Synthesis and photoresponse of PbBiSrCaCuO films

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To my parents

Abstract

Thin films of PbBiSrCaCuO superconductor have been produced by means of single target magnetron rf sputtering followed by a heat treatment. The effects of deposition and post-annealing parameters on film properties were investigated. It was found that film thickness decreases near the discharge center, possibly due to the preferential ion bombardment of the film during deposition. Superconducting films with the high T_c 2223 phase could be obtained after a heat treatment as short as 60 min. A structural transition from the semiconducting phase to the low T_c 2212 phase took place in the film during the preannealing in O_2 (20 min). During the subsequent annealing in air (40 min), a gradual structural transition from the 2212 phase to 2223 phase occurred when the annealing temperature and duration were increased. The resulting films showed $T_{\rm c} \sim 107$ K and $J_{\rm c}$ exceeding 8x10³ A / cm² at 79 K. For all stages of the transition, the phases revealed in the temperature characteristics of electrical resistance and magnetic susceptibility are consistent with those identified in the XRD spectra of the film. Heat treatments of shorter duration or at lower temperatures resulted in films with mixed 2212 and 2223 phases, in which a superconducting percolation path could still be established at temperatures as high as 100 K. The evolution of film compositions with annealing time suggested that Pb is a precursor of the chemical reactions behind the accelerated formation of the 2223 phase.

The photoresponse of PbBiSrCaCuO film was investigated at temperatures below, around, and beyond T_c . Consistency was found between photoresponse and temperature derivative of film resistivity near T_c , suggesting that the photoresponse is bolometric in origin. Other bolometric signatures include the long recovery time and linear dependence of photoresponse with supplied current. Below $T_{\rm c}$, a fast response appeared when the power density of optical excitation exceeded a certain threshold. The effect of bias temperature on transient structure, magnitude, and time delay of the fast response showed that this response is also bolometric. A bolometric model was developed using the solutions of the problem of linear heat flow in a solid bounded by a pair of parallel planes. The photoresponses predicted by this model were in good agreement with those obtained experimentally. Beyond T_c , it was found that a nonbolometric photoresponse coexists with the bolometric counterpart in electrically biased films. These components superimpose linearly and can be extracted from the responses measured with forward and reverse bias currents. The nonbolometric component also manifested itself as the response of electrically unbiased films. Its behavior was consistent with prediction of a model based on the Seebeck effect. In this model the film was depicted as a number of parallel layers having different thermopowers and forming a tilt angle to the substrate surface. Such a structure can be seen as the equivalent of a number of thermocouples connected in series along the length of the film. Upon thermal heating of the film, the temperature gradient in the individual thermocouples results in Seebeck voltages that add up to the transverse nonbolometric voltage.

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Résumé

Des couches minces supraconductrices de PbBiSrCaCuO ont été produites par pulvérisation cathodique de cible simple assistée par magnétron rf, suivie d'un traitement thermique. On a étudié les effets des paramètres de dépôt et de recuit sur les propriétés du film. On a constaté une décroissance de l'épaisseur du film au voisinage du centre de décharge, possiblement occasionnée par le bombardement ionique préférentiel sur le film durant le dépôt. Des films supraconductrices ayant la phase d'haute T_c 2223 pouvaient être produits après un traitement thermique aussi bref que 60 min. Une transition de la phase semiconductrice vers la phase de basse $T_{\rm c}$ 2212 avait lieu dans le film durant la pré-cuisson dans O₂ (20 min). Au cours du recuit ultérieur dans l'air (40 minute), une transition structurelle progressive de la phase 2212 à la phase 2223 s'effectuait au fur et à mesure que la température et la durée de recuit augmentaient. Les films qui en résultent montrent $T_{\rm c}\sim 107~{\rm K}$ et $J_{\rm c}$ dépassant $8{\rm x}10^3~{\rm A}$ / cm² à 79 K. À toutes les étapes de la transition structurelle, les phases révélées dans les caractéristiques de résistance électrique et susceptibilité magnétique correspondent à ceux identifiés dans les spectres XRD du film. Les traitements thermiques à durée plus courte ou température plus modérée ont produit des films ayant la phase composée de 2212 et 2223 dans lesquels un chemin de percolation supraconducteur pouvait néanmoins être formé à des températures aussi élevées que 100 K. L'évolution stoichiométrique du film durant le recuit suggère que le Pb soit un précurseur des réactions chimiques accélérant la formation de la phase 2223.

La photoréponse des couches de PbBiSrCaCuO a été examinée aux températures au-dessous, autour et au-dessus de T_c . On a trouvé une corrélation entre la photoréponse et la dérivée en température de la résistivité de la couche autour de T_c , ce qui suggère l'origine bolométrique de la réponse. Les autres indices comprennent le temps de recouvrement étendu ainsi que l'augmentation linéaire de la photoréponse avec le courant de polarisation. Au-dessous de $T_{\rm c}$, une photoréponse rapide s'est manifestée lorsque la densité de puissance de la stimulation optique dépassait un certain seuil. L'effet de la température d'opération sur la forme transitoire, l'amplitude et le retard temporel a démontré que cette réponse est également bolométrique. Un modèle bolométrique a été établi à partir des solutions du problème de propagation linéaire de chaleur dans un solide borné par une paire de parois parallèles. Les photoréponses dérivées de ce modèle concorde avec celles obtenues expérimentalement. Au-dessus de T_c , on a observé une réponse nonbolométrique en plus de la réponse bolométrique dans les films mis sous tension. Ces composantes superimposent linéairement et peuvent être déduites des photoréponses mesurées du film alimenté de courants directs et inverses. La composante nonbolométrique s'est également manifestée en tant que la photoréponse mesurée des films nonalimentés. Son comportement était comparable à celui dérivé d'un modèle basé sur l'effet Seebeck. Le film a été modélisé en une structure de plusieurs couches parallèles ayant différentes thermopuissances et à un angle par rapport à la surface du substrat. Une telle structure peut être considérée comme l'équivalent de nombreux thermocouples branchés en série suivant la longueur du film. Lors de l'échauffement thermique du film, les gradients de température induits dans ces

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Acknowledgements

I would like to express my gratitude to my thesis supervisor, Professor Ishiang Shih, for his invaluable guidance and assistance over the years. Special thanks are due to Gaston Lortie for his help in the pressing of sputter targets. Also instrumental was the assistance of David Comeau in the programming for the bolometric photoresponse model. This thesis work was made possible thanks to the financial support and access to research facilities of Defence R-D Canada.

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There are four subjects investigated in this thesis work. These are:

- thin film synthesis of Pb doped BiSrCaCuO superconductor by magnetron rf sputtering;
- (ii) kinetics of the formation of superconducting phases in PbBiSrCaCuO films;
- (iii) photoresponse of superconducting PbBiSrCaCuO films; and
- (iv) photoresponse of normal state PbBiSrCaCuO films.

Each subject is treated in a separate chapter that follows the present chapter.

The purpose of this introductory chapter is to provide the necessary background for a better understanding of the context in which the above subjects were investigated. It is organized as follows. The first section reviews the significant milestones in theory and material research in the field of superconductivity. The second section presents selected superconducting properties that are relevant to the thesis work. The specific characteristics of the BiSrCaCuO superconductor and a review of the previous work on thin film synthesis of this compound are outlined in the subsequent sections. Finally, the motivation behind the thesis work and the thesis objectives will be stated.

1.1 Historical background

Superconductivity is the ability of certain materials to conduct direct current with zero electrical resistance. For a material to be superconducting, it has to be cooled below a critical temperature (T_c) , must not carry electric current exceeding a critical density (J_c) , and must not be exposed to magnetic field more intense than a critical field (H_c) . If one of these conditions fails, the superconducting state is destroyed and the material exhibits the so-called normal resistive state. The zero electrical resistance may be the better known attribute of superconductors, but is not the only one. These materials exhibit also particular magnetic and thermal properties, and should rather be considered a particular state of low temperature matter than just superconductors.

Superconductivity was discovered in 1911 by H. Kamerlingh-Onnes [1.1] while studying properties of metals at liquid helium temperature. He passed a current through a pure Hg wire and measured its resistance as the temperature decreased gradually. At 4.2 K the resistance vanished. Kamerlingh-Onnes later observed the same occurrence in other metals such as Pb and Sn at temperatures near 4 K. The technological developments in the 1920s allowed cryogenic equipment to become more common and more laboratories began investigating superconductivity. In 1933, W. Meissner and R. Ochsenfeld [1.2] discovered that superconductors are more than a perfect conductor of electricity, they do not allow a magnetic field to penetrate them. When the material is placed in an external magnetic field, an electric current will be set up in the surface layer such that its

magnetic field will oppose the applied field. This is commonly referred to as the Meissner effect.

After the discovery of the Meissner effect, different theoretical models have been proposed to account for the superconducting phenomenology. In 1935, F. London and H. London [1.3] proposed a model to explain the Meissner effect and predict how far a magnetic field could penetrate into a superconductor. This model, referred to as the classical model, incorporates the properties of zero resistance and perfect diamagnetism into electromagnetic constitutive relations known as the London equations. These equations are empirically based and not deduced from any microscopic mechanism within the material. Although the classical model can be used to estimate relevant parameters of a superconducting system, it does not account for the properties subsequently observed in superconductors. In 1950, V. Ginzburg and L. Landau [1.4] intuited a description of superconductivity that integrated the electrodynamic, quantum mechanical, and thermodynamic properties of superconductors. The Ginzburg-Landau theory provided derivation for the London equations and accounted for most properties of superconductor. However, it does not offer an explanation as to how superconductivity occurs. It was not until 1957 that J. Bardeen, L. Cooper, and R. Schrieffer [1.5] proposed a model, known as the BCS model, that actually explained how superconductivity occurs. This model is expressed in terms of advanced ideas of quantum mechanics, but the main idea is that superconductor has a more ordered state than normal conductor where electrons travel coherently in pairs without losses. These electron pairs are called Cooper pairs. The BCS model correlates well with the Ginzburg-

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Landau and London predictions. About the same time, A. Abrikosov [1.6] predicted the existence of type II superconductors in considering a particular case of the Ginzburg-Landau equations. He classified accordingly superconductors into type I and type II in relation to their magnetic properties. Type I superconductors exclude the applied magnetic field by establishing circulating currents on its surface that counteract the applied field. The field is excluded as long as it remains below the critical field. When it is increased beyond the critical field, it penetrates the material completely and the material is no longer superconducting. Type II superconductors are characterized by the lower critical field H_{c1} and upper critical field H_{c2} . When the field is smaller than H_{c1} or exceeds H_{c2} , the material behaves like a type I superconductor. When the field is between H_{c1} and H_{c2} , the material is in a mixed state, also called the Abrikosov regime. It remains electrically superconducting but allows the field to penetrate it partially in quantized amounts of flux. These quanta are comprised of circulating vortices of current and the flux is contained in the vortices. Five years after the BCS theory, B. Josephson [1.7] predicted that Cooper pairs as well as single electrons could tunnel without resistance from one superconductor end to another through a thin insulating layer. As such, a current would flow in the absence of an applied voltage. He further predicted that an ac current would flow when a dc voltage was applied across the junction. These predictions have since been experimentally confirmed and are referred to respectively as the dc and ac Josephson effects.

Since the early days it was realized that, as T_c decreases in the presence of magnetic field or supplied current, most operations of

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superconducting devices had to be performed at rather low temperatures. The inconvenience of cryogenic requirement motivated the search for superconductors with higher $T_{\rm c}$ values. Despite more than two decades of research effort following the BCS theory, the highest T_c achieved was only 23 K in the Nb₃Ge compound (Fig. 1.1). The breakthrough came, however, in 1986 with the report of superconductivity at 30 K in LaBaCuO ceramics by G. Bednorz and K. A. Muller at the IBM Zurich Research Laboratory [1.8]. Later that year, Tanaka's group at the University of Tokyo showed that the substitution of Sr for Ba led to an increase of T_c to 42 K [1.9]. These results triggered a worldwide shift in research direction from studying metals and alloys to examining oxide ceramics. This paid off with the report of 90 K superconductivity in the YBaCuO compound in 1987 [1.10], and even higher T_c 's in the BiSrCaCuO [1.11] and TlBaCaCuO compounds [1.12] shortly after. These CuO superconductors are referred to as high T_c superconductors. The evolution of T_c 's since the discovery of superconductivity is shown in Fig. 1.1.

1.2 Superconducting properties

This section presents a short review of selected superconducting properties that are relevant to the thesis work. Because this work is about high T_c superconductor, the particularities of the latter with respect to traditional superconductors will be emphasized.

As noted in the previous section, current density and magnetic field join temperature in a triumvirate that governs whether or not a superconductor conducts current with zero resistance. Furthermore, these three critical values at which the transition to normal state

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takes place vary in a fixed relationship to the temperature, field, and current to which the material is exposed. For instance, for type I superconductor the temperature dependence of H_c is:

$$H_{\rm c} (T) \sim H_{\rm c}(0) \left[1 - (T / T_{\rm c})^2\right]$$
 (1.1)

and the temperature dependence of J_c is:

$$J_{\rm c} (T) \sim J_{\rm c}(0) \left[1 - (T / T_{\rm c})\right]^{3/2} \tag{1.2}$$

It follows that the farther below T_c a superconductor is cooled, the greater the field and current density it will withstand before reverting to normal resistivity. At T_c , H_c and J_c become zero. Likewise, it was found that the smaller the field applied to the material, the greater the critical temperature and current become. In particular, the field dependence of J_c is stronger in high T_c superconductors than in traditional superconductors. Even in a moderate field, the critical current of the former is found significantly reduced.

There are two length scales that characterize superconductors: the penetration depth λ and the coherence length ξ . A given superconductor with $\xi > \lambda$ will be type I. Conversely, a superconductor with $\xi < \lambda$ will be type II. The penetration depth λ is the distance over which an applied magnetic field is shielded by the superconductor. When the surface current is set up due to the Meissner effect, it does not actually flow on the material surface but penetrate to some extent below the surface. According to the classical model, the magnetic field inside a type I superconductor decreases exponentially with distance x below the surface:

$$H(x) = H_0 \exp(-x / \lambda)$$
 (1.3)

H becomes very small at depths of ~ 4 λ below the surface; most values of λ are in the range of 10-100 nm. On the other hand, the coherence length is a parameter of the Cooper pairs in the BCS theory. The notion of Cooper pairs, *i.e.* two electrons attracted to each other strongly enough to form a bound state, is presented schematically in Fig. 1.2. This notion suggests that attractive interaction between two electrons can arise indirectly via lattice deformation [1.13]. The first electron passes through a given region of the lattice and attracts the ions which move inwards from their equilibrium positions. This distorted region has a net positive charge, and hence a nearby second electron is attracted to it. The largest separation between the two electrons over which the bound state can extend is referred to as the coherence length. The energy required to break the bound state is called the energy gap, $E_{\rm g}$. According to the BCS theory, the energy gap at 0 K is proportional to the critical temperature:

$$E_{\rm g}(0) \sim 3.53 \, {\rm k}T_{\rm c}$$
 (1.4)

High T_c superconductors stand out as an extreme type II material that is highly anisotropic at the same time. They are called extreme type II in reference to their coherence length being significantly smaller than their penetration depth. For instance, the coherence length of Bi₂Sr₂CaCu₂O_y (~ 3 nm) is two orders of magnitude below its penetration depth (~ 300nm) [1.14-1.16]. Note that this order of coherence length is also 10 to 100 times below that of traditional superconductors. The degree of anisotropy can be qualitatively assessed from the ratio of ξ values in the *ab* plane and

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along the c axis, ξ_{ab} / ξ_c . Referring to Table 1.1, it is seen that this ratio can be as high as 29. Such a strong anisotropy reflects the fact that high T_c superconductors superconduct in the *ab* plane only, *i.e.* resistivity is zero in the *ab* plane but finite normal to this plane. As a result of the quasi two-dimensional transport, the upper critical value of the magnetic field is also larger when the field is applied in the *ab* plane than when it is oriented along the *c* axis (see Table 1.1).

The thermal properties of superconductors depart considerably from those of normal metals. When the heat is transferred to a normal metal, a portion of it creates additional lattice vibration and the remainder increases the kinetic energy of the electrons. At low temperatures the specific heat C_n of the normal state varies as $AT + BT^3$, where A and B are constants. The first term is due to electronic excitations and the second term is due to lattice vibrations. At the transition to superconducting state, the specific heat jumps to a much larger value C_s at just below T_c . Then, C_s decreases rapidly with decreasing temperature to become eventually smaller than C_n at a given temperature. Below this temperature C_s exhibits an exponential dependence on 1/T. For the high T_c superconductors, the temperature dependence of specific heat remains unclear. There have been reports of the specific heat jump at T_c for YBaCuO, but not for BiSrCaCuO and TIBaCaCuO.

