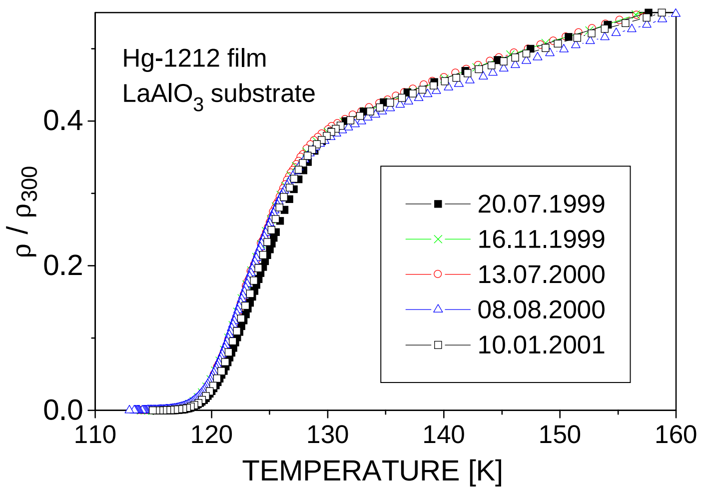

Fig. 4. The long-time stability of superconducting transition of Hg-1212 thin film

4. Conclusion remarks

We have prepared Tl- and Hg-based cuprate thin films on various, including low loss substrates at microwave frequencies. The zero resistance critical temperatures for the best Tl-2212 films are about 100-104 K and 115-117 K for Hg-1212 thin films. The critical current density reaches value $1x10^4$ A/cm^2 at 77 K for Tl-2212 film and $1x10^4$ A/cm^2 at 100 K for Hg-1212 film. The Tl-based films were patterned and some structures (microstrips, sandwich junctions, coplanar tranmission lines) were prepared. The Hg-based films are till now not satisfactory homogeneous for preparation of some structures. Some Hg-1212 thin films contain also Hg-1223 phase and are at present under investigations.

Acknowledgements

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References

[1] R.S. Aga, S, Yan, Y. Xie, S. Han, J.Z. Wu, Q. Jia, and C. Kwon, Appl. Phys. Lett. **76** (2000) 1606
[2] A.Tsukamoto, K. Takagi, Y. Moriwaki, T. Sugano, S. Adachi, and K. Tanabe, Appl. Phys. Lett. **73** (1998) 990
[3] E.R. Soares, K.F. Raihn, A.A. Davis, R.L. Alvarez. P.J. Marozick, and G.L. Hey-Shipton, IEEE Trans. Appl. Supercon. **9** (1999) 4018
[4] Š. Chromik, Mi. Jergel, F. Hanic, S. Jimenez, Ma. Jergel, V. Štrbík, C. Falcony, Š. Beňačka, J.C. Cheang-Wong, and E. Andrade, Thin Solid Films **373** (2000) 129
[5] G. Plesch, Š. Chromik, V. Štrbík, M. Mair, G. Gritzner, Š. Beňačka, I. Sargánková, and A. Bučkuliaková, Physica C **307** (1998) 74
[6] Š. Chromik, A. Sin, V. Štrbík, paper in preparation
[7] Š. Chromik, M. Jergel, Š. Gaži, V. Štrbík, F. Hanic, C. Falcony, M. Vaško, and Š. Beňačka, Physica C (2001) in print
[8] V. Štrbík, Š. Chromik, M. Jergel, D. Machajdík, Š. Beňačka, and A.P. Kobzev, J. of Superconductivity **11** (1998) 65
[9] V. Štrbík, A. Plecenik, Š. Chromik, Š. Beňačka, M. Zuzčák, D. Machajdík, and M. Kunc, Acta Physica Slovaca **50** (2000) 571
[10] S.N. Putilin, E.V. Antipov, A.M. Abakumov, M.G. Rozova, K.A. Lokshin, D.A. Pavlov, A.M. Balagurov, D.V. Sheptyakov, and M. Marezio, Physica C **338** (2000) 52
[11] S.H. Yun and J.Z. Wu, Appl. Phys. Lett. **68** (1996) 862