Two step synthesis of $TlBa_2Ca_2Cu_3O_x$ films on Ag substrates by spray pyrolysis of metal-acetylacetonates

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Recibido el 13 de agosto de 2008; aceptado el 24 de noviembre de 2008

A two-step synthesis process was performed to obtain $TlBa_2Ca_2Cu_3O_x$ (Tl-1223) superconductor films. The synthesized films were obtained under different thallium diffusion conditions in a two-zone furnace precursor films were deposited at 550°C on silver substrates using the spray pyrolysis technique from acetylacetonates (2, 4-pentanedionates) as reagents. Second, a thallium diffusion process is carried out to incorporate Tl in the films. For this task Tl_2O_3 pellets, as a Tl source, were used at 750°C. Different oxygen flow rates at atmospheric pressure were used in order to get the thallous oxide p(Tl_2O) partial pressure in the range of 6.9×10^{-4} to 6.1×10^{-2} atm. The Tl-1223 phase was obtained in all cases, though for a low p(Tl_2O), the films presented the $BaCuO_2$ phase mixed with the Tl-1223 one. Critical temperature (T_C) values for these films were in the range of 90 to 102 K.

Keywords: Superconductors; thin films; spray pyrolysis.

El proceso de síntesis de dos pasos fue realizado para obtener películas superconductoras de $TlBa_2Ca_2Cu_3O_x$ (Tl-1223). Las películas sintetizadas fueron obtenidas bajo diferentes condiciones de difusión de talio en un horno de dos zonas. En el primer paso, las películas precursoras se depositaron a 550°C sobre substratos de plata usando la técnica de rocío Pirólitico a partir de acetilacetonatos (2,4-pentanedionatos) como reactivos. En el segundo paso, se llevó a cabo un proceso de difusión de talio para incorporar Tl en las películas. Para ésta tarea, se usaron pastillas de Tl_2O_3 como fuente de talio a 750°C. Se usaron diferentes razones de flujo de oxígeno a presión atmosférica para obtener presiones parciales de óxido taloso p(Tl_2O) en el intervalo de 6.9×10^{-4} to 6.1×10^{-2} atm. La fase Tl-1223 se obtuvo en todos los casos, aunque a bajas presiones parciales de p(Tl_2O), las películas presentan la fase $BaCuO_2$ mezclada con la fase Tl-1223. Los valores de temperatura crítica para estas películas se encuentran en el intervalo de 90 a 102 K.

Descriptores: Superconductores; películas delgadas; rocío pirolítico.

PACS: 74.78.Bz; 74.62.Bf; 74.72.Jt; 81.15.Rs

1. Introduction

Tl-Ba-Ca-Cu-O high-temperature superconducting (Tl-HTS) films have been the subject of extensive research activity. In particular the Tl-1223 phase is of interest because of its electronic properties, high-critical current, low anisotropy, and great flux pinning [1]. Tl-1223 films have been reported to have a zero-resistance temperature up to 112 K and a critical current density, under zero magnetic field, of the order of 10^4 A/cm^2 at 77 K [2]. However, Tl-based superconductors have been reported to have difficulties in controlling the formation of single superconducting phase due to their volatility at the typical growth temperatures used for these cuprates. In order to overcome this difficulty, *ex-situ* growth methods have been used extensively for the synthesis of Tl-HTS thin films such as the two-step process. This process consists in first depositing a non-superconducting precursor film with the required Ba-Ca-Cu oxides composition onto a substrate, by either d.c. or rf sputtering, screen printing, spray pyrolysis or any other deposition technique [3,4,5], and then placing this precursor film in a furnace for thallination and conversion to a Tl-HTS material phase. Chemical processes such as spin coating have also been used to deposit the precursor films, but the preparation time is too long, and requires a post annealing treatment at 600 °C for several hours (10 h) [6]. Similarly, the screen-printing method needs several steps, first the sol and later the gel formation with posterior conversion into oxides at high temperatures (800 °C) for very long times (50 h) [7]. Spray pyrolysis is a very simple, low-cost deposition technique that has been used extensively for the synthesis of Tl-HTS precursor films using metal nitrate solutions, although in this case, several deposition cycles (heating – cooling) are required to obtain the adequate precursor film synthesis and thickness [8,9]. Similar thermal treatments are required in precursor films deposited by electrodeposition techniques.