1.3 BiSrCaCuO superconductors

One particular aspect of the BiSrCaCuO superconductor is that it has a multiphase structure. This structure, identified as $Bi_2Sr_2Ca_{n-1}$ Cu_nO_y by Tarascon *et al.* [1.17], comprises at least three phases with *n*

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= 1, 2, and 3. The first phase, $Bi_2Sr_2CuO_y$ (*n*=1) with $T_c \sim 10\text{-}20$ K, was discovered in 1987 by Michel *et al.* [1.18]. Shortly after, by adding Ca to this compound, Maeda *et al.* [1.19] reported finding the $Bi_2Sr_2CaCu_2O_y$ (*n*=2) and $Bi_2Sr_2Ca_2Cu_3O_y$ (*n*=3) phases with T_c 's of 85 K and 110 K respectively. These phases are usually denoted by their cation ratio as the 2201, 2212, and 2223. Their unit cell structures and lattice constants are shown in Fig. 1.3. It is seen that they differ mainly in the number of CuO_2 planes between Bi_2O_2 along the *c*-axis. The structure has a pseudotetragonal symmetry and contains up to four formula units. For the 2212 phase for instance, it can be denoted by a stacking of atomic planes in the sequence of :

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Bi₂O₂ / SrO / CuO₂ / Ca / CuO₂ / SrO / Bi₂O₂ / SrO / CuO₂ / Ca / CuO₂ / SrO / Bi₂O₂

Similarly to the other high T_c superconductors, the Bi₂Sr₂Ca_{n-1} Cu_nO_y are type II superconductors with a strong anisotropy due to their layered nature. The anisotropy manifests itself in the difference of H_c , J_c , and ξ values in the ab plane and along the c axis. These values are shown in Table 1.1, together with the counterparts of other high T_c superconductors [1.20-1.36]. The ratio of the ab plane to c-axis data is larger for the BiSrCaCuO, indicating a higher degree of anisotropy. One notes also the extremely short coherence length of BiSrCaCuO along the c-axis. As a result, it is possible only to make use of the transport properties along the ab (CuO) planes, which in turn requires an epitaxial c-axis orientation for thin films. The shorter coherence length also makes it more challenging to achieve uniform superconducting properties as these vary with local changes in the sample properties on the scale of ξ .

1.4 Thin film synthesis of BiSrCaCuO superconductor

The need for thin films of superconductor stems from the requirements of fundamental studies and a variety of electronic applications. After the discovery of Bi₂Sr₂Ca_{n-1}Cu_nO_y superconductors, much effort has been devoted to the thin film synthesis of these materials. However, most of the attempts to obtain single crystal films were hampered by the predisposition of the 2212 and 2223 phase to intergrow [1.30, 1.37]. The difficulty encountered is actually twofold. Firstly, because the BiSrCaCuO compound contains up to four metals plus oxygen, it is challenging to maintain precise stoichiometry so as to avoid occurrence of multiple phases in the film. Secondly, the low $T_{\rm c}$ 2212 phase appears to grow more rapidly than the more desired high $T_{\rm c}$ 2223 phase and, as a result, impedes the growth of the latter [1.17]. Various methods have been used to enhance the 2223 phase, including optimizing stoichiometry [1.38-1.41], adjusting heat treatment conditions [1.17, 1.42-1.45], depositing films onto heated substrates [1.46], and elemental substitution [1.47-1.51]. These approaches yielded inconsistent results until Takano et al. [1.47] discovered that the introduction of Pb into BiSrCaCuO compound increases significantly the volume fraction of the 2223 phase. This method has since proved to be effective despite the problematic loss of Pb [1.52] during the heat treatment of the films.

The methods for growing BiSrCaCuO films can be divided into two categories, *ex-situ and in-situ*, depending on whether or not an external treatment of the film is required after its growth. The *ex-situ* method consists of two separate steps. The film is first grown on an unheated substrate by various means, such as rf and dc sputtering

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[1.30, 1.37, 1.52-1.55], thermal and e-beam evaporation [1.56-1.59], laser ablation [1.60], chemical vapor deposition [1.61], and spray pyrolysis [1.62, 1.63]. The as-deposited film is usually amorphous; therefore in order to form superconducting phases in the film a subsequent heat treatment in air or O_2 is essential. The *in-situ* method requires that the film be deposited onto an intentionally heated substrate in the first step. During the deposition, the substrate is kept at temperatures substantially lower than those prescribed for the exsitu heat treatment. A number of groups opted for reactive film growth in partial O₂ atmosphere in this step [1.71-1.73]. After the deposition, substrate heating is removed and the film is oxygenated in an O_2 or ozone atmosphere. At the same time, the film is gradually or stepwise cooled down to room temperature. Occasionally, a low temperature heat treatment of the film is further carried out in flowing O_2 or in air in order to enhance superconducting phases in the film. Magnetron sputtering has been used quite extensively for the *in-situ* deposition of BiSrCaCuO films [1.66-1.72]. The other techniques in use include ion beam sputtering [1.73, 1.74], electron cyclotron resonance sputtering [1.75], molecular beam epitaxy [1.76-1.78], and laser ablation [1.79-1.81].

Table 1.2 shows the correlation between the heat treatment conditions and formation of superconducting phases in the films prepared *ex-situ*. It is seen that films with T_c above 54 K were obtained following a heat treatment in the temperature range of 840-890 °C. Examination of annealing data reveals an even smaller range, 850-870 °C, for the majority of these films. Not only this range is narrow, it lies just below the melting point of BiSrCaCuO. Hence, precision control of annealing temperatures appears critical for the *ex-situ* route.

With respect to other deposition techniques, it is noted that sputtering was used more extensively in the *ex-situ* process. This may be due to the fact that, being the preferred technique for preparing thin films of alloys and complex materials, sputtering was the natural technique to experiment with when BiSrCaCuO superconductors were first discovered. The extensive use of this technique may account for the larger number of reports of 2223 phase formation in sputter deposited films. Referring to the data in Table 1.2, annealing periods from 20 to 50 hrs combined with the addition of Pb seem compulsory to obtain the 2223 phase in these films. Unfortunately, these two requirements are hardly compatible. Because Pb evaporates at the required annealing temperatures, the Pb content in the film decreases drastically after long periods of heat treatment [1.54]. One approach to minimizing the loss of Pb was to perform the heat treatment in a sealed enclosure [1.52].

The high temperatures required for the heat treatment is the main factor limiting the choice of the substrate materials. At these temperatures, chemical reaction and large thermal stress between the film and substrate were found to occur. Hung *et al.* [1.64] investigated the interactions between BiSrCaCuO films and Al₂O₃, Si, SiO₂, and fused quartz substrates. At temperatures above 800 °C, chemical reactions took place and destroyed superconductivity in the films grown directly on these substrates. Further, the high thermal stress caused cracking of the films deposited on quartz. These authors had some success in reducing the effects of chemical reaction and thermal stress with the use of ZrO_2 / Zr -Si-O buffer layers. However, the highest value of T_c measured on the buffered films remained below 70 K. Nasu *et al.* [1.65] grew epitaxial ZrO_2 film by electron beam

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evaporation as a buffer for BiSrCaCuO on Si substrates. After the heat treatment the film showed a $T_c \sim 50$ K. Mei *et al.* [1.52] attempted to grow Pb doped BiSrCaCuO films directly on Al₂O₃ substrate. Since the film reacts with Al₂O₃, the heat treatment could only be performed at low temperature (~ 800 °C) for a short period of time (~ 1 hr). The best film obtained using this approach exhibited a predominant 2212 phase and $T_c \sim 30$ K. As can be seen in Table 1.2, better results could only be obtained when the films were prepared on compatible substrates such as MgO, SrTiO₃, and LaAlO₃. Beside these substrates, BeO is another substrate reported to be compatible with BiSrCaCuO films [1.62].

Table 1.3 shows the correlation between the temperature, oxygenation conditions, and T_c for the films prepared *in-situ*. The substrates onto which these films were deposited were biased at temperatures in the range of 525-821 °C. In similarity to the *ex-situ* process, magnetron sputtering seems to be the preferred technique for the film deposition. The substrate temperatures for the sputter deposited films are in the range of 525-715 °C. These are considerably lower than the temperatures required for the *ex-situ* heat treatment, 850-870 °C. In most of the *in-situ* processes reported for BiSrCaCuO films, the post-deposition oxygenation of the film is performed by venting the deposition chamber gradually to atmospheric pressure of O₂.

Although the low temperatures of the *in-situ* process allow for a larger choice of substrate materials and result in better film morphology, they seem to provide just enough energy for the nucleation of the 2212 phase. There was no sign of the 2223 phase in the reported characteristics of the films prepared *in-situ*. As shown in

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Table 1.3, the typical values of T_c measured on these films are merely 56-80 K. The largest volume fraction of the 2212 phase was reported by Jedamzik *et al.* [1.72]. These authors grew reactively Pb doped BiSrCaCuO film on MgO substrate in a mixture of Ar and O₂. The substrate temperature was kept at 537 °C since partial melting of the film was observed at 540 °C. After the deposition, it was necessary to increase the substrate temperature to 600 °C while the film was immersed in 280 torr of O₂ to obtain the 2212 phase ($T_c \sim 80$ K). Similar results were reported by Fujita *et al.* [1.74], who further annealed the film in air at 500 °C.

1.5 Motivation and thesis objectives

As pointed out earlier, the extent to which a superconductor is able to withstand bias current or magnetic field is determined by the discrepancy between its operating temperature and T_c . Devices operating at the liquid nitrogen temperature, for instance, would require materials with T_c 's exceeding 77 K as much as possible. From this point of view the Bi₂Sr₂Ca₂Cu₃O_y superconductor with $T_c \sim 110$ K is a quite attractive candidate, considering the toxicity of TlBaCaCuO and the lower T_c values of other cuprate compounds. For potential electronic applications, it is further required that the Bi₂Sr₂Ca₂Cu₃O_y superconductor be prepared in a thin film form. High quality films are of primary importance for the development of devices such as superconducting quantum interference devices (SQUID), microwave filters, and infrared detectors.

One conclusion drawn from the survey in section 1.4 is that thin film synthesis of single phase Bi₂Sr₂Ca₂Cu₃O_y superconductor proves

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to be difficult. Although the mechanisms of the *in-situ* process are not fully understood, the results obtained seem to indicate that the 2223 phase cannot nucleate on substrates at temperatures substantially lower than those prescribed for the *ex-situ* heat treatment. Furthermore, control of stoichiometry is more difficult as elemental losses increased with increasing substrate temperature [1.66]. On the other hand, while there were reports of the 2223 phase formation in the films prepared *ex-situ*, most of those films also contain a significant fraction of the 2212 phase and remain polycrystalline. The lengthy period of heat treatment required to grow the 2223 phase (20-40 hrs) is an impediment to the production time and cost, making the *ex-situ* process less viable commercially. Furthermore, methods have to be devised to compensate for the loss of Pb after such a long heat treatment. The presence of Pb in the film is believed necessary to promote the growth of the 2223 phase.

Considering the higher potential for achieving Bi₂Sr₂Ca₂Cu₃O_y superconductor films using the *ex-situ* route, the shortcomings of this method will need to be addressed. A closer look at these shortcomings, *i.e.* long annealing period, evaporation of Pb, and phase intergrowth, reveals that they are interrelated. To solve them, one possible solution would be shortening the period of annealing. In doing so the loss of Pb would be reduced. By preserving a sufficient Pb content in the film, the 2223 phase might grow more rapidly to be formed within a short period of heat treatment. This idea is examined further in this thesis work.

The first objective of this thesis is to investigate the *ex-situ* fabrication of Bi₂Sr₂Ca₂Cu₃O_y superconductor films. More specifically,

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the investigation is carried out on: (i) the use of magnetron rf sputtering to obtain the desired film properties; and (ii) the kinetics of the phase formation in the film under a short heat treatment. Magnetron sputtering technique is selected for the film growth in this work because it offers unique advantages. Firstly, sputtering allows for deposition of films with properties close to the bulk properties of the target, that are predictable and stable. This feature eases the stoichiometry control that is needed to minimize the phase intergrowth. Secondly, using sputtering film uniformity may be achieved over large areas. This feature makes this technique more suitable for the ultimate production of useful devices. Thirdly, the planar magnetron is well established as a highly efficient sputter source, making the process more attractive commercially. Once the films are prepared with desired properties, the formation of superconducting phases is examined under a short heat treatment.

A promising application of thin film superconductors is their use as optical detectors. The early studies on the electrical response of thin films of traditional superconductor showed that the photoresponse could be either bolometric or nonbolometric in origin [1.82-1.84]. Bolometric mechanism relies on changes in the biased state resistivity of the film as the film is heated up in absorbing optical radiation. This explains the prevalence of bolometric response in the vicinity of T_c where the resistivity change per unit temperature is large. Nonbolometric mechanism was found predominant in the films held at temperatures below T_c and exposed to energies that exceed the superconducting energy gap. Under this mechanism, the incident photons break the Cooper pairs, reducing the relative fraction of Cooper pairs to normal electrons in the superconductor. As a result of

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the decreasing fraction, the critical current value of the film's weak links decreases [1.85]. So long as these links are current biased at slightly below the critical value, incident radiation is seen as the appearance of a voltage across the links. Devices that make use of the bolometric and nonbolometric mechanisms were demonstrated but not widely in use. One obvious limitation is the stringent cryogenic requirement for their operation.

The second objective of this thesis is to investigate the photoresponses of BiSrCaCuO films. Such an interest stems from the prospect of operating superconductor detectors at or above the liquid nitrogen temperature. From the photoresponse characteristics, one can also extract important information on the underlying mechanisms, thermal properties, and microstructures of BiSrCaCuO film. The investigation is carried out for a wide range of temperatures, covering both the superconducting and normal states.

The organization of the thesis is as follows. Details of the thin film synthesis by magnetron rf sputtering are presented in Chapter 2. Chapter 3 describes the kinetics of superconducting phase formation in the heat treated films and outlines the results on superconductivity obtained under a short annealing. Photoresponses and experimental evidences of underlying mechanisms are discussed in Chapters 4 and 5 respectively for films in the superconducting and normal states. Chapter 6 summarizes the principal findings of this study with emphasis on the original contributions of the author.

Table 1.1 - Characteristics of various high T_c superconductors reported in the literature. Data are shown for crystals and thin films, along the *ab* plane and the *c*-axis. T_c 's are measured in the absence of magnetic field and electric current, J_c 's are measured at T = 77 K and H = 0 T except where noted, and H_{c2} 's are extrapolated values (for T =0 K).

Material	$T_{ m c}$	$J_{ m c}$	$H_{ m c2}$	ξ (nm)	References
	(K)	(kA/cm ²)	(T)		
LaSrCuO (ab plane)	41	40 a	30	3-5	1.20, 1.21
LaSrCuO (c-axis)		6^{a}	8		1.20
LaSrCuO (film)	30				1.22
YBaCuO (ab plane)	90	120	383	1.1 - 1.3	1.23 - 1.25
YBaCuO (c-axis)			74	0.2	1.23, 1.25
YBaCuO (film)	88	100	134		1.26, 1.27
Bi-2212 (<i>ab</i> plane)	84	10	680	2.7	1.28, 1.29
Bi-2212 (c-axis)		0.002	45	0.18	1.28, 1.29
Bi-2212 (film)	83	4.4	440		1.30, 1.31, 1.36
Bi-2223 (<i>ab</i> plane)	106	536 a	500	2.9	1.32, 1.33
Bi-2223 (c-axis)		135~a	56.5	0.1	1.32, 1.33
Bi-2223 (film)	106	100	500		1.34, 1.35,1.36

 $^a\,$ Measured at $T\sim 2$ - 4 K.

Table 1.2 - *Ex-situ* growth of BiSrCaCuO films: correlation between heat treatment conditions and formation of superconducting phases on various substrates. T_A and t_A denote respectively the maximum annealing temperature and annealing time.

Deposition	Substrate	$T_{ m A}$	$T_{ m A}$	$T_{ m c}$	Phase	Ref.
technique		(°C)	(hr)	(K)		
rf sputtering	Al ₂ O ₃	800	1	30	2212	1.52
	$SrTiO_3$	830	1	54	2212	1.52
		840	40	104	2223	1.52
	LaAlO ₃	843	40	90	2212 / 2223	1.52
	MgO	840	40	90	2212 / 2223	1.52
		855	20	105	2212 / 2223	1.53
		855	50	90	2212 / 2223	1.54
		870	1	80	2212	1.37
dc sputtering	MgO	870	0.33	80	2212	1.55
		870	12	80	2212 / 2223	1.30
Thermal	SrTiO ₃	870	1	83	2212	1.56
evaporation	MgO	860	2	80	2212	1.57
E-beam	SrTiO ₃	850	0.1	80	2212	1.58
evaporation	MgO	890	5	107	2223	1.59
Laser ablation	MgO	850	1	84	2212	1.60
CVD	MgO	865	2	80	2212	1.61
Spray	BeO	850	1.5	83	2212	1.62
pyrolysis	MgO	845	15	100	2212 / 2223	1.63

Table 1.3 - In-situ growth of BiSrCaCuO films : correlation betweensubtrate temperature, oxygenation conditions, and T_c .

Deposition	$T_{ m substrate}$	Post-deposition	<i>T</i> _c (K)	Ref.
technique	(°C)	oxygenation		
Magnetron	715	$400 ext{ torr } O_2$	56	1.66
sputtering	700	300 torr O ₂	75	1.67
	525	none	< 30	1.68
	680	$760 torr O_2$	74-82	1.69
	530	760 torr O_2	60	1.70
	665	$700 ext{ torr } O_2$	36	1.71
	537	$280 \text{ torr } O_2$	80	1.72
Ion beam	700	annealed at 880 °C in O ₂	65	1.73
sputtering	640	annealed at 500 °C in air	80	1.74
ECR	570-590	760 torr O ₂	58-64	1.75
MBE	780	15 µtorr ozone	65	1.76
Laser ablation	821	760 torr O ₂	79	1.79
	700	$750 \text{ torr } O_2$	50	1.80
	800	$750 \text{ torr } O_2$	71	1.81



Fig. 1.1 – Evolution of critical temperatures since the discovery of superconductivity. T_c values are shown for a number of superconductors only.



Fig. 1.2 – Schematic representation of the attractive interactions between two electrons via lattice deformation. The first electron passes through a given region of the lattice and attracts the ions which move inwards from their equilibrium positions (dashed circles). This distorted region has a net positive charge, hence a nearby second electron is attracted to it. Adapted with permission from Fig. 44.13 of Ref. 1.13. Chapter 1 – Introduction



Fig. 1.3 - Fundamental unit cells of Bi₂Sr₂Ca_{n-1}Cu_nO_y superconductor with n = 1, 2, and 3. Only half of the cell is shown. The other half is identical and stacks on top of the first as shown by the dashed lines. The lattice constants are: $a \approx b \approx 5.4$ Å, $c \approx 24.4$ Å (n=1), 30.7 Å (n=2), and 37 Å (n=3).

Chapter 2. Synthesis of BiSrCaCuO superconductor films

2.1 Introduction

The intent of this chapter is to present results of the thin film synthesis of BiSrCaCuO superconductors. Despite the extensive research into thin films of high T_c superconductors [2.1-2.3], the number of reports on preparation of BiSrCaCuO superconductor films with single crystal quality have been scarce. Because the BiSrCaCuO compound contains up to four metals plus oxygen, it is difficult to maintain precise stoichiometry so as to avoid occurrence of multiple phases in the film. Another difficulty stems from the fact that the low T_c Bi₂Sr₂CaCu₂O₈ phase grow more rapidly than the high T_c Bi₂Sr₂Ca₂Cu₃O₁₀ phase [2.3]. The introduction of Pb into the film appeared to promote the growth of the high T_c phase [2.4-2.5], but the increased number of metallic elements made stoichiometry control even more difficult. In the subsequent parts of this thesis the Pb doped BiSrCaCuO compound is referred to as PbBiSrCaCuO.

Both the *ex-situ* and *in-situ* approaches to thin film synthesis of PbBiSrCaCuO were used by different researchers [2.4-2.7] with varying degrees of success. In this study the *ex-situ* approach was selected because it eased the control of stoichiometry and process variables [2.8]. This approach consisted of two steps. First, PbBiSrCaCuO films were prepared on unheated substrates by means of single target magnetron sputtering. Second, the prepared films underwent a heat treatment so as to form the desired crystal structure. The synthesis of PbBiSrCaCuO films by single target sputtering is the main subject of the work described in this chapter.

In order to obtain the desired film stoichiometry from single target sputtering, the ability to control the cation ratio of the multicomponent target is critical. This is increasingly important as the content of Pb in the film appears to be a variable determining the crystalline structure formed during the heat treatment. In this work, a method was devised to prepare high purity PbBiSrCaCuO targets for the sputter deposition. The experimental details and characteristics of the prepared targets are presented in section 2.2. The selection of the substrates for the film growth and their characteristics are reported in section 2.3. Section 2.4 provides the details of the magnetron sputter deposition, and the subsequent sections are devoted to the effects of deposition variables on various film characteristics. Finally, the conclusions are presented in section 2.10.

2.2 Preparation of sputter targets

The preparation of PbBiSrCaCuO sputter targets consisted of a blending of precursor powders, followed by solid state reactions and pressing of the reacted powder compound. The powder materials (supplied by Johnson Matthey) were 99.999% purity PbO, Bi₂O₃, SrCO₃, CaCO₃, and CuO. To study the effect of Pb on the formation of high T_c phases, attempts were made to prepare targets with varying concentrations of Pb. To promote the growth of the Bi₂Sr₂Ca₂Cu₃O₁₀ phase, the cation ratio of the other metals was set to be Bi:Sr:Ca:Cu = 2:2:2:3. It was found in preliminary experiments that nearly half of the amount of Pb evaporated during the sintering of the powder compound. To compensate for the loss of Pb, a large amount of Pb was initially introduced in the compound. However, for compounds of Pb:Bi:Sr:Ca:Cu = x:2:2:2:3, a partial liquid state reaction was found to occur at the sintering temperature when x > 2, resulting in fractures of the pressed targets. This constraint sets the upper limit of Pb concentration to x = 2. The experimental details of the target preparation follow.

The stoichiometric weight M_j of each precursor powder j was computed from:

$$M_{\rm j} = n_{\rm i}\,\mu_{\rm j}\,M_{\rm t}\,/\,\Sigma\,n_{\rm i}\,\mu_{\rm j}\,,\qquad(2.1)$$

where n_j is the number of moles required to obtain the nominal composition of Pb:Bi:Sr:Ca:Cu = 2:2:2:2:3, μ_j is the molecular weight, and M_t is the total weight of the target. M_t is typically ~ 35 g for a disk target with a diameter of ~ 50 mm and a thickness of ~ 4 mm. The weighing process was performed using an electronic balance (Mettler AE-240) of 10- μ g resolution. Prior to this process, the hygroscopic carbonates were heat treated at 120 °C so as to remove the residual water. Table 2.1 shows the calculated and weighed stoichoimetric amounts. It is seen that the relative difference between them is negligible. Also shown in Table 2.1 is the melting temperature T_m for each component. The lowest value of T_m 's, 860 °C for Bi₂O₃ [2.9], defined the upper limit of sintering temperatures at normal pressures for the target.

The precursor powders were mixed and mechanically ground in a micro mill (Retsch MS) until an average grain size of ~ $2 \mu m$ was obtained. The mixture was sintered at 790 °C in air for 12 hours in a single zone furnace (Lindberg model 56822). The purpose of the sintering was to remove carbon atoms from the carbonate components and to react the mixture. The values of the sintering temperature and duration were selected such that the mixture could be well reacted without releasing a too large amount of Pb. To avoid interdiffusion and contamination, the mixture was placed in a high purity MgO container and kept inside the furnace when it was cooled to room temperature. To achieve a complete reaction, the mixture were reground and sintered again twice, each time with an increase in the sintering temperature by 10 °C. Figure 2.1 shows a SEM photograph of the sintered PbBiSrCaCuO powder compound. It is seen that the grain size is relatively uniform and is $\sim 2 \ \mu m$ in average. After the final sintering a reduction of ~ 9.5% of M_t was seen. This reduction may account for the evaporation of Pb and the reduction of carbon content through the released CO_2 gas.

The sintered PbBiSrCaCuO powder was pressed under a pressure of 1.4 kbar into a disk of 50-mm diameter. This pressure and diameter required the use of a large hydraulic press and an assembly of high strength mold and pistons. The diagram of the cylinder mold assembly is shown in Fig. 2.2. It was found that the disk could easily be fractured, except for a limited range of values of pressure and pressing duration. To minimize the risk of target fracture, four pressing cycles were performed with gradually increased values of pressure (by an increment of 0.175 kbar). Each cycle, which consisted of raising, holding, and releasing the pressure, enabled a gradual

increase of the strength of the disk. The period of time during which the powder was kept under pressure was 50 seconds per cycle. To distribute the pressure uniformly over the disk area, the disk was rotated around the cylinder axis by 90° prior to each pressing cycle. The pressed disk was sintered again at 810 °C in air for 12 hours. The temperature profile of the final sintering, as recorded with a thermocouple located in the furnace, is shown in Fig. 2.3. Figure 2.4 shows a SEM photograph of the surface of the resulted target. The surface appears to be relatively smooth and lacks the visual evidence that a liquid state reaction has occurred.

Even after the last sintering the disk remained too fragile to be used directly as a sputter target. To reinforce the disk, it was bonded to a Cu base plate which served as a mechanical support (Fig. 2.5). The base plate, being clamped to the water cooled magnetron gun, served also as a heat sink for the target. This prevents the target heating induced in part by the rf power supplied to the magnetron gun during the film deposition. For an effective target bonding, the surfaces of the disk target and base plate were polished down to level of 600 grit sand paper so that they are flat with respect to one another. Then, the target was attached to the plate using ~ 5 g of silver epoxy and was placed under a weight of ~ 250 g until the epoxy had cured.

2.3 Characteristics of substrates

The choice of the substrate matters in many respects. The BiSrCaCuO superconductor is a brittle ceramic material. In thin film form, if its thermal expansion coefficient mismatches that of the substrate, it may crack when being heat treated. If it reacts chemically

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with the substrate material, superconductivity may be weakened or destroyed. In addition, the orientation of the thin film crystal depends on the crystalline structure of the substrate and the lattice matching between the film and substrate.

In the preliminary experiments, PbBiSrCaCuO films were successively grown on the monocrystalline substrates made of (100) ZnO, (0001) Al₂O₃, (100) SrTiO₃, (100) MgO, and (100) LaAlO₃ (all supplied by Target Materials Inc.). It was found that films reacted chemically with the ZnO and Al₂O₃ substrates during the heat treatment and turned weakly superconducting or non-superconducting. The film grown on the other substrates showed good superconducting properties. MgO and LaAlO₃ substrates were used more extensively than SrTiO₃ for the film growth in subsequent experiments because of the high cost of the latter substrate. Table 2.2 summarizes the principal properties of the MgO and LaAlO₃ substrates.

The surface roughness of the substrates was examined using a surface profiler (Sloan Dektak 3030). This profiler shifted the sample linearly under a stationary 25- μ m stylus. The moving sample was mechanically interfaced with a precision planar surface which established referencing for profiling evaluation. The typical scan length was 10 mm. Figure 2.6 compares the surface profiles of the MgO, LaAlO₃, and SrTiO₃ substrates (over a 250 μ m area) with that of a glass slide (Corning 2497). Although well polished, the substrate surface is seen to contain steps that are nearly one order of magnitude below typical film thicknesses. For this reason, only the films deposited on glass slide were used for the thickness measurement in this thesis work.

2.4 Magnetron sputter deposition

The magnetron sputter deposition of PbBiSrCaCuO films was performed in Ar in a cylindrical chamber with horizontal axis. Figure 2.7 shows a schematic diagram of the chamber and its components. The inner diameter and the depth of the chamber are respectively 57 and 28 cm. Inside the chamber, a planar magnetron gun (Corona C-2) was mounted in front of a rotating substrate table; the separation between them was between 6 and 8.5 cm along the axis normal to the table. This magnetron gun can hold targets with a diameter of up to 5 cm. An rf generator (Advanced Energy RFX-600) supplied power at 13.56 MHz to the magnetron gun through an impedance matching network (Advanced Energy ATX-600). The reflected power was negligible under the experimental conditions used in this work. The chamber was evacuated by means of a turbomolecular pump (Balzers THS-512). A freon cooled Meissner coil installed in the chamber accelerated the removal of water vapor at sub-millitorr pressures.

Prior to the deposition, the chamber was evacuated until a base pressure of 10⁻⁶ Torr was reached. High purity Ar was fed into the chamber at a rate of 9 sccm through a piezoelectric valve which, together with control electronics (Tylan FC 280), provided a gas flow accuracy of ~ \pm 0.5 %. Using a throttle valve, the pumping speed was adjusted to a rate such that the desired Ar pressure (~ 4 mTorr) could be maintained under continuous pumping. The sputtering pressure was monitored using a precision capacitance manometer (Vacuum General 80-6A). The pre-sputtering was carried out for a period of 5 min at an rf power level of 100 W. The deposition was performed usually at a lower power level (~ 80 W) to enhance the uniformity of film growth and reduce target heating. Unless stated otherwise, no intentional heating was applied to the substrate during the deposition.

2.5 Thickness measurements of the sputtered films

For a better control of the superconducting properties, it is important to obtain films with uniform thickness and composition. The first series of experiments was performed to investigate the thickness variation of sputtered films on the substrate. The film thickness was determined by means of surface profilometry as described in section 2.3. It was seen that the substrates intended for film growth have a rough surface, making reliable thickness measurements difficult. Hence, films were prepared specially on glass slides (Corning 2497) for the present experiments. During the film deposition, the slide was tape masked partially so that steps could be created along the slide. Figure 2.8 shows the deposition geometry and the arrangement of the slides on the substrate table. After the deposition, the mask was removed and the sample was cleaned with propanol to eliminate any residual adhesive. The variation of film thickness on the slide was determined by scanning the steps between the film and the slide at different locations along the slide. The film level was taken at least 1 mm away from the film edge to avoid errors due to masking accumulation and shadowing.

Figure 2.9 shows a photograph of a PbBiSrCaCuO film obtained after a deposition period of 100 min. The film appears to have a smooth texture and perceptible change in color. From the discharge center towards the edge, the color transition is from a dark opaque brown to a lighter transparent yellow. This appearance suggests that the film is thickest at the center and tapered off towards the edge, as expected for a

typical sputter deposited film. However, the thickness measurement revealed a different result. Figure 2.10 shows the film thicknesses, d, measured at different locations on the slide, for different periods of deposition time. The separation between the target and substrate table was 8 cm. The rf power and Ar pressure were respectively 80 W and 3 mTorr. It is seen that d is depleted near the discharge center, x = 0, but remains relatively constant away from the center. Towards the edges, *i.e.* |x| > 4 cm, d decreases rapidly. The area in which thickness uniformity was achieved was slightly larger than the projection of the target area on the slide. Within this area, the thickness data gave a deposition rate of ~ 10 nm / min.

In order to confirm whether the thickness depletion observed near the projection of target center was an artifact of the deposition geometry, a Cr film was sputter deposited for a period of 60 min under conditions similar to the ones described above. The thickness variation of the Cr film on the glass slide was also plotted in Fig. 2.10 for comparison. Unlike the PbBiSrCaCuO film, the thickness of the Cr film is the largest at the center and decreases gradually towards the edge. The dissimilarity in thickness characteristics suggests that the thickness depletion is inherent to the PbBiSrCaCuO compound rather than an artifact of the deposition geometry.

2.6 Film densification

The decrease in the thickness of PbBiSrCaCuO films around the discharge center could be due to an increase in the film density. The speculated increase of film density may be a result of local heating of the substrate. The microstructural change of sputtered films with substrate

temperatures was predicted by Movchan and Demchishin in the structure zone model [2.10]. According to this model, the microstructure of sputtered films can be classified in terms of three zones, depending mainly on the ratio of the substrate temperature, $T_{\rm s}$, to the melting temperature of the film, $T_{\rm m}$. When $T_{\rm s} / T_{\rm m} < 0.3$, zone 1 structure occurs having tapered columns with void boundaries. Zone 2 structure usually occurs when $0.3 < T_{\rm s}$ / $T_{\rm m} < 0.5$. This zone is associated with columnar, platelet, or whisker grains separated by dense intercrystalline boundaries. Zone 3 structure, which occurs when $T_{\rm s}$ / $T_{\rm m}$ > 0.5, is characterized by epitaxial growth on the substrate. A fourth zone, zone T ("transition"), was later identified by Thornton [2.11, 2.12] as an intermediate regime between zones 1 and 2. This zone is characterized by densely packed fibrous grains. Although no intentional heating was applied to the substrates during film growth, local heating around the discharge center may have been caused by the preferential ion bombardment in this area. One possible source of the energetic ions was the O ions produced during the sputtering of the oxide target [2.13]. If the substrate temperature was sufficiently high, a structural transition from zone 1 to either zone T or zone 2 may have resulted locally. The ensuing increase in volume density at the center of the sputtered film may be responsible for the observed thickness depletion.

The speculated local increase of film density is consistent with two experimental observations. Firstly, the change in color across the film may be explained in terms of film opacity. The smaller optical transmittance of the film at the center may be associated with the more densely packed grains of zone T. Towards the edges, the zone 1 microstructure, which consisted of loosely packed columns with void boundaries, would allow more light to transmit. Secondly, the higher

density in the central area would subject the films in this area to a higher tensile stress when heat treated. This is in agreement with the observation that the central films were more prone to flaking during post-deposition heat treatment. Further details on this observation are provided in Chapter 3.