Thallium diffusion has been performed in either one-or two-zone furnaces in order to obtain thallium based superconductor films. A one-zone furnace has been used to obtain superconductor films consisting of a mixture of Tl-2212 and Tl-2223 phases [10,11]. In these works, precursor films had been previously deposited by spray pyrolysis from acetylace-

tonates as reagents. However, the Tl-1223 phase has been difficult to obtain reliably in the one-zone furnace. Other types of superconductor films have also been obtained from acetylacetonates [12]. Processing in a two-zone furnace is thought to be the most appropriate for Tl-HTS films since, in principle, it allows for independent control of the diffusion temperature, and the partial pressure of both oxygen and Tl-oxide, each of which are critical thermodynamic variables for the formation of a given Tl-HTS phase. Reported phase diagrams indicate that the optimal conditions for obtaining the $TlBa_2Ca_2Cu_3O_{9-x}$ phase in a two-zone furnace correspond to p(Tl_2O) of $2-3.5\times10^{-3}$ atm in 1 atm of O_2 [13]. Several substrates have been used for $TlBa_2Ca_2Cu_3O_{9-x}$ thin films, mainly single crystals such as MgO, $LaAlO_3$ and YSZ [14], and on a few metallic substrates, such as silver, haste alloy or nickel [15]. Silver substrates are the ones that do not require a buffer layer to avoid surface reactivity with the superconducting cuprates [16]. Tl-1223 films on polycrystalline YSZ were obtained in a two-zone furnace at p(Tl_2O) of $2-3\times10^{-3}$ atm in 1 atm of O_2, at a sample temperature of 860°C and 735–750°C for the thallium source. In this case, the precursor films were deposited by spray pyrolysis using nitrates as reactants, and a post annealing treatment at 600°C for 8 hrs. after the thallium diffusion process was required [17]. Other authors have reported similar types of procedures for the synthesis of Tl-1223 films on Ag substrates, although in that case the films were obtained after a 30 min. thallium diffusion at a p(Tl_2O) of 1.1×10^{-3} atm. in 1 atm of O_2 [18]. Similarly, the synthesis of Tl-1223 films on polycrystalline Ag using the spin coating technique for precursor film deposition required post-annealing treatment at 600°C in an oxygen flow for 10 hours.

In this work, the process to synthesize films of the $TlBa_2Ca_2Cu_3O_y$ phase on silver substrates from acetylacetonates reagents by spray pyrolysis technique and two-zone furnace is described. Aceylacetonates have been used extensively for metallic oxide layers deposition using the spray pyrolysis technique, but they are not among the usual reagents used to prepare precursor films for Tl-HTS. However, these reagents seem to offer better advantages than nitrates since a single deposition cycle is usually required to obtain precursor films with equivalent characteristics and without further annealing treatments, as is shown in this paper. Also, different partial pressures of thallous oxide in a two-zone furnace thallination process, and the effect of this parameter, on the structural and electrical characteristics of the films, were studied.

2. Experimental Details

Tl-1223 superconductor thin films were synthesized following a two step process. In the first step, precursor films with a chemical stoichiometry close to $Ba_2Ca_2Cu_3Ag_{0.2}$ were deposited by ultrasonic spray pyrolysis technique using a spraying solution prepared from Ba, Ca, Cu and Ag acetylacetonates (2, 4-pentanedionates) dissolved in N, N- Dimethylformamide, (N,N-DMF). For this task a 0.006M concentration was prepared from the latter reagents. Silver foil from Goodfellow (99.9%) was cut to $10\times5\times0.25$ mm plates to be used as substrates. In order to get them with a low surface roughness, one face was mechanically polished using 1.0 μm and 0.1 μm grit size diamond suspension. The precursor film deposition time was 40 minutes at 560°C, without any further annealing treatment. A commercial ultrasonic humidifier, operating at 750 KHz, was used to generate the mist of the previous solution. Air was used as carrier gas at a flow rate of 5.0 l/min. About 60 ml of the spray solution was employed for the 40 min. of deposition.

Thallium diffusion in the precursor films was carried out in a two-zone furnace using a reactive chamber consisting of a 30 cm long high purity alumina tube with 0.9 cm of inner diameter. As the source of thallium, a 0.1 gram Tl_2O_3 pellet was used and placed inside a gold boat. The precursor film and the Tl_2O_3 pellet were put inside the alumina tube with a separation of 24 cm between them. The thallium source was heated to 750°C and the precursor film to 850°C at a rate of 350°C/h and 400°C/h, respectively. These temperatures were maintained during the thallium diffusion process and then the furnace was switched off to cool it down to room temperature. An O_2 gas flow was introduced into the furnace chamber at different rates: 40, 20, 10, 5 and 0.5 cm^3/min, in such a way that the partial pressure of the generated thallous oxide (Tl_2O) at the thallium source was calculated for these flows to be: 6.9×10^{-4} atm, 1.9×10^{-3} atm, 4.9×10^{-3} atm, 1.4×10^{-2} atm and 6.1×10^{-2} atm. respectively at a total pressure of $\sim$1 atm (oxygen partial pressure 0.99 – 0.93 atm). The variation in p(Tl_2O) (6.9×10^{-4} – 6.1×10^{-2} atm in $\sim$1 atm of O_2)was obtained by varying the oxygen flow, and it was calculated following the method reported by Holstein [19]. A JEOL, JSM-6300, Electron Microscope, equipped with an EDS system was used to estimate the chemical composition as well as the surface morphology of both, the

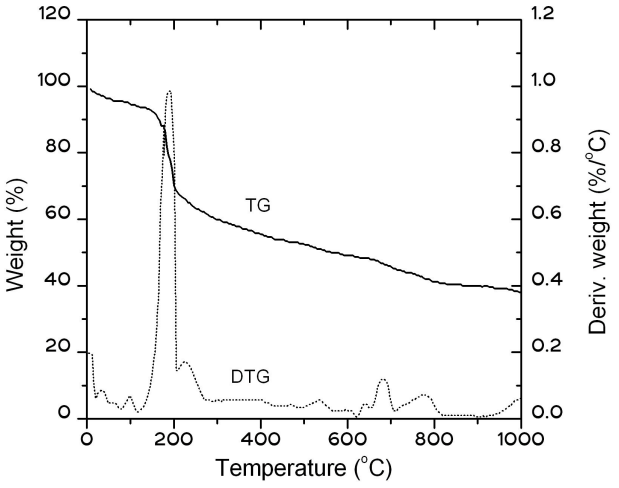

FIGURE 1. Thermogravimetric (TG, DTG) data for homogenized acetylacetonate mixture of Ba:Ca:Cu = 2:2:3.

precursor and the thallinated films. The crystalline structure of the films was evaluated with a Siemens D-5000 Diffractometer, (Cu Kα, 0.15406 nm). Electrical characteristics of the films, such as resistance vs. temperature (R vs. T), were measured using the conventional four-probe technique. R vs. T measurements were carried out using mechanical contacts and a constant current of 100 mA. The film thickness was measured in a Dektak^3 surface profiler system from Veeco.