2.7 Resputtering

Beside film densification, another possible cause for the decrease of thickness is film erosion due to resputtering, *i.e.* bombardment of the growing film by energetic ions. Resputtering of YBaCuO films was reported by Rossnagel and Cuomo [2.13] for single target magnetron sputtering, and by Shah and Carcia [2.14] for multitarget magnetron sputtering. According to the former authors, a large number of O ions were produced during the sputtering at the oxide target. These ions were accelerated away by the negative bias voltage (with respect to the plasma), and were neutralized by loosing their electron through collisions in the plasma. In a low pressure plasma, the neutrals had a small cross section for momentum transfer collisions and could reach the growing film. Shah and Carcia [2.14] found that when the substrate was sequentially positioned under each of the multiple targets, film erosion occurred only under the Y₂O₃ and Ba₂CO₃ but not under the CuO targets. Their observation led to the speculation that, not only neutralized O⁻ but other neutrals inherent to each oxide may contribute as well to film erosion.

The relevance of the above results to the films deposited from the PbBiSrCaCuO targets is unknown because the yield of O⁻ ions is different. A quantitative study of this occurrence is beyond the scope of

this thesis. However, it remains a possibility that, in addition to film densification, resputtering contributed to some extent in the central thickness depletion and even in the variation of film thickness along the slide. From the application viewpoint, it is desirable to control the ion bombardment of the growing films so as to maximize the usable film area. A straightforward method is to decrease the rf power and increase the plasma pressure so as to reduce the kinetic energy of the neutrals that reach the film. Another method consists in positioning the substrate at a small angle with respect to the main stream of neutrals. However, these methods were not adopted in this thesis work because they lower the deposition rate and affect the thickness uniformity of the film.

2.8 Film composition

After the thickness measurement, the composition of sputtered films was measured at different locations on the substrate. This was necessary to determine the film homogeneity and locations where film stoichiometry close to the high T_c Bi₂Sr₂CaCu₂O₈ could be obtained. The quantitative measurement of film composition was performed by means of electron probe microanalysis (EPMA). The film was inserted in the chamber of an EPMA analyzer (Cameca) and the chamber was evacuated to a pressure of ~ 10⁻⁶ Torr. After this, an electron beam with a diameter of 5 µm and current of 10 nA was directed to the film under an accelerating potential of 15 kV, and the characteristic energies of Xray emitted from the excited film atoms were detected. The emission intensities were monitored at specific wavelengths and compared with standards taken from elemental samples. The analyzer was programmed to detect only pre-identified elements and, therefore, was

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operated in conjunction with energy dispersive X-ray spectroscopy (EDX). The initial identification of elements was carried out using the EDX analyzer of a scanning electron microscope (Noran-Adem).

Several samples of PbBiSrCaCuO films prepared on (100) MgO substrates were used for the composition determination. Due to the limited space in the chamber of the EPMA analyzer, the area of the substrates for the growth of films for the composition determination was set to be $3 \times 10 \text{ mm}^2$. The spatial dependence of composition was assessed by examining the samples prepared 4 mm apart one another on the substrate table, from the discharge center outwards. To minimize the effects of unwanted X-ray from excited substrate atoms, films that are thicker than the lateral penetration depth of the electron beam (~ 0.5 um) are required. All the films intended for the EPMA analysis are 1-µm thick.

The initial identification of elements in the films confirmed the presence of all starting metallic elements of the sputter target and no evidence of impurities. Because carbonate powders were used in the preparation of the target, the possibility that some carbon impurity might remain in the sintered target was examined. No sign of carbon atoms (Z = 6) could be found in the EDX spectra, suggesting that the presence of carbon in the target, if any, was reduced to at least the noise level. Figure 2.11 shows the average atomic concentration of the metals in the film, normalized to Cu = 3, at various locations with respect to the discharge center (x = 0). For each film, the metal concentrations were averaged out from the line scan data. It is seen that, away from the discharge center, the deviation of the film composition from the nominal composition Bi:Sr:Ca:Cu = 2:2:2:3 increases gradually. For x < 2.5 cm,

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i.e. within the projection area of the sputter target on the substrate table, this deviation is relatively small. For x > 2.5 cm, deviation becomes more important. This behavior is consistent with that expected from the sputtering of a target directly facing the substrate table.

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One notable result in Fig. 2.11 is the ratio of the Pb concentration to the other metals is about half that selected for the target preparation. The deficiency of Pb may be due to: (i) preferential resputtering of the film by O⁻ ions or sputtered species from the target; and (ii) the sintered target was already Pb deficient. In the former case, the ratio of Pb concentration to the other metals would exhibit a dependence on the film location. However, referring to Fig. 2.11, it is seen that this ratio varies rather slightly within the projection area of the target. Such a behavior favors the thesis of Pb deficient target. It appears likely that some amount of Pb escaped by evaporation during the target sintering. Likewise, a loss of Pb in thin films and crystals of PbBiSrCaCuO after the heat treatment has been reported by other researchers [2.15-2.16].

2.9 Superconductivity in heat treated films

In light of the above results, films with desired composition and thickness uniformity could be achieved within the projection area of the target on the substrate table. To determine whether the high T_c phase could be formed in these films, one of them was subjected to a heat treatment. The selected film was grown to a thickness of ~ 1 µm at distance x = 1.8 cm from the discharge center. Referring to Fig. 2.11, it is seen that the nominal composition of this film is close to Pb:Bi:Sr:Ca:Cu:O ~ 1:2:2:2:3. The heat treatment was performed in a tube furnace successively in flowing O₂ and in air. Details of the heat treatment are provided in Chapter 3 of this thesis. Briefly, the film was pre-annealed in flowing O_2 (500 sccm) for 20 min, heat treated in air for 40 min, and air quenched to room temperature. The annealing temperatures of the film in O_2 and air were respectively 830 and 865 \circ C. After the heat treatment, the electrical resistance of the film, R, was measured as a function of temperature, T. In this experiment, Rwas taken as the ratio of the voltage developed across the film when a small current (I = 1 mA) traversed the film. The *R*-*T* characteristic of the film is shown in Fig. 2.12. When the film was cooled from room temperatures down to ~ 125 K, R decreased linearly with decreasing T, showing a metallic behavior. When T was reduced further, R decreased sharply and reached superconductivity value at $T \sim 106$ K. This critical temperature is close to that of the $Bi_2Sr_2Ca_2Cu_3O_{10}$ phase [2.17]. suggesting the presence of this phase in the film. Subsequent analysis of the film, presented in Chapter 3, corroborated this speculation. This result shows the evidence that magnetron sputtering is effective as a technique to prepare superconductor films with the high $T_{\rm C}$ phase.

2.10 Conclusions

This chapter reported on the synthesis of PbBiSrCaCuO superconductor films by means of single target magnetron rf sputtering. It described in the first place the experiment devised to prepare the sputter targets of PbBiSrCaCuO. The procedure consisted of a blending of precursor powders, followed by solid state reactions and pressing of the reacted powder compound. Experimental conditions were determined for each step, which resulted in high quality sputter targets for magnetron sources. During the sintering of the powder compound, an important amount of Pb appeared to evaporate and had

to be compensated by introducing a larger amount of Pb in the compound. The compositional analysis of the sputtered films suggested that the target was likely composed of Pb:Bi:Sr:Ca:Cu:O ~ 1:2:2:2:3with low carbon content. The magnetron sputter deposition was performed in a laboratory type coater which enabled the process to be scaled. Thin films of PbBiSrCaCuO were deposited onto monocrystalline (100) MgO and (100) LaAlO₃ substrates. Several effects of the sputter deposition that had not been reported elsewhere were observed. For instance, surface profiling over a film length of 12 cm showed the evidence of a depletion of film thickness around the discharge center. This depletion was found to be consistent with the structure zone model of sputtered films, in which an increase in film density at the center area could be predicted. Beside film densification, it is believed that the depleted film thickness was also a result of film erosion due to the bombardment of growing film by energetic ions. The composition of the sputtered films was examined at different locations on the substrate. The EPMA data confirmed that a significant loss of Pb had occurred during the target sintering and film deposition. The deviation of film composition from nominal composition of the target was found to increase with increasing distance between the film and the discharge center.

In light of the experimental results, films with desired composition and thickness uniformity could be achieved within the projection area of the target on the substrate table. After a specific heat treatment, one of these films showed superconductivity with a T_c ~ 106 K. This critical temperature suggested the presence of the high T_c Bi₂Sr₂Ca₂Cu₃O₁₀ phase in the film. An extensive investigation on

the effects of the heat treatment on the formation of the superconducting phases is presented in the next chapter.

j	$n_{ m j}$	μ_j (g/mol)	$M_{ m j\ computed}\ ({ m g})$	$M_{ m j\ weighed} \left({ m g} ight)$	$T_{\mathrm{m}^1}(^{\mathrm{o}}\mathrm{C})$
PbO	2	223.19	9.4894	9.4890	886
Bi_2O_3	1	465.96	9.9056	9.9059	860
$SrCO_3$	2	147.63	6.2768	6.2773	1497^{2}
$CaCO_3$	2	100.09	4.2555	4.2556	899
CuO	3	79.54	5.0727	5.0726	1326
$M_{ m t}$			35.0000	35.0004	

Table 2.1 - Stoichiometric weights and melting temperatures of theprecursor powders used in the preparation of PbBiSrCaCuO targets

 1 at 1 atm 2 at 69 atm

Table 2.2 - Room temperature characteristics of the supportingsubstrates of PbBiSrCaCuO films

Substrate material	MgO	LaAlO ₃
Crystal orientation	(100)	(100)
Crystal system	cubic	rhombohedric
Lattice constant (nm)	a = 0.42	$\alpha = 0.54$
Thermal expansion coefficient (K-1)	$8 \ge 10^{-6}$	10-5
Thermal conductivity (W / cm.K)	3.4	0.12
Specific heat capacity (J / kg.K)	1003	
Thickness (µm)	200 and 50	0 200
Maximum area (cm ²)	. 1	1
Surface roughness (nm)	3	8



Fig. 2.1 - SEM photograph of the sintered PbBiSrCaCuO powder compound



Fig. 2.2 - Diagram of the apparatus for the pressing of the sputter target. This apparatus comprises a cylindrical mold and press system and two rotating pistons. Dimensions are in centimeter unit.



Fig. 2.3 - Temperature profile of the final sintering of the pressed PbBiSrCaCuO disk



Fig. 2.4 - Surface morphology of a sintered PbBiSrCaCuO target



Fig. 2.5 - Sintered PbBiSrCaCuO target on Cu base plate. The target is intended for use with a Corona 2-inch magnetron gun (model C2).



Fig. 2.6 - Surface profiles of different supporting substrates for PbBiSrCaCuO films. The profile of a glass slide (Corning 2497) is also shown for the purpose of comparison.



Fig. 2.7 - Schematic diagram of the sputter deposition facility



Fig. 2.8 - Schematic arrangement of the masked slide on substrate table prior to the sputtering deposition



Fig. 2.9 - Photograph of a PbBiSrCaCuO film deposited on the glass slide



Fig. 2.10 - Thickness profiles of several PbBiSrCaCuO films for different periods of deposition time. The separation between the target and substrate table was 8 cm. The rf power and Ar pressure were respectively 80 W and 3 mTorr. The thickness profile of a Cr film deposited under similar conditions is also shown for the purpose of comparison.



Fig. 2.11 - Atomic concentrations normalized to Cu = 3, as measured on sputtered PbBiSrCaCuO films at different locations on the substrate table.


Fig. 2.12 - R-T characteristic of a heat treated PbBiSrCaCuO film

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Chapter 3. Formation of superconducting phases in PbBiSrCaCuO films

3.1 Introduction

Since the discovery of superconductivity in the multiphase $Bi_2Sr_2Ca_{n-1}$ Cu_nO_y [3.1], there has been extensive work devoted to the synthesis of thin films of this compound. Chapter 2 described the magnetron sputtering synthesis with emphasis on properties of the sputtered films. The intent of this chapter is to report on the effects of heat treatment conditions on the growth of superconducting phases in these films.

Thin films of Bi₂Sr₂Ca_{n-1}Cu_nO_y may be synthesized in at least two superconducting phases which differ mainly in the number of CuO₂ planes between Bi₂O₂ along the *c*-axis. These phases are commonly referred to by their cation ratios as 2212 with n = 2 and $T_c \sim$ 80 K, and 2223 with n = 3 and $T_c \sim 110$ K. Under normal preparation conditions, the low T_c 2212 phase develops more rapidly and impedes the growth of the high T_c 2223 phase [3.2]. As an attempt to promote the growth of the 2223 phase, the effect of Pb doping has been investigated [3.3-3.4]. To achieve zero resistivity at above 100 K in PbBiSrCaCuO films, thermal annealing for 20-40 hrs at temperatures close to the melting point of the film has been used. This process suffered from low yields because it was difficult to regulate annealing temperatures over a lengthy period of time. Moreover, the composition of metal constituents of the film appeared to vary with annealing time. The difficulty in compensating adequately elemental losses during prolonged treatments, especially the loss of Pb, may have contributed to the low yield of single phase 2223 films. Finally, the long thermal annealing was unattractive for both fundamental study and application purposes.

Although the formation of single phase 2212 films after a short annealing (~ 1 h) has been reported before [3.5], the accelerated growth of single phase 2223 films has received little attention. In a paper by Tanaka *et al.* [3.6], it was suggested that Pb acts as an accelerator of the chemical reaction required for the formation of 2223 phase. During the investigation of BiSrCaCuO films containing codeposited PbO layers, these authors found that films with 2223 dominant multiphases could be developed after one hour of annealing. However, it remained questionable whether a single high T_c phase could be segregated after a short heat treatment. As an attempt to address this question, the main object of this chapter is the kinetics of phase formation in PbBiSrCaCuO films under a short annealing. In the following sections, after the description of the thermal annealing and characterization techniques, the effects of annealing conditions on the film properties will be presented and discussed.

3.2 Apparatus for thermal annealing

The annealing apparatus is intended for treatments of PbBiSrCaCuO films at temperatures of up to 900 °C in air and O₂. Figure 3.1 shows a schematic diagram of this apparatus. It consists mainly of a cylindrical tube (5 cm diameter) inserted in a resistively heated furnace (Lindberg 54233). The tube material, Al₂O₃, was selected for its high melting point and chemical stability in the annealing temperature range. The end caps of the tube were loose enough so that only a slight overpressure occurred inside it. Films to be treated were placed with the film side upwards on a flat Al_2O_3 piece in a boat made of the same material. This configuration raised the film to about the vertical midpoint of the tube. The boat carrying the film could be moved from one end to the center of the tube. Ar and O_2 of 99.995% purity were allowed to flow through the tube at rates of up to 1000 sccm. The flow rate was monitored by a flowmeter placed at the entrance of the tube. For heat treatments in O_2 , Ar flush was used to vent out atmospheric gas in the tube prior to annealing. The temporal characteristic of furnace temperature could be programmed and regulated with a feedback temperature controller (Eurotherm 818P).

In the course of the work on thermal annealing, it was found that the actual temperature of the furnace could deviate considerably from its set point and, therefore, required careful monitoring. An accelerated rise of temperature to the set point, for instance, may result in temperature overshoots. Furthermore, temperature varies along the tube as a result of unequal heat distribution. Because the formation of superconducting phases is highly sensitive to annealing temperature, it is important to assess the extent of temperature deviation. For this purpose, calibrated type K thermocouples were used to record temperatures at different sites in the tube. The recorded data were fed to a computerized acquisition system (Acro System 900). Figure 3.2 shows the temporal characteristic of the temperature measured at the tube center when the furnace temperature was set to 860 °C and the thermal elements were set to deliver full power. It reveals the occurrence of an overshoot of ~ 30 °C above the set point. Following the overshoot, the decreasing temperature is seen to reach

the set point only after a period of ~ 25 min. The noise of the characteristic, ~ 4 °C, is also considerable. The observed temperature overshoot and noise are believed to have caused flaking and evaporation of the films treated under this condition. As an attempt to remedy this problem, the thermal power of the furnace was lowered to ~ 30% of its maximum level. The *T*-*t* characteristic recorded under this condition (Fig. 3.3) has negligible overshooting and instability. However, temperature tends to decrease gradually after reaching the set point because of the low thermal power. Through the subsequent tests it was found that temperature drifts could be minimized by moving the sensor of the characteristic recorded at the film site. Figure 3.4 shows the characteristic recorded at the film site when the sensor was placed right above the film on the outer side of the tube. It is seen that, after the desired temperature was reached, temperature was kept to 1 °C stability over the period that follows.