3. Results and discussion

Figure 1 shows the thermal decomposition of a mixture of barium, calcium, and copper acetylacetonates in a 2:2:3 chemical stoichiometry. From the figure, it is observed that a noticeable loss of weight occurs at 200°C, approximately. The remaining mixture is then slowly decomposed at higher temperatures, probably due to the slow decomposition of barium and calcium acetylacetonates. This result might indicate that a mixture of the oxides of barium, calcium, and copper is obtained in the precursor films. It is known that prior to decomposition, the acetylacetonates are subjected to melting at relatively low temperatures, thus, on contact with the substrate, they can melt and conform well to the substrate's surface. In addition, depending on the solvent and deposition conditions, the solid or partially molten metal-organic material may eventually vaporize as it approaches the substrate, and then the film might undergo a true chemical vapor deposition (CVD) reaction [20]. Upon deposition, the precursor films were characterized by means of EDS. The average chemical composition of the precursor films was 29.5 ± 0.8, 25.7 ± 0.7 and 44.9 ± 0.8 %at for Ba, Ca and Cu respectively. The precursor films' chemical composition was slightly higher in Ba with respect to the nominal $Ba_2Ca_2Cu_3$ composition (28.6, 28.6 y 42.8 %at). The silver content, $\sim$1.2 %at, was measured on powder obtained from a precursor film to avoid the substrate signal, and corresponded approximately to $Ag_{0.2}$ (1.4 %at), added to the precursor films.

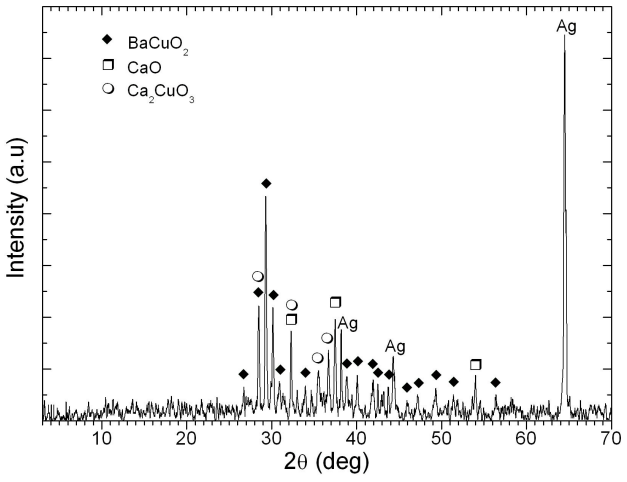

FIGURE 2. X-ray diffraction pattern of a precursor film.

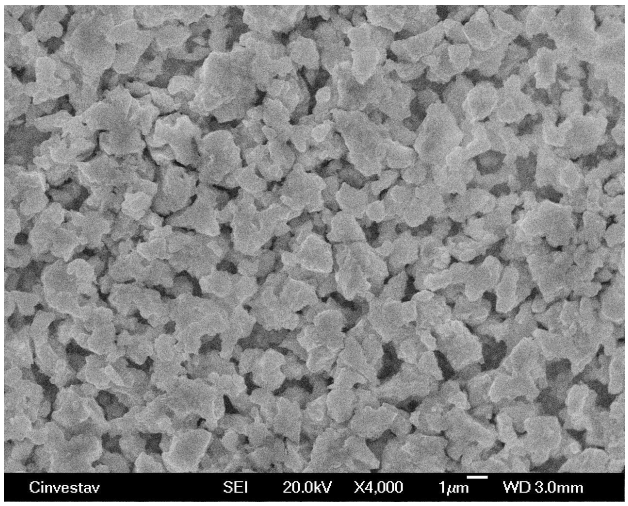

FIGURE 3. Typical SEM image of precursor films.

The precursor films were about 4 μm thick. Fig. 2 shows a typical X-ray diffraction pattern for these films: they are polycrystalline and the diffraction peaks observed corresponded to $BaCuO_2$, CaO, and Ca_2CuO_3 as indicated in the diffraction pattern. Fig. 3 shows the granular morphology of these films, with particle size of 2 to 3 μm. Table 1 summarizes the experimental conditions and chemical composition of both precursor and superconducting films as measured by EDS. The characteristics of the precursor films prepared by spray pyrolysis from acetylacetonates compare well with those obtained from metal nitrates using a more complex process involving a post-deposition annealing at high temperatures [9,18]. Films synthesized from acetylacetonates can generally be obtained in a one-deposition cycle and do not require additional annealing treatments, while in the case of nitrates, the films have to be prepared in about 6 cycles of deposition at 275°C and an annealing at 600°C for 5 min., in order to get films of a thickness of ~ 3 μm.

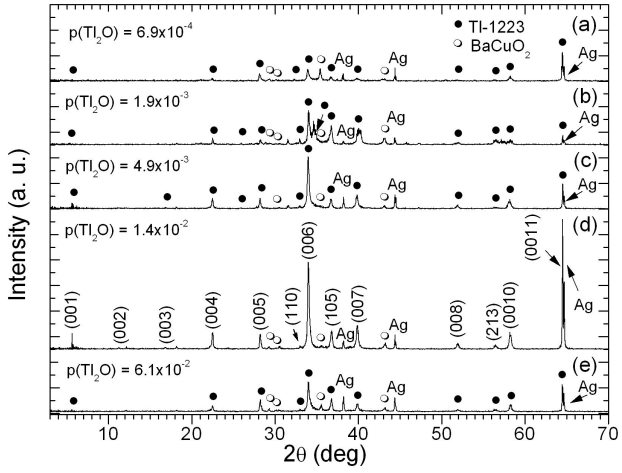

FIGURE 4. X-ray diffraction patterns of the superconducting films obtained under different p(Tl2O).

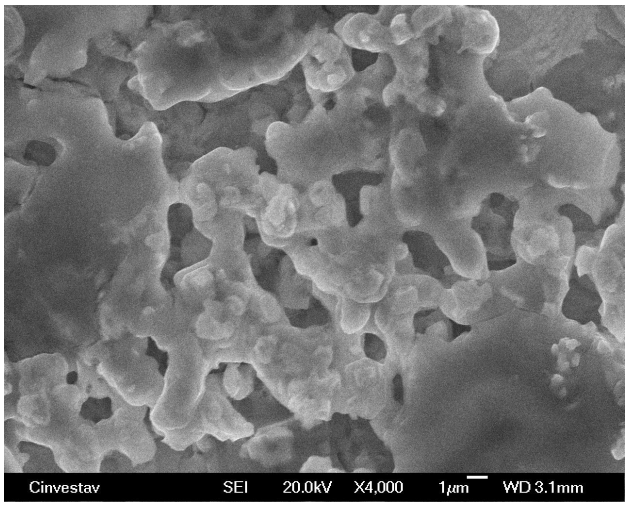

FIGURE 5. SEM image of thallinated films.

Figure 4 shows the X-ray diffraction patterns for the superconducting films after thallium diffusion at different partial pressures of thallous oxide p(Tl_2O). In all cases, peaks associated with the $TlBa_2Ca_2Cu_3O_y$ phase were observed, and with predominance, the peaks associated to the $(00l)$ reflections suggesting a preferential crystalline orientation with the c-axis normal to the films surface. However, there is also the presence of peaks related to $BaCuO_2$, the strongest at the lowest p(Tl_2O) studied and in much less intensity for the rest of the cases. The intensity of the diffraction peaks, as an indication of the crystalline quality, increases with increasing p(Tl_2O) up to a maximum at p(Tl_2O)=1.4×10^{-2} atm. There is a competing effect between the better formation of the superconducting phase as the p(Tl_2O) is increased as well as the volatility of the Tl-related compounds [21]. The (006) diffraction peak was used to estimate the crystallite average size through the Scherer formula [22]. The crystal size for all samples is listed also in Table I. It can be observed that it is proportional to the diffraction peak intensity in the superconducting phase. Fig. 5 shows the surface morphology

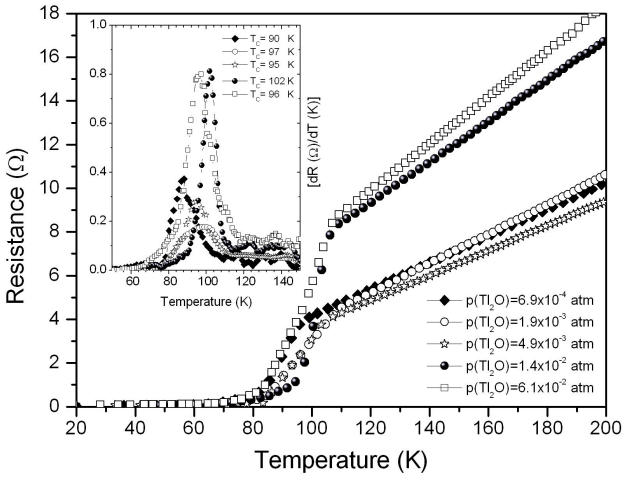

FIGURE 6. R vs. T curve of superconducting films. The inset shows the dR/dT vs. T plot.