After the overshooting problem had been solved, temperature was monitored at different points along the longitudinal axis, x, of the tube. The center of the tube was taken as x = 0 and the temperature sensor was placed at x = 0 on the outer side of the tube. Results of the treatment in air is shown in Fig. 3.5. The T(x) plot reveals that temperature peaks near the center of the tube and decreases away from the center. This behavior is predictable since the temperature sensor is located at the center. In the central part of the tube the temperature gradient is less than 1 °C per centimeter of film. It is further seen that T peaked at $x \sim 3$ cm, an indication that the heat distribution was asymmetrical around x = 0. Also shown in Fig. 3.5 is the temperature measured at x = 0 cm for different rates of O₂ gas flow. When the flow rate was kept at below 1000 sccm, the change in temperature with the flow rate was less than 1 $^{\circ}$ C. Comparing, one notes also that the temperature at the center differs only slightly whether the treatment is performed in O₂ or in air.

Nearly all of the PbBiSrCaCuO films were treated at x = 0. Because the film was located at a distance from the temperature sensor, there was a deviation between the temperature set point, T_0 , and the temperature at the film site, T. Figure 3.6 displays the relation between T_0 and T in the range from 840 to 880 °C. This relation can be described by the following equation:

$$T_0 = 0.95 \ T + 31.5 \tag{3.1}$$

that was used for temperature conversion. Note that it is T, not T_0 , that will be referred to as the annealing temperature in the subsequent sections.

3.3 Electrical characterization

Electrical characterization was performed as part of the investigation on the superconducting properties of the annealed films. The parameters extracted from this characterization are the critical temperature, T_c , and the critical current density, J_c , of the film. The values of T_c and J_c were determined by measuring the film resistance, R, as a function of temperature and current. The determination of zero resistance was limited by the instruments sensitivity. The value of J_c was defined as the current density beyond which the voltage generated across the film exceeded 1 μ V.

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The resistance of the film was measured using the four-point probe technique (Fig. 3.7). The electrical contacts formed on the film (typical film area ~ $10 \times 3 \text{ mm}^2$) were colinear and spaced 2 mm apart. A dc current was supplied through the two outer contacts and the voltage drop between the inner two was evaluated. Because very little current flew in the voltage leads, the voltage drop due to the contact resistance was negligible. In some experiments, the contacts were made of Ag thermally evaporated onto the film through an Al mask. Otherwise, contacts were made using Ag paint to attach 120-µm diameter Au wires to the film. When the film was to be preserved for subsequent analysis, Ag paint was removed from it by ultrasound cleaning in CH₃OH solvent. Inspection was also carried out to discriminate superconductivity simulated by defects in the film. One common type of defects leading to simulated superconductivity is fissures that open up in the film at low temperatures, isolating the current and voltage leads (Fig. 3.7). As such, the voltage drops to zero with the current remained constant, even when the film was not superconducting. The described condition was checked by allowing the current from lead 1 to lead 3 and measuring the voltage between leads 2 and 4. If the same result is obtained as when injecting the current in leads 1 and 4 and measuring the voltage between leads 2 and 3, one concludes that the film contains at least one superconducting path.

The experimental setup for the electrical characterization of PbBiSrCaCuO films is schematically shown in Fig. 3.8. To enable the resistance measurement at temperatures down to 77 K, the film was thermally anchored to a Cu block at the cold end of a low temperature probe. The probe consists of a stainless steel cylindrical tube having a diameter of 15 mm, which can be inserted into a liquid nitrogen (LN₂) Chapter 3 – Formation of superconducting phases in PbBiSrCaCuO films 56

dewar. The Cu block is an extension of a steel rod that fits down the center of the probe. Two ports are provided on top of the probe, one for vacuum pumping and gas filling and the other for venting. Prior to inserting the probe into the LN₂ dewar, a mechanical pump was used to evacuate the probe for at least 10 min. This step was carried out to prevent condensation of water vapor inside the probe at the low temperatures. After this, the probe was filled with approximately 0.1 atm of He gas that provided thermal contact between the Cu block and LN₂ refrigerant. To reduce the temperature gradient across the Cu block, the 15-cm cold end of the tube wall was also made of Cu. Following immersion of the probe in LN_2 , the resistance of the film was measured repeatedly until its temperature reached 77 K. The film temperature was monitored using a Si diode imbedded in the block. The dc currents driving the film and the Si diode were respectively supplied by a current source (Keithley 224) and a voltmetermultiplexer control unit (HP 3497A). The latter unit was also used to acquire the voltages developed across the film and the Si diode. Data were fed to a computer which calculated and plotted the R-Tcharacteristic of the film. The Si diode was calibrated periodically against a cryogenic temperature sensor (LakeShore DT-470) that replaced the film in the setup. The repeatability and accuracy of the latter sensor were respectively 10 and 50 mK.

In the later phase of the thesis work, electrical characterization was further performed in a Gifford-McMahon closed cycle cryocooler. This cooler was originally the cooling unit of a commercial laser spectrometer (Laser Photonics LS-3). For the purpose of this work, the laser diode at the cold head of the cooler was replaced with the PbBiSrCaCuO film. The cold head was decoupled mechanically from the 3 Hz cycling vibration of the cooler. The temperature range of the cold head is 10-300 K. In the lower end of this range (10-100 K), temperature stability of better than 0.3 mK was achieved with the use of an integrated temperature controller. The latter interfaced with a Si temperature sensor imbedded in the cold head and a tightly coupled wire-wound heater. As the cooler allows for optical access to the film through an integrated window, it was mainly used in the low temperature measurement of photoresponses (Chapter 4).

3.4 Magnetic characterization

An accepted technique for characterizing superconductivity is to measure the magnetic susceptibility, χ , of the material. This technique allows to determine T_c as the temperature below which the film exhibits perfect diamagnetism. Because the detection of diamagnetism is possible only in a large volume of homogeneous and superconducting material, this technique provides further insight as to whether the entire film is superconducting or consists merely of a superconducting island in a nonsuperconducting sea.

The measurement was performed in a low temperature ac susceptometer (Lakeshore Cryotronics 7000) as illustrated in Fig. 3.9. The film is thermally anchored to a temperature regulated probe which is inserted into a liquid He cooled chamber. The vertical position of the probe is controlled by a stepping motor so that the film can be moved precisely between a primary coil and either one of the two oppositely wound sensing coils. The primary coil consists of a solenoid in a transformer circuit driven by an ac current to generate fields of up to 800 A/m at frequencies from 5 to 1000 Hz. The sensing coils are arranged such that the phase sensitive detector (lock-in amplifier) connected to them produces a vanishing signal in the absence of the film. When the film is introduced next to one of the sensing coils, its magnetic moment is detected inductively by the coils and the lock-in amplifier produces an out-of-balance voltage, v. This voltage is proportional to the magnetic susceptibility as:

$$v = \gamma^{-1} \left(V_{\rm f} H_{\rm f} \right) \chi, \tag{3.2}$$

where V_f is the film volume, H and f are respectively the rms amplitude and frequency of the applied magnetic field, and γ is a coefficient dependent upon the film and coil geometry [3.7]. The coefficient γ can be inferred from Eq. 3.2 by measuring the output voltage with a standard of known susceptibility and of geometry comparable to the film sample. Both the in-phase and out-of-phase components of v (with respect to the current driving the primary coil) are measured. They are respectively proportional to the real, χ' , and imaginary, χ'' , part of the complex susceptibility $\chi = \chi' + j\chi''$. χ'' represents the lossy component that is due to the motion of the vortices in type II superconductors.

To investigate the uniformity of superconducting area, the 10 x 3 mm^2 PbBiSrCaCuO film was further cut into three equal parts for separate measurements. Each of these parts was oriented normal to the applied field in order to maximize the output voltages. Only when most of the film material was superconducting, a transition from normal paramagnetic state to diamagnetic state could be evidenced in the χ -T characteristic. The T_c value was defined as the temperature below which the film turns diamagnetic.

3.5 Microstructural characterization

The microstructures of the annealed PbBiSrCaCuO films were examined by means of electron probe microanalysis (EPMA), scanning electron microscopy (SEM), and X-ray diffraction (XRD). The EPMA technique is the same as the one described in Chapter 2 (section 2.8). The SEM and XRD techniques are described below.

Scanning electron microscopy is commonly used in surface analysis of thin films. The SEM technique makes use of an electron beam that is focused onto different spots of the film sample. For each spot, some characteristic of the sample must be measured so as to reproduce its image. The most commonly measured characteristic is the rate of secondary electrons emitted from the film, that is detected with a scintillator in conjunction with a photomultiplier. The source of incident electrons consists of a current driven thermoionic filament, such as W. The emitted electrons are focused into nanometer diameter beam by two successive magnetic lenses. This beam is then deflected by a pair of scanning coils in order to scan the electron spot in a raster pattern across the sample. The micrographs of the films produced in this work were obtained from the JEOL 5800 SEM instrument. The focused beam of this instrument has energy in the range from 0.3 to 30 keV, enabling spatial resolutions of up to 3.5 nm. At the room temperature, superconductor films exhibit metallic behavior, *i.e.* good electrical conductivity, so that no special preparation is required for these samples. On the other hand, the as-deposited films are insulating and, when examined in the SEM, need to be coated with a thin conducting carbon film. This coating was necessary to prevent a rapid build up of electric charges on these samples when scanned by a

beam of high energy electrons. Charging phenomena, in the absence of a coating layer, may result in image distortion and thermal damage of the sample.

The multiphase nature of BiSrCaCuO superconductors makes it imperative to determine information on the crystal lattice, crystal orientation, and which other phases are present. In this work, this information is obtained by means of X-ray diffraction. This technique relies on reflecting monochromatic X-rays off a crystal lattice and evaluating the angles for which the Bragg law for constructive interference holds. This is done by scanning the X-ray source and detector together and recording the intensity of the reflected beam against the incident angle. The result is a characteristic pattern from which the crystal structure can be inferred. Referring to the illustration in Fig. 3.10, the Bragg law can be expressed as:

$$\lambda = 2d\,\sin\theta\tag{3.3}$$

where λ and θ are respectively the wavelength and incident angle of the X-ray, and *d* is the spacing between crystal plans. In the experiments, a Phillips PW1710 diffractometer with Cu K α X-rays ($\lambda \sim$ 1.54 Å) was used. The detector was scanned over 2 θ at 2 degrees / min. At this scan rate, reproducibility of the diffractometer is estimated to be within 0.1 degree for values of 2 θ . For the purpose of identification, the measured patterns were compared against the indexed XRD signatures of bulk Bi₂Sr₂Ca_{n-1}Cu_nO_y superconductors (Fig. 3.11), according to Tarascon *et al.* [3.8].

3.6 Effects of annealing temperature

In the first series of experiments, the effects of annealing temperature on the formation of superconducting phase in PbBiSrCaCuO films were investigated. Most of these films were grown to a thickness of 1 µm by means of magnetron rf sputtering. The deposition was performed in 4 mTorr of Ar using an rf power of 80 W. The separation between the target and the substrate table was 8 cm. The substrates used were (100) oriented monocrystalline MgO, LaAlO₃, and SrTiO₃, each having an area of $10 \times 3 \text{ mm}^2$. No intentional heating was applied to the substrates during the deposition. Details on properties of the sputtered films were presented in Chapter 2. After the deposition, the film was annealed in the apparatus described in section 3.2. The heat treatment was carried out first in flowing O_2 (500 sccm), at a slight overpressure, and then in air. The temperatures of annealing in $O_2(T_{A1})$ ranged from 810 to 830° C, and those in air (T_{A2}) from 830 to 870° C. The annealing time in O₂ and air (t_{A1} and t_{A2}) was respectively 20 and 40 min. After the heat treatment, the film was withdrawn from the tube furnace and air quenched to room temperature.

Figure 3.12 shows the X-ray diffraction (XRD) spectra of the films treated at different temperatures in air after a preannealing at 830 °C in O₂. Although the XRD patterns have not been indexed, they match the signatures of bulk Bi₂Sr₂Ca_{n-1}Cu_nO_y [3.8] as shown in section 3.5. Accordingly, it was possible to denote the Bragg diffraction peaks by the number of the CuO₂ layers in the unit cell, *n*. When the treatment in air was carried out at temperature equal to that in O₂, $T_{A2} = 830$ °C, it is seen that the 2212 phase formed readily in the film.

As T_{A2} was increased, a gradual structural transition from the 2212 to 2223 phase occurred. In effect, at $T_{A2} = 830$ °C only the (00*l*) Bragg diffraction peaks of 2212 phase are seen in the XRD spectrum. The structure of the film treated at 840 °C remains predominantly 2212 phase. However, there is indication of the presence of high T_c phase in this sample as a small (0010) peak of 2223 phase appears next to the (008) peak of 2212 phase (intensity ratio ~ 1/12). The intensity of the high $T_{\rm c}$ peak increases significantly as $T_{\rm A2}$ was increased to 850 °C, at which a mixture of (00l) oriented 2212 and 2223 phases is found in the XRD spectrum. Beyond this temperature, the phase transition appears to be highly susceptible to temperature changes. For instance, the ratio of the (0012) peak of 2212 phase to the (0014) peak of 2223 phase decreases from 60% at 850 °C to 20% at 855 °C. When T_{A2} was increased to 865 °C, the resulting film developed into nearly 2223 single phase and the 2212 peaks are barely visible in the XRD spectrum. The presence of a small peak associated with the 2201 phase $(n = 1; T_c \sim 10 \text{ K})$ is also noted at $2\theta = 22^{\circ}$. When T_{A2} exceeded 870 °C the films suffered from a loss of material, possibly due to evaporation.

To corroborate the above results, the *R*-*T* characteristics of the films were measured and related to the XRD data. In this experiment the current density supplied to the films was ~ 3 A / cm². Figure 3.13 displays the *R*-*T* characteristics recorded on the treated films. For all of these films, the superconducting phases revealed by these characteristics are consistent with those identified in the XRD spectra. The film treated at $T_{A2} = 830$ °C shows a T_c of ~ 77 K and 12 % resistance drop near 110 K, indicating the occurrence of a predominantly 2212 phase. As the volume fraction of the 2223 phase increased in the film treated at 840 °C, the resistance drop near 110 K

becomes larger (~ 42 %). The film with mixed 2212 and 2223 phases, as obtained after the treatment at $T_{A2} = 850$ °C, shows an onset temperature, T_{onset} , of 115 K and a T_c of 99 K. The broad transition width ($\delta T / T_c >> 0.01$) and the resistance tail suggest that different parts of the film have different transition temperatures [3.9]. In this case, the film resistance goes to zero when a percolation path is established. According to the Bruggeman effective medium approximation [3.10], the occurrence of a high $T_{\rm c}$ superconducting percolation indicates that the volume fraction of 2223 phase in the film is at least 33%. This is consistent with the XRD data showing a $\{(0010)\}$ / (0010)+(008)} peak ratio that exceeds 70%, where (0010) and (008) are respectively the main peaks of the 2223 and 2212 signatures. Finally, the films annealed at T_{A2} in the range from 855 °C to 870 °C exhibit single phase behavior, such as sharp resistive transition at $T_{\rm c} \sim 107$ K, and a R(150 K) / R (250 K) ratio close to the ideal value of 0.6. The critical current density J_c of these films was estimated to exceed 8 x 10^3 A/cm² at T = 79 K using the 1-µV criterion. The measurement of the transport J_c was limited to the above value because the contact resistance may have caused warming of the sample at higher current values. The temperature dependence of J_c is shown in Fig. 3.14. It is evident from this dependence that the experimental data follows a power law: $J_{\rm c} \propto (1 - T / T_{\rm c})^n$, with *n* found to be 2.4. This value is larger than the one predicted by Deutscher and Muller, n = 2 [3.11]. These authors assumed that J_c was determined by Josephson tunneling at the grain bounderies in order to derive the power law dependence.

Although a resistance measurement may be satisfactory for films that are known to be homogeneous and superconducting, only a susceptibility measurement can confirm whether the film area contains more than just a superconducting path. Figure 3.15 displays together the R-T and γ -T characteristics of a single phase 2223 film annealed at T_{A2} = 865 °C. The *R*-*T* characteristic was measured in the absence of a magnetic field, using a current density of 3 A / cm^2 . The χ -T measurement was performed in ac magnetic fields (frequency of 1 kHz) for two intensities, 25 and 800 A / m. The film is seen to exhibit perfect diamagnetism ($\chi' = -1$) at temperatures below 103 K for H = 25A / m, and below 90 K for H = 800 A / m, while showing zero resistance at below 107 K in the R-T characteristic. The T_c values obtained from susceptibility measurement decrease with increasing field intensity and are smaller than the one obtained from resistance measurement, without an applied field. This result is consistent with the expected effect of magnetic field on T_c 's. Referring to the χ' data, the sharp temperature transition from normal paramagnetism to diamagnetism suggests that the film is homogeneous and superconducting over a large film area. This observation is further supported by the weak dependence of the transition temperature upon field intensity. In effect, the transition shifts only by ~ 3 K towards lower temperatures when the field is increased from 25 to 800 A / m. This behavior is in contrast to that of heterogeneous films, of which the temperature shift and broadening of the transition are sensitive to field intensity. Another evidence of the superconducting homogeny of the studied film is that the χ " peaks around T_c remain fairly small. These peaks are believed to be a measure of the resistive losses of multiconnected superconducting-normal areas of the film [3.12].

To confirm the above, susceptibility measurement was further carried out on a mixed 2212 and 2223 phase film (annealed at T_{A2} = 850 °C) for different field intensities. The results obtained, as shown in Fig. 3.16, were compared against the preceding results on the single phase film. It is evident from the χ' data that the normal-diamagnetic state transition broadens with increasing field intensity. At T = 90 K, χ ' approaches 65% of the diamagnetic limit for H = 20 A/m, whereas it is less than 25% for H = 800 A / m. The broadening of the transition indicates that the film is heterogeneous and its different parts have different $T_{\rm c}$ values. Because of this, although the film resistance decreases to zero at $T_c = 99$ K (see Fig. 3.13), the superconducting percolation is not dense enough at temperatures as low as 77 K for the film to exhibit perfect diamagnetism. The χ " data reveals a continuous shift of the χ " peak towards lower temperatures when *H* is increased. The temperature shift of the mixed phase film, 16 K, is about five times the shift observed on the single phase film, with both films subjected to comparable changes in *H*. Because χ " is related to resistive losses, it peaks at the temperature where the resistive losses across the Josephson junctions of the film are the highest. Such losses occur when the field induced current exceeds the Josephson current. Therefore, the larger shift of χ " peak agrees with the fact that the intergrain coupling strength is weaker in a mixed phase film than in a single phase film.

3.7 Effects of annealing time

The kinetics of the 2223 phase formation was investigated on the PbBiSrCaCuO films annealed for different periods of time. The annealing temperatures in O₂ and in air, T_{A1} and T_{A2} , were respectively 830 °C and 865 °C. The films used were sputter deposited under identical conditions prior to the heat treatment; these sputtering conditions were described in section 3.6. Figures 3.17 and 3.18 display respectively the XRD spectra and *R-T* characteristics of the treated films. After the first 5 min of preannealing in O_2 , the film resistance is seen to increase with decreasing temperature, suggesting a semiconductive behavior. However, after 10 min of preannealing, the film starts to exhibit some superconducting sign as its resistance decreases with decreasing temperature. The XRD spectrum of this film shows a predominant 2212 structure with preferred (001) orientation and a weak (001) oriented 2201 structure. The additional presence of CaPbO₄ impurity at $2\theta = 31.6^{\circ}$ is also noted. The early formation of CaPbO₄ in PbBiSrCaCuO compound was proposed by Hatano et al. [3.13] as a mechanism which impedes transitions from the 2201 to 2212 or 2223 phase. This theory was substantiated by the report of Osborne *et al.* [3.14] of a correlation between the CaPbO₄ and 2201 peaks in the first 30 min of annealing of moderately Pb doped BiSrCaCuO films. The presence of these correlated peaks was not commented in the work of Tanaka et al. [3.6] on heavily Pb doped films. However, the secondary phases of the XRD spectra of their films seem to contain these peaks during the first 10 min of heat treatment. Referring to Fig. 3.17, it is seen that while the $CaPbO_4$ peak remains in the film preannealed for up to 20 min, the (006) peak of the 2201 phase decreases considerably. This observation suggests that the evaporation of Pb during preannealing was not sufficient to eradicate completely the early formed CaPbO₄. However, those Ca atoms released with the loss of Pb allowed for a gradual incorporation of CaCuO layers into 2201 lattices to form 2212 or 2223 phases. In effect, mixed 2212 and 2223 phases were seen in the film which underwent an additional 5 min of heat treatment in air. As the content of Pb decreased further in this film, the CaPbO₄ peak disappeared in its

XRD spectrum. Although the $\{(0010) / (0010) + (008)\}$ peak ratio of the 2212 and 2223 phases is just slightly above 33 %, a $T_{\rm c}$ of above 100 K is obtained in the *R*-*T* characteristic, suggesting that a superconducting percolation path could be established in this film. As the annealing progressed in time, a gradual structural transition from the 2212 to 2223 phase occurred so that the 2223 volume fraction is seen to increase. For the films with t_{A2} being increased from 5 min to 30 min, the intensity ratio between the $(00\underline{10})$ peak of 2223 and (008)peak of 2212 rises steadily from 58 % to 122 %. An increase of the onset temperature is also seen in the R-T characteristics with $T_{\rm c}$ remaining unchanged. After $t_{A2} = 40$ min the phase transition becomes more rapid, leading to the formation of a nearly single phase 2223 with a strong (001) preferred orientation. In this sample, while the peaks of 2212 phase mostly disappear, the (006) peak of 2201 phase appears near the (0010) peak of 2223 phase. An observation similar to the one presented here on the presence of minor 2201 phase in predominantly 2223 films was reported by Takano et al. [3.15]. In a study on the reaction mechanism of the high T_c formation in PbBiSrCaCuO system, Kijima [3.16] proposed that a disproportionate reaction of:

$$2 \operatorname{Bi}_{2} \operatorname{Sr}_{2} \operatorname{Ca} \operatorname{Cu}_{2} \operatorname{O}_{y} \rightarrow \operatorname{Bi}_{2} \operatorname{Sr}_{2} \operatorname{Ca}_{2} \operatorname{Cu}_{3} \operatorname{O}_{y'} + \operatorname{Bi}_{2} \operatorname{Sr}_{2} \operatorname{Cu}_{y''}$$
(3.4)

may partly be responsible for this phase conversion in the presence of a large concentration of Pb. While this interpretation is supported by the result for $t_{A2} = 5 \text{ min (Pb/Cu} \sim 15\%)$, the result for $t_{A2} = 40 \text{ min (Pb/Cu} \sim 3\%)$ suggests that Pb is unlikely to be a precursor for the above reaction.

Figure 3.19 shows the SEM photographs of the films treated above. After the first 10 min of heat treatment in O₂, the film surface is seen to be uniformly smooth, defect free, and composed of very small grains. By the end of the treatment in O_2 , $t_{A2} = 20$ min, the film becomes blackened with platelike grains emerged on the film surface. This morphological change suggests that solid state reactions occurred mainly in the second half of the treatment in O_2 . Referring to Fig. 3.18, this morphological change is seen to coincide in time with the transition from semiconductive to superconductive structure in the film. The first 5 min of the ensuing treatment in air results in films with better defined platelike grains. The shape and disposition of the grains in the films treated for $t_{A2} = 10-30$ min suggest that a partial liquid state reaction occurred during annealing. Consequently, these films are composed of larger grains (size of 5-10 µm) which are stacked parallel to the substrate. The visual evidence of melting is present in the morphology of the film treated for $t_{A2} = 40$ min. This suggests that the 2223 phase is obtained at temperatures nearing the melting point. The orientation of the grains in all micrographs seems to indicate a preferred *c*-axis growth of the films.

3.8 Effects of film composition

To establish the effect of film composition on the volume fraction of the 2223 phase, Seshu Bai *et al.* [3.17] reviewed the literature on the compositions and major processing features. These authors suggested that, to obtain a single or nearly single phase BiSrCaCuO, a prolonged heat treatment combined with simultaneous deficiencies of Bi and Sr with respect to the 2:2:2:3 cation ratio are required. The compositional requirement had previously been proposed by other groups [3.18-3.19]

as a condition necessary for the formation of the 2223 phase. To determine whether this condition applies for a short annealing, compositions of the films treated for different periods of time were measured by means of EPMA. Details on the measurement technique and heat treatment parameters were presented in sections 2.8 and 3.7 respectively. Figure 3.20 shows the average atomic concentrations, normalized to the sum {Bi+Sr+Ca+Cu} with a nominal value of $\{2+2+2+3\}$, as a function of annealing time. In contrast to what indicated by the other groups, all of the films examined were found to be simultaneously Bi- and Sr-rich with respect to the 2:2:2:3 ratio. It is also seen that concentrations of individual metals varied appreciably with annealing time throughout the 20 min of preannealing and the first 10 min of annealing. Coincidingly in this period, the concentration of Pb decreased steadily. This correlation corroborates the role of Pb as a precursor of the solid state reactions occurred in this period. Referring to Fig. 3.17, one should note that the volume fraction of the 2223 phase in the film became substantial towards the end of this period. Following this, a much slowlier decrease in the Pb concentration was observed as the transition from the 2212 to 2223 phase completed. After 40 min of annealing in air, a small but detectable amount of Pb remained in the nearly single phase film. This result is consistent with the observation that the reduction of Pb concentration to essentially zero results in a halt in the 2212-to-2223 transition [3.6, 3.14]. It is noted also that the nominal composition of this film is close to the 2:2:2:3 ratio, which is in agreement with the one reported by Mei et al. [3.4].

3.9 Effects of substrate material and film thickness

The possibility of accelerated formation of the 2223 phase in PbBiSrCaCuO films deposited on substrates other than MgO was further examined. In such experiments, sputtering conditions identical to those described previously were used to grow 1-µm thick films on monocrystalline substrates made of (100) MgO, (0001) Al₂O₃, (100) SrTiO₃, and (100) LaAlO₃. For the annealing conditions, T_{A1} , T_{A2} , t_{A1} and t_{A2} were selected to be respectively 830°C, 865°C, 20 min and 40 min. After the annealing, the films deposited on ZrO and Al₂O₃ substrates were non-superconducting and strongly discolored, suggesting that a chemical reaction had occurred between the film and substrate. Conversely, the films grown on LaAlO₃ and SrTiO₃ substrates showed superconductivity with T_c and J_c exceeding 100 K and 8 x 10³ A / cm² respectively.

The same annealing conditions were also applied to films with various thicknesses. Figure 3.21 shows the XRD spectra of some of the films deposited on LaAlO₃ substrates. It is seen that the phase structure remains predominantly 2223 significantly for the thickness range of 0.4-1 μ m. The lower limit of film thickness for which the short annealing process applies was not determined.

3.10 Conclusions

PbBiSrCaCuO films have been synthesized using an *ex-situ* approach in view of determining whether films with a high T_c 2223 phase could be obtained within a short annealing time (~ 60 min). After the magnetron sputter deposition, the films underwent a heat

treatment in an apparatus set up for precision annealing. The effects of annealing conditions on the formation of superconducting phases in the film were systematically studied.

It was found that the films preannealed in O₂ at relatively low temperatures (810 to 830 °C) had initially a semiconductive structure. During the 20 min preannealing, a solid state reaction occurred, resulting in a transition towards a superconductive structure in the film. At the end of the preannealing period, the low $T_{\rm c}$ 2212 phase was formed readily. During the subsequent treatment in air, a gradual structural transition from the 2212 phase to 2223 phase occurred as the annealing temperature and duration were increased. Experimental evidences of the phase transition were first obtained from measurements of the XRD spectra. Subsequently, these evidences were further confirmed by the *R*-*T* and χ -*T* characteristics of the treated films. For all films, the superconducting phases as revealed by the R-Tand γ -T characteristics are precisely consistent with the phases identified in the XRD spectra. Under specific conditions, nearly single 2223 phase was achieved in the films treated for 40 min in air. These films, found to be homogeneous and highly oriented, exhibit a $T_{\rm c} \sim 107$ K and a J_c exceeding 8×10^3 A / cm². The uniform superconductivity achieved over a large film area was corroborated by the weak dependence of $T_{\rm c}$ on magnetic field intensity. These results were reproducible for at least three different substrate materials, MgO, LaAlO₃ and SrTiO₃. The treatments of shorter duration or at lower temperatures resulted in heterogeneous films with mixed 2212 and 2223 phases, in which a superconducting percolation path could be established at temperatures as high as 100 K.

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The evolution of film compositions with annealing time suggested that Pb is a precursor of the reactions accounting for the rapid phase transition. It was seen that concentrations of individual metals varied appreciably with annealing time throughout the 20 min of preannealing and the first 10 min of annealing. Coincidingly in this period, the concentration of Pb decreased steadily. This correlation suggests the role of Pb as a precursor of the solid state reactions occurred in this period. By the end of this period, the XRD spectra shows that the volume fraction of the 2223 phase in the film became substantial. Following this, a much slowlier decrease in the Pb concentration was observed as the transition from the 2212 to 2223 phase completed. After 40 min of annealing, a small but detectable amount of Pb remained in the nearly single phase film. This result is consistent with the observation that the reduction of Pb concentration to essentially zero results in a halt in the 2212-to-2223 transition.

The results obtained in this chapter demonstrate that accelerated formation of the high T_c phase in PbBiSrCaCuO films is possible. For the first time, experimental evidences are presented on the complete 2212 to 2223 phase transition in a period as short as 60 min [3.20, 3.21]. The devised processes resulted in high quality films and can be scaled to commercial systems for the production of superconductor devices. It is noted that few groups have reported high quality PbBiSrCaCuO films despite a much longer heat treatment. This work enables also the production of PbBiSrCaCuO films with controlled properties for the investigation of their photoresponses.

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Fig. 3.2 - *T*-*t* characteristics recorded at the centre of the tube with thermal power of the furnace set to maximum level. The annealing temperature was set to 860 °C. The characteristic recorded reveals occurrence of a temperature overshoot of ~ 30 °C above the set point.





Fig. 3.3 - *T*-*t* characteristic recorded at the centre of the tube with thermal power of the furnace lowered to 30 % of its maximum level. The annealing temperature was set to 860 °C. The recorded characteristic reveals negligible temperature overshooting.



Fig. 3.4 - T-t characteristics recorded at the film site with the temperature controller sensor placed above the film on the outer side of the tube. The annealing temperature was set to 860 °C.



Fig. 3.5 - Temperature gradient across the tube furnace (lower horizontal scale) and effect of O_2 flow rate on annealing temperature at x = 0 (upper horizontal scale). $T_0 = 860$ °C. The solid lines are provided as visual aids.



Fig. 3.6 - Relation between the temperature set by the controller, T_0 , and the actual temperature at the film location, T, at the center of the tube. The solid line depicts the equation $T_0 = 0.95 T + 31.5$.



Fig. 3.7 – Illustration of the four point probe technique for electrical characterization of PbBiSrCaCuO films. Superconductivity may be simulated by fissures that open up at low temperatures, isolating current and voltage leads.



Fig. 3.8 - Experimental setup for the low temperature characterization of electrical parameters of PbBiSrCaCuO films



Fig. 3.9 - Schematic diagram of the low temperature ac susceptometer used for the magnetic characterization of PbBiSrCaCuO films. Reproduced with permission of Lake Shore Cryotronics Inc.



Fig. 3.10 - Illustration of X-ray diffraction by a crystal lattice.



Fig. 3.11 - Indexed XRD signatures of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ superconductors with n = 1, 2, and 3, according to Tarascon *et al.* [3.8].





Fig. 3.12 - XRD spectra of the PbBiSrCaCuO films treated at different annealing temperatures T_{A2} . The Bragg diffraction peaks are denoted by the number of the CuO₂ layers in the unit cell. $T_{A1} = 830$ °C, $t_{A1} = 20$ min, and $t_{A2} = 40$ min.





Fig. 3.13 - *R*-*T* characteristics of the PbBiSrCaCuO films treated at different annealing temperatures T_{A2} . The film resistance is normalized to the resistance measured at T = 250 K. $T_{A1} = 830$ °C, $t_{A1} = 20$ min, and $t_{A2} = 40$ min.



Fig. 3.14 - Temperature dependence of the critical current density of a PbBiSrCaCuO film. The fitting solid line depicts the relation $J_c \propto (1 - T/T_c)^{2.4}$.
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Fig. 3.15 – Temperature dependence of electrical resistance, R, and magnetic susceptibility, χ , of a nearly single phase PbBiSrCaCuO film. The ac field frequency is 1 kHz. The χ (T) results are shown for two applied field magnitudes. The solid lines are provided as visual aids.



Fig. 3.16 - In-phase and out-of-phase components of the magnetic susceptibility of a mixed 2212 and 2223 phase PbBiSrCaCuO film. Results are shown for different magnitudes of the applied field and a field frequency of 1 kHz. The solid lines are provided as visual aids.



Fig. 3.17 - XRD spectra of the PbBiSrCaCuO films treated for different periods of time in O₂ (t_{A1}) and in air (t_{A2}). The Bragg diffraction peaks are denoted by the number of the CuO₂ layers in the unit cell. T_{A1} = 830 °C, T_{A2} = 865 °C.



Fig. 3.18 - *R*-*T* characteristics of the PbBiSrCaCuO films treated for different periods of time in O₂ (t_{A1}) and in air (t_{A2}). The film resistance is normalized to the resistance measured at T = 250 K. $T_{A1} = 830$ °C, $T_{A2} = 865$ °C.

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 $t_{A2} = 20 \min$



 $t_{A2} = 30 \min$



Fig. 3.19 – SEM photographs of the PbBiSrCaCuO films treated for different periods of time in O₂ (t_{A1}) and in air (t_{A2}). All photographs are shown at 2000 X magnification. The film resistance is normalized to the resistance measured at T = 250 K. T_{A1} = 830 °C, $T_{A2} = 865$ °C.









Fig. 3.21 - XRD spectra of PbBiSrCaCuO films with various thicknesses deposited on LaAlO₃ substrate.

Chapter 4. Photoresponse of PbBiSrCaCuO films at superconducting temperatures

4.1 Introduction

A promising application of superconductors is the use of these materials as optical detectors. This was the motivation behind the first studies on the electrical response of thin films of conventional superconductor to optical radiation [4.1-4.3]. The early researchers found that the photoresponse could be classified into either bolometric or nonbolometric in origin. Bolometric mechanism relies on changes in the biased state resistivity of the film as the film is heated up by absorption of optical radiation. This explains the prevalence of bolometric response in the vicinity of $T_{\rm c}$ where the resistivity change per unit temperature is large. Nonbolometric mechanism was found predominant in the films held at temperatures below $T_{\rm c}$ and exposed to photon energies that exceed the superconducting energy gap. Under this mechanism, the incident photons break the Cooper pairs, reducing the relative fraction of Cooper pairs to normal electrons in the superconductor. As a result of the decreasing fraction, the critical current value of the film's weak links decreases [4.4]. So long as these links are current biased at slightly below the critical value, incident radiation is seen as the appearance of a voltage across the links. Devices that make use of the bolometric and nonbolometric mechanisms were demonstrated but not widely in use. One obvious limitation is the stringent cryogenic requirement for their operation.

Chapter 4 – Photoresponse at superconducting temperatures

Following the discovery of cuprate superconductors in recent years, renewed interest in their photoresponse was sparked by the prospect of operating superconductor detectors at above the liquid nitrogen temperature [4.5]. Attention was further drawn to the possible use of photoresponse to diagnose the thermal properties and energy gap of the new materials. Actually, the findings of the initial studies on photoresponse yielded more questions than answers. In investigating YBaCuO films, several authors have interpreted the observed response as being solely bolometric in origin [4.6-4.13], whereas a comparable number have reported nonbolometric response [4.14-4.21]. For both mechanisms there has been scarcely reports on any other cuprate materials than YBaCuO. Further, none of the reports on nonbolometric response provided direct evidence of the energy gap in high T_c superconductors.

This chapter reports on the first experimental study on the photoresponse of PbBiSrCaCuO films. The film samples investigated were prepared by magnetron sputtering technique as described in the previous chapters. The primary purpose of this study was to determine the characteristics and origins of the response of Bi-based cuprate material. From there, any similarity with the counterparts in the YBaCuO material could be drawn. The scope of the study as presented in this chapter was limited to the temperature ranges below and around T_c . Details of a separate study on the normal state photoresponse are presented in Chapter 5. In the following, a review of the bolometric and nonbolometric responses observed by the other authors will first be presented. Sections 4.5 and 4.6 report on the details of photoresponse measurement and the results obtained, respectively. In order to differentiate bolometric from nonbolometric

responses, one technique used was to compare the measured response with that predicted by a bolometric model. The method for modeling the bolometric response is described in section 4.7, followed by a discussion on the origin of the measured response.

4.2 Observation of bolometric photoresponse

The investigations on YBaCuO films by various groups [4.6-4.13] led to the conclusion that the photoresponse observed in these films is bolometric in origin. To confirm the bolometric origin, two experimental techniques have been used. The first technique consists in measuring the temperature dependence of photoresponse and comparing it with the temperature derivative of film resistance. The second technique relies on the correlation between photoresponse and modulation frequency of incident radiation. The principles underlying these techniques are elaborated below.

Figure 4.1 depicts the principle of bolometric detection that makes use of the *R*-*T* characteristic of superconductor film. Upon absorbing incident radiation, the film temperature rises from *T* to *T* + ΔT , resulting in an increase of film resistance from *R* to *R* + ΔR . As long as a direct current, *I*, is supplied to the film, an output voltage is obtained as:

$$V = I \,\Delta R \approx I \,(\mathrm{d}R/\mathrm{d}T) \,\Delta T \tag{4.1}$$

It is seen that, if ΔT varied negligibly in the measuring temperature range (usually within the resistance transition), the temperature dependence of V would follow that of dR/dT. The latter could be extracted numerically from the experimental R-T characteristic to be compared with V(T). A correlation between them would corroborate the bolometric origin of V.

One could estimate the temperature rise ΔT in Eq. 4.1 using a simple thermal model of the film. As schematically shown in Fig. 4.2, this model consists of a film with heat capacity C connected to the heat sink through a substrate with thermal conductance G. The heat equation for this film for a time varying source of radiation is [4.22]:

$$C \left(\frac{d\Delta T}{dt} \right) + G \Delta T = P \exp\left(i2\pi ft\right)$$
(4.2)

where P and f are respectively the peak power and modulation frequency of the incident radiation. The solution of the above equation yields a steady state amplitude:

$$\Delta T = (P / G) \left[1 + 4 \pi^2 f^2 \tau^2 \right]^{-1/2}$$
(4.3)

where $\tau = C / G$ is the thermal time constant. Introducing Eq. 4.3 in Eq. 4.1, one obtains:

$$V = I \left(P / G \right) \left(\frac{dR}{dT} \right) \left[1 + 4 \pi^2 f^2 \tau^2 \right]^{-1/2}$$
(4.4)

It follows that, for a given temperature, the frequency dependence of V is also indicative as to whether or not it is bolometric in origin.

The measuring conditions and detectivity of the bolometric response previously observed in YBaCuO films are summarized in

Table 4.1. The detectivity, D^* , is the signal to noise ratio per irradiance per linear dimension of the film:

$$D^* = V \Delta f^{1/2} / V_{\rm n} p A^{1/2} \tag{4.5}$$

In this expression, Δf is the bandwidth in which the rms noise voltage V_n is measured, p is the power density of incident radiation, and A is the illuminated film area. From Table 4.1, it is seen that the thickness of the investigated films is typically in the range from 200 to 350 nm. Aside from one exception, these films were shined by modulated cw light with relatively low power (from a few mW to a few tens of mW). The bolometric origin of photoresponse at temperatures near T_c was confirmed by means of the experimental techniques described above. The films are seen to exhibit bolometric behavior over a wide spectral range, from visible to far infrared wavelengths. The measured detectivities of the films were in the order of 10^8 cm.Hz^{1/2}/W. The rather large difference between the reported time constants was a result of different definitions given to the time constant by the authors.

4.3 Nonbolometric mechanisms

Nonbolometric photoresponse is a term used by many authors to refer to signals that were too fast or had too weak temperature dependence around T_c to be due to a bolometric mechanism. Most of the reported nonbolometric responses were observed in granular films that were excited by laser pulses [4.17-4.20]. Given the presence of the naturally formed weak links in granular films, Cooper pair breaking was often suggested as the possible mechanism. However, photoresponse of granular films was also discussed in terms of light induced dissociation of vortex-antivortex pairs [4.17]. Most surprisingly, some reports of nonbolometric response were extended to epitaxial YBaCuO films. To explain the presence of nonbolometric signal in non-granular films, the reporting authors evoked either optically induced supression of superconductivity [4.16, 4.21] or photoenhanced flux creep [4.14, 4.15]. A brief account of the suggested nonbolometric mechanisms is given below.

The breaking of Cooper pairs by above-gap photons was well documented for conventional superconductors, as described in section 4.1. The effect of pair breaking was discussed in different terms depending upon the microstructure of the film. For granular films, the increased portion of normal electrons had the effect of lowering the weak link's critical current to a value below the supplied current. For epitaxial films, the pair breaking was postulated to suppress superconductivity briefly so that the film exhibits a finite resistance prior to recombination of normal electrons. In both cases, this mechanism manifests itself in the dependence of photoresponse on radiation wavelength. As the energy of incident photon must exceed the gap energy to break Cooper pairs, a threshold exists in the radiation wavelength beyond which photoresponse disappears. Considering the range of 1 to 50 meV estimated for the gap of YBaCuO [4.23-4.25], the cutoff wavelength (between 1 mm and 30 μ m) would fall into the far infrared range. If the response is originated by the pair breaking mechanism alone, experimental evidence of the gap may be found by measuring the cutoff wavelength.

Under the conditions where the pair breaking mechanism could not possibly prevail, the dynamics of the response was presented in

terms of motion of magnetic flux vortices in the film. For a bulk superconductor it is an established fact that, when it is placed in an external magnetic field, an electric current will be set up in the surface laver such that its magnetic field will oppose the applied field. The applied field can only penetrate a short distance at the surface of the sample, referred to as the magnetic penetration depth, because the magnetic induction becomes extinct inside the sample. Thin films of high $T_{\rm c}$ superconductor, however, behave differently in a magnetic field. If the field is weak, it will fully be expelled. When the field exceeds a threshold value, it penetrates partially into the film. Because of the Lorentz force, a fraction of the electrons with velocities normal to the field start to circle around some axis, creating the so-called vortex lines. The closer to the axis, the faster the electrons circle. At some distance from the axis, their speed exceeds the critical value so that the core of the vortex is in the normal state. Therefore, any random motion of the vortices across the film results in dissipative losses that are seen as the appearance of a voltage drop. Quite often, the vortices are pinned by potential wells arising from the film's inhomogeneities [4.4]. A dc current supplied to the film may exert a Lorentz force on the vortices larger than the pinning force. In this case, the film is said to be in the flux flow regime and has a finite resistivity. When the Lorentz force is comparable with the pinning force, the film is in the flux creep regime with zero resistivity.

It should be stressed that the earlier measurements of photoresponse were performed actually in the absence of an external magnetic field. It is a peculiar but established fact, however, that superconducting films that are thinner than the magnetic penetration depth (or that are thin and granular) may contain vortices even in the

total absence of the field. These vortices consist of pairs of opposite helicity bound together at below a specific transition temperature. These pairs are non-dissipative even without pinning [4.26]. The zero resistance regime, of course, cannot prevail if a supplied current converts it into the flux flow regime. However, pinning is always present and helps maintain the film's zero resistance for finite currents. When the film is shined by a laser pulse, the temperature of the film may exceed a threshold temperature, resulting in dissociation of vortex-antivortex pairs. Under this condition, the motion of the unbound vortices may give rise to finite resistance across the film. The threshold temperature is referred to as the Kosterlitz-Thouless phase transition temperature [4.27], $T_{\rm KT}$, and has been extended to superconductors by Halperin and Nelson [4.28]. According to these authors, superconductor films exhibit the following temperature dependence of the *I-V* characteristics around $T_{\rm KT}$:

$$\begin{array}{cccc} T << T_{\rm KT} & V = 0 & \mbox{when } I < I_{\rm c} & (4.6 \ a) \\ & V \sim (I - I_{\rm c})^{\rm n}, \ n > 3 & \mbox{when } I > I_{\rm c} \\ \\ T = T_{\rm KT} & V \sim I^{3} & (4.6 \ b) \\ T > T_{\rm KT} & V \sim I & \mbox{for small } I & (4.6 \ c) \end{array}$$

It follows that T_{KT} can be determined through examination of the *I-V* characteristics at different temperatures. Furthermore, Gubser *et al.* [4.29] predicted the following *R-T* characteristic of the film near T_{KT} :

$$R / R_{\text{max}} = a \exp \left\{ -2 \left[b(T_{\text{c}} - T_{\text{KT}}) / (T - T_{\text{KT}}) \right]^{1/2} \right\}$$
(4.7)

where a and b are constants, and R_{max} is the film resistance at temperatures just above T_{c} . A correlation between the measured R-T

characteristic and that predicted by Eq. 4.7 would confirm also that the film exhibits a Kosterlitz-Thouless phase transition. The photoresponse due to the dissociation of vortex-antivortex pairs should peak near $T_{\rm KT}$.

Rather than evoking the phase transition, other authors [4.14, 4.15] explained the origin of photoresponse in terms of light enhanced vortex motion. These authors postulated that the photon energy would be transferred to the vortices via the phonons in the lattice. The enhancement of vortex motion or the transition from the flux creep to flux flow regime would lead to an increase in film resistivity, thereby generating a photoresponse. At low temperatures where the thermal vortex motion is negligible, Yeh and Tsuei [4.30] suggested that photon energy acted to de-pin the vortices from the potential well associated with film's inhomogeneities. This, again, results in a change in film resistivity. This regime may be identified by the exponential current dependence of film resistance. Further, the film resistance would be a function of the pinning potential, U_0 , that must be overcome in order for the vortices to move, *i.e.* $R \sim \exp(-U_0 / kT)$.

4.4 Observation of nonbolometric photoresponse

The evidences of nonbolometric photoresponse have been reported for YBaCuO films with different combinations of thickness and microstructure. A summary of the experimental conditions and photoresponse characteristics is presented in Table 4.2. Most optical measurements were performed at visible or near infrared wavelengths. The commonly reported nonbolometric signatures consisted of the small time constant and weak temperature dependence of the response, mainly at temperatures below T_c . In certain reports the nonbolometric interpretation relied also on the fact that the response peaked at temperatures well below the derivative of film resistivity. Apart from one report, the nonbolometric response was detected either in thick granular films (thickness exceeding 250 nm) or thin epitaxial films (thickness smaller than 100 nm). It was interpreted by various physical mechanisms as described in the following.

The observation of nonbolometric response in YBaCuO films was first reported by Leung *et al.* [4.18]. These authors investigated the electrical response of thick, highly granular films to modulated cw light and pulsed light. They found that the response to cw light peaked at below T_c , where the temperature derivative of film resistivity was zero. Because this behavior is different from that predicted by the derivatives, it was interpreted as a nonbolometric signature. Furthermore, the response of 1 µm-thick films to pulsed light showed a time constant of only 20 ns, which the authors estimated too small to be due to a bolometric process. Because the authors failed to reproduce and observe the above results in less granular films, they suggested the Cooper pairs breaking as the mechanism behind the resistive losses in intergrain weak links.

In complement to Leung's study, Kwok *et al.* [4.19] investigated specifically thin, non-granular YBaCuO films. Their optical measurement was performed on films with a thickness of 80 nm, using pulsed light excitation. Photoresponse was recorded with a transient digitizer of 15 ns resolution. At temperatures below T_c , a fast response was observed. The time constant of the response, 15 ns, was limited by the resolution of the digitizer. When the bias temperature was

increased to a value near T_c , a slow component was seen superimposed onto the fast response. The slow component became the sole component above T_c . The temperature dependence of the slow component was consistent with the derivative of film resistivity, indicating that this component is bolometric in origin. On the other hand, the fast component was believed to be nonbolometric as it remained temperature invariant below T_c and dropped to zero at T_c . The authors suggested that the nonbolometric response was due to photoinduced Cooper pair breaking. However, they did not elaborate on the fact that, unlike the previous study by Leung *et al.* [4.18], a nonbolometric response was detected in non-granular films in this study.

The observation of nonbolometric responses in thin, epitaxial films was further confirmed by Frenkel *et al.* [4.14]. The latters observed a fast nonbolometric response at temperatures below T_c when 40-nm thick, epitaxial YBaCuO films were shined with laser pulses. They reported also a bolometric response at temperatures above T_c . Similar to the above results, the nonbolometric response differs in that it shows a subnanosecond time constant and a weak temperature dependence.

Semenov *et al.* [4.16] offered an explanation for the nonbolometric response observed in thin, epitaxial YBaCuO films. Their experiment was performed at temperatures slightly above the zero resistivity T_c . Films with a thickness of 70 nm were shined with laser pulses of 5 ps duration. For small laser fluences, the authors detected a fast response with subnanosecond time constant. As the fluence rose, a slow response was seen superimposed onto the fast response. These results are consistent with those reported for films

with comparable thickness and microstructure [4.14, 4.19]. Beside the time constant, the authors found that the fast response stands out in that it has a short dynamic range. They suggested that this response, as for epitaxial films, was the result of an avalanche production of quasiparticles, leading to suppression of superconductivity. The saturation of the nonbolometric response was due to the change in film resistance from the near zero value at the operating point to the entirely normal resistance. The time constant of the slow response corresponded with the heat diffusion time, indicating that it is bolometric in origin.

To examine the effect of the probing time scale, Johnson [4.21] reproduced the above experiment for the temporal regime between 10 ps and 10 ns. The films used in the optical measurement were epitaxial and had a thickness in the range of 20-80 nm. Like the above authors [4.14, 4.19], Johnson observed a nonbolometric response at below T_c and a bolometric response above T_c . The nonbolometric response has a smaller time constant and shorter dynamic range, and is weakly dependent on temperature.

Another study on the photoresponse of epitaxial YBaCuO films was reported by Zeldov *et al.* [4.15]. Unlike the previous studies, photoresponse was measured on relatively thick films (thickness in the range of 250 - 600 nm). Modulated cw light was used to illuminate the films and the recorded response was plotted as a function of temperature. Evidence of nonbolometric response was shown as the large deviation between the peak response and the peak derivative of film resistance. This nonbolometric signature is similar to the one that Leung reported for thick, granular films [4.18]. Zeldov speculated that, for epitaxial films, the mechanism behind the nonbolometric response is photoenhanced flux creep.

Finally, Leung's study on thick, granular YBaCuO films was repeated by Culbertson *et al.* [4.17]. The samples examined by the latters exhibited a much wider width of resistance transition, indicating a higher degree of granularity. In examining the temperature dependence of *I-V* characteristics near T_c , Culbertson noted the additional presence of a Kosterlitz-Thouless phase transition. The *R-T* characteristics near $T_{\rm KT}$ were shown to be consistent with the theoretical prediction expressed in Eq. 4.7. The response to modulated cw light, as a function of temperature, exhibits a large component near $T_{\rm KT}$ where the derivative of film resistivity is nearly zero. This component is interpreted as the evidence of photodissociation of vortex-antivortex pairs at the Kosterlitz-Thouless transition temperature.

4.5 Experimental details

The photoresponse measurement has been performed on the PbBiSrCaCuO superconductor films fabricated in this thesis work. All samples were prepared by means of magnetron rf sputtering and postdeposition heat treatment. The details of the synthesis and characteristics of these films were reported in Chapters 2 and 3. The photoresponse was measured on both single phase 2223 films and granular films with mixed 2212 and 2223 phase. The granular films have a minimum thickness of 200 nm. For thinner samples, it was found that the larger current density and the more pronounced effects of local defects and nonuniformity degraded significantly superconductivity.

In order to better define the active area of the samples, wet etching was used to pattern some of them into meander lines with an aspect ratio of ~ 25. First, a 1-µm thick layer of positive photoresist was spun coated onto the film at 7000 rpm. To harden the resist, the sample was baked at 90 °C for 20 min, followed by cooling in the air for 15 min. After this, it was exposed to ultraviolet light for about 6 min through a photomask. The light source of the mask aligner (Karl Suss MJB-3) consisted of a Hg lamp providing an output of ~ 200 W in the spectral range of 350-450 nm. The photomask was prepared commercially by Adtek Inc. according to the configuration provided by the thesis author (Fig. 4.3). The exposed resist was removed after immersion of the sample in a solution of dilute developer (1:3 volume ratio of microposit developer to deionized water) for about 2 min. The step that followed consisted in hardening the remained resist with a heat treatment at 90 ^oC for 10 min. The unwanted film area of the sample was etched for 5 s in a room temperature solution of 1% HCl. After the etching, the sample was sprayed with acetone so as to remove the residual resist on the film pattern. Finally, Ag electrodes were formed on the film by vacuum evaporation. During the evaporation a sheet of Al was placed on the sample, serving as a mask with the four square windows aligned to the four rectangular contact pads of the film pattern.

To determine the origin of the photoresponse, the characteristics of the latter to short light pulses were investigated. Two infrared laser sources were used to illuminate the film during the measurement. The first source consisted of a *Q*-switched solid state Nd:YLF laser (Lightwave Electronics 110) that supplied pulsed light (175 μ J) at the wavelength of 1.047 µm. The transient characteristic of the pulse was monitored using an InGaAs photodetector (Newport 818-BB). The second source was an experimental TEA CO₂ pulsed laser with more than 90% of its power emitted at the wavelength of 10.6 µm. A Ge photon drag detector (Rofin 7441) having sub-nanosecond response time was used to monitor the laser output. The nominal gas composition for the laser source was $CO_2:N_2:He = 3:3:14$. In the early experiments, it was found that the stability of the incident pulse depends on the gas pressure. When the laser cavity was at ambient pressures (gas flow rate ~ 200 sccm), the peak power of the incident pulse fluctuated in the range of 80-90 kW. In addition to high voltage sparks, there was occurence of secondary spikes and the beam size varied between pulses. By increasing the gas pressure by 0.3 atm, the laser pulse became more reproducible and stable with a peak power of 95 kW and average energy of 25 mJ. The average beam size, as determined from the witness spot of the laser discharge on graphite, was ~ 0.1 cm^2 . A set of optical attenuators were used in conjunction with the laser sources to reduce and vary the power incident on the film samples. The laser damage threshold of PbBiSrCaCuO film was measured to be ~ 50 mJ / cm^2 at the CO₂ laser wavelength. The threshold at the Nd:YLF laser wavelength may be about three times smaller on the basis of the spectral dependence of film reflectance [4.31]. The damage threshold was defined as the lowest incident energy that induced a measurable change in the film resistance.

Figure 4.4 shows the schematic experimental setup for the measurement of resistivity and photoresponse of the film. This setup allowed for data acquisition in the temperature range from 20 to 300 K. The film was thermally anchored to the cold head of a Gifford-McMahon closed cycle cryocooler. The optical access to the film was provided through a 60 K radiation shield and a KRS-5 infrared window. An integrated temperature controller provided temperature stability of better than 0.3 mK for the cryocooler in the measuring temperature range. The controller was interfaced with a Si temperature sensor imbedded in the cold head and a tightly coupled wire wound heater. A low noise current source (Keithley 224) was used to supply dc currents of up to several mA to the film. Upon illumination, the voltage generated across the film was recorded with a digitized oscilloscope (HP 54542A) via a high impedance amplifier (gain ~ 30 dB). For the data acquisition, the highest sampling rate of the oscilloscope was set at 2 Gs/s, *i.e.* data were acquired every 500 ps. The size and intensity of the laser beam incident on the film were adjusted by means of a set of optical attenuators (0-60 dB), focal lenses, and diaphragms.

4.6 Results

The photoresponse was measured on both single phase 2223 films and granular films with mixed 2212 and 2223 phase. In the first series of experiments, photoresponse to far infrared light has been specifically measured. Figure 4.5 displays a typical transient response of a granular film to CO₂ laser pulses. The thickness of the film was 240 nm. The densities of power and energy contained in the incident pulse were measured to be respectively ~ 54 kW / cm² and 15 mJ / cm². During the measurement a constant current of 10 mA was supplied to the film; the latter was temperature biased near the midpoint of resistance transition, T = 105 K. As seen in Fig. 4.5, the photoresponse exhibits a

longer recovery time with respect to the incident pulse. A quantitative comparison of the time constants of both signals is provided in Table 4.3. Whereas the rise time is about the same for these signals, the recovery time of the photoresponse is about 3.5 times that of the incident pulse. Even after the pulse had become extinct ($t > 3 \mu s$), the photoresponse continued to decay, suggesting that it may be thermal in origin. The temperature dependence of photoresponse lends further support to this possibility. Figure 4.6 shows plots of resistance, R, and responsivity, r, of the same film as a function of temperature. Here, r denotes the peak voltage of photoresponse normalized to the peak power of incident pulse. The resistance transition is seen to be typical of granular films, *i.e.* it is widely stretched from $T_{\text{onset}} \sim 110 \text{ K}$ to $T_{\text{c}} \sim 75 \text{ K}$. Within this transition, a strong temperature dependence of r is noted. With T decreasing from T_{onset} to the transition midpoint, r increases to a maximum. When T decreases further towards $T_{\rm c}$, r drops to nearly zero. This behavior is consistent with the prediction of the temperature derivative of resistance, dR/dT. According to Eq. 4.1, such an agreement indicates that the observed photoresponse is bolometric in the resistance transition region. The variation of photoresponse with the supplied current also showed a linear dependence, in consistency with Eq. 4.1.

To examine the possible nonbolometric mechanisms at temperatures below T_c , the optical measurement was further performed in the range of 20 - 90 K [4.31]. The investigated samples consisted of granular films with a thickness of 220 nm. Their *R-T* characteristic exhibited $T_{onset} \sim 110$ K and $T_c \sim 90$ K when the supplied current was set to 1 mA. For low densities of incident pulse (*i.e.* a few kW / cm²), no sign of photoresponse was observed. However, when the incident power was increased to a large value, a fast signal appeared. Figure 4.7 shows the

transient responses recorded at different bias temperatures when the incident pulse reaches a density of ~ 260 kW / cm². The CO₂ laser pulse, reproduced with a photon drag detector, was further shown for the purpose of comparison. To ease the visual comparison, for every bias temperature the peak photoresponse was normalized such that it equals the peak voltage of the incident pulse. It is seen in Fig. 4.7 that the photoresponse at T = 20 K decays faster than the laser pulse. One possibility behind this peculiar result is that the laser pulse was too fast to be reproduced accurately by the photon drag detector, but could be replicated with the PbBiSrCaCuO film thanks to some faster mechanism. However, this possibility appears unlikely considering the sub-nanosecond time constant of the photon drag detector. On the other hand, the fast response may be interpreted as well in terms of bolometric effects as follows. After an initial fraction of the pulse, the laser energy delivered to the film could be sufficient to increase the film temperature from the bias value, at below $T_{\rm c}$, to a value slightly beyond $T_{\rm c}$. Hence, the film started to exhibit a bolometric response after a finite period of illumination. Conversely, the bolometric response disappeared after the laser energy had decayed to a level where the cooling rate became more important than the heating rate. As a result, the film may have responded only to the central portion of the pulse, which explains the seemingly fast response. If this contention holds, the film should have responded to a larger portion of the pulse when the bias temperature approached $T_{\rm c}$, resulting in photoresponse with larger time constants. Referring to Fig. 4.7, it is obvious that the time constant of the response increases with increasing bias temperatures. At $T \sim T_c$, the decay time of the response becomes effectively longer than that of the laser excitation. Figure 4.8 displays the response on a smaller time scale for different values of bias temperature. It reveals that the time delay

between the laser pulse and photoresponse, both simultaneously recorded, decreases when T is increased toward T_c . On the basis of the above contention, the time delay is believed to coincide with the period of laser heating required to elevate film temperature to T_c , where a bolometric response can be generated. Figure 4.8 shows also that the photoresponse magnitude increases with increasing bias temperature. This attribute is, again, consistent with that anticipated from the bolometric mechanism. If the temperature variation of thermal properties of the film is small at temperatures below T_c , the temperature rise in the film should roughly be the same regardless of the bias temperature. Therefore, when the film is biased at temperatures closer to T_c , higher resistance values can be attained upon laser illumination, resulting in larger output voltages.

The above characteristics of photoresponse were further validated at the near infrared wavelength. In a series of experiment, photoresponse to Nd:YLF laser pulse was measured on several films. Figure 4.9 shows the temperature dependence of the resistance R and responsivity r of a single phase, meanderline film. The film has an active area $A \sim 7 \text{ mm}^2$ and a thickness of 210 nm. The power and energy densities of the laser pulse incident on the film were respectively 1.7 kW / cm² and 6 μ J / cm². It was noted that superconductivity degraded after the chemical etching of the film. In this example, the resistance transition of the film was shifted towards lower temperatures by ~ 7 K after the etching. The gradual decrease to zero resistance may be due to the large current density ($J \sim 10^4$ A / cm²) that results from the small cross section of the meanderline. Similarly to the results obtained at the far infared wavelength, a correlation was found between the temperature dependence of r and that of dR / dT. In addition, it was

found that r increases linearly with increasing bias current. The photoresponse exhibited also a slow recovery after the completion of the laser excitation. As shown in Table 4.4, the rise time, fall time, and pulse width of the photoresponse are many times larger than the time constants of the incident pulse. All these attributes suggest that the observed photoresponse is bolometric in origin. The optical measurement of the same sample at below T_c revealed no evidence of nonbolometric components.

4.7 Modeling of the bolometric photoresponse

As seen in the previous section, the transient characteristics of the photoresponse suggested that it is bolometric in origin. One possible approach to confirming this is to compare the experimental characteristics with those predicted by a bolometric model. Such a comparison allows one to either corroborate or discard the nonbolometric theory. The bolometric model can be established in relating the output voltage, V(t), with the evolution of film resistance, $\Delta R(t)$, upon thermal excitation of the film:

$$V(t) = I \Delta R(t) \tag{4.8}$$

In this equation ΔR (t) represents the increase of film resistance from the initial value, at bias temperature $T_{\rm b}$, to the value at $T_{\rm b} + \Delta T$:

$$\Delta R(t) = R[T_{\rm b} + \Delta T(t)] - R[T_{\rm b}]$$
(4.9)

where $\Delta T(t)$ is the rise of film temperature due to the applied thermal excitation. In Eq. 4.9, the temperature-to-resistance conversion relies

on the experimental *R*-*T* characteristic of the film. Because the resistance value at T_b is a constant, in practice the modeling comes to evaluating the transient resistance at $T_b + \Delta T(t)$.

The modeling method employed in this work consists, first, in using a heat transfer model and the thermal data of the film to compute ΔT as a function of space and time. Next, to account for the spatial variation of ΔT in the film, the film is modeled as m parallel layers with resistance R_i and temperature T_i , i = 1,...,m. For a given time t, T_i is calculated from the spatial function of ΔT and the T_i -to- R_i conversion is made for each layer using the R-T characteristic. Once R_i is obtained for every layer, the overall resistance of the film at time t is taken as the equivalent of m parallel resistors. The following provides details of the heat transfer model and computation behind the above operations.

The heat transfer model is adapted from solutions of the problem of linear heat flow in a solid bounded by a pair of parallel planes [4.22]. To simplify the problem, a number of assumptions have been made. The film is treated as a slab with thickness d in which heat flows in the region 0 < x < d, *i.e.* from top surface to bottom surface. The film is thermally isolated at x = 0 and has a finite thermal boundary resistance R_{bd} to the substrate at x = d. The substrate is biased at T = 0 K, acting as a perfect heat sink. The temperature rise in the film results from the absorption of thermal energy of density ε (per unit film area) within a penetration depth δ . The spatial distribution of initial temperature along the film is assumed to be exponential:

$$\Delta T_0(x) = (\varepsilon / C \delta) \exp(-x / \delta) \qquad 0 < x < d \qquad (4.10)$$

where C is the heat capacity per unit volume of the film. Under the above conditions, the temperature rise as a function of space and time is expressed as:

$$\Delta T(x,t) = 2 \sum_{n=1}^{\infty} \exp\left(-\alpha_n^2 D t\right) \frac{(h^2 + \alpha_n^2) \cos(\alpha_n x)}{(h^2 + \alpha_n^2)d + h} \int_{0}^{d} \Delta T_0(x) \cos(\alpha_n x) dx$$
(4.11)

In Eq. 4.11, D and k are respectively the thermal diffusivity and conductivity of the film, and α_n is the n^{th} positive root of:

$$\alpha (\tan \alpha d) = h \tag{4.12}$$

where:

$$h = 1 / (R_{\rm bd} k)$$
 (4.13)

The numerical solutions of $\Delta T(x, t)$ are obtained using MATLAB programming software (version 6.1). The codes of the scripts and functions written to this end (by David Comeau, Defence R-D Canada) are as follows. The script *input_film_data.m* is meant to acquire the parameters of the film and of the thermal excitation. The function *roots_alpha.m* is intended for the numerical computation of the roots α_n (Eq. 4.12). It was found that the solutions of $\Delta T(x, t)$ were hardly affected by *n* for n > 100; consequently, only the first 100 roots of α_n are retained for the evaluation of Eq. 4.11. This evaluation is performed using the function *film_temp.m*. The latter retrieves the coefficients of Eq. 4.11 that were acquired under the script *input_film_data.m*, generates a time vector, and provides values of $\Delta T(t)$ for a given value of *x*.

The photoresponse is calculated using the script heat_prop.m. As described above, this is done by evaluating the transient resistance of the film at $T_b + \Delta T(t)$ in two steps. First, experimental data of the *R*-*T* characteristics are stored in the function resis_parallel.m for several values of bias current. Next, by modeling the film as 20 parallel layers, the resistance of each layer is derived from the layer's temperature; the latter was determined previously from the function film_temp.m. The temperature-to-resistance conversion is made by interpolating the data stored in resis_parallel.m.

4.8 Discussion

The results obtained experimentally point to a purely bolometric photoresponse in both epitaxial and granular PbBiSrCaCuO films with thicknesses of 200-250 nm. The optical measurement was performed at temperatures below and around T_c . In the vicinity of T_c , the measured responses exhibited several bolometric signatures. Firstly, consistency was found between the temperature dependence of photoresponse and that of temperature derivative of film resistivity. Secondly, the recovery time of the response was many times longer than that of the optical excitation. Thirdly, the response magnitude increased linearly with increasing supplied current. At temperatures below T_c , a fast response appeared when the power density of optical excitation exceeded a threshold. However, the effect of bias temperature on the transient structure, magnitude, and time delay of the response indicated that the response is also bolometric in origin.