TABLE I. Experimental conditions, chemical composition and critical temperature of thallinated films.

Sample	O2 Flow rate (cm3/min)	p(Tl2O) (atm)	%at Tl	%at Ba	%at Ca	%at Cu	Crystal size (Å)	TC (K)
M96B	40	6.9×10^{-4}		30.0	25.7	44.3	294	90
			14.6	24.2	23.1	38.1		
M105A	20	1.9×10^{-3}		30.0	25.0	45.0	326	97
			22.2	26.2	19.8	31.9		
M104A	10	4.9×10^{-2}		29.8	26.6	43.6	351	95
			18.6	25.7	21.5	34.2		
M102B	5	1.4×10^{-2}		29.2	25.5	45.3	392	102
			15.9	24.8	20.2	39.0		
M03A	0.5	6.1×10^{-2}		29.7	25.3	44.9	338	96
			13.6	23.5	22.0	40.9		
Ideal chemical composition			12.5	25.0	25.0	37.5		

of these films. In this SEM micrograph, the grains of the Tl-1223 phase appear in a plate like morphology, showing an average size of about 10 μm.

Fig. 6 shows the R vs. T characteristic curves for the samples studied, and the inset shows the derivative of these data. The onset transitions (Tc) was estimated from the peak location of these derivative data. The T_C values were in the range of 90 K to 102 K, as shown in Table 1. Since the critical current density in polycrystalline HTS is highly limited by the grain boundaries, the decoupling of the grains may be visualized when plotting dR/dT vs. temperature (inset). The main peak in this type of plot shows the superconducting transitions within the grains, while smaller peaks on the low-temperature side are due to the superconductor transition of intergranular regions [23]. In this case, the main peak is not as sharp as it should be. This indicates that there is not a good superconducting transition within the grains that constitute the films. This is, probably, the reason for the low T_C values, on average, observed in these samples. However, there are no noticeable small peaks on the low temperature side, suggesting a relatively good superconductor transition in the inter-granular regions. Since the critical temperature in polycrystalline HTS is highly limited by the grain boundaries, the interconnection between the grains might be poor, but from the dR/dT vs. temperature data shown in the inset of Fig. 5, there is no clear sign that they are. It is possible that the presence of $BaCuO_2$ and an incomplete transformation of the precursor material into a superconducting phase are responsible for these results. In addition, even though X-ray diffraction measurements suggest that the $TlBa_2Ca_2Cu_3O_{8.5}$ crystalline phase is predominant in the films, it is not dis-

carded that an oxygen deficiency in the films might lead to the low T_C values obtained.

4. Conclusions

$TlBa_2Ca_2Cu_3O_x$ films were deposited on untextured polycrystalline silver substrates by a two-step method using spray pyrolysis. Firstly, precursor films were synthesized from acetylacetonates (2-4, pentanedionates). Secondly, different Tl_2O partial pressures, determined by the oxygen flow at atmospheric pressure in the two-zone furnace, were used during thallium diffusion of the films. In all cases, polycrystalline films were obtained with the Tl-1223 phase with a preferential c-axis orientation perpendicular to the substrate surface. Also found was the presence of $BaCuO_2$, especially at low p(Tl_2O). The largest crystallite grain size and the best overall characteristics were obtained for a p(Tl_2O) = 1.4×10^{-2} atm. In this case, the best superconducting transition occurs at a T_C= 102 K.

Acknowledgements

The authors appreciate the technical assistance of J. Garcia-Coronel, M. Guerrero-Cruz, A.B. Soto-Guzman, and Z. Rivera Álvarez, Phys. Dept., CINVESTAV-IPN. We are also grateful for the financial support from CONACyT-Mexico.

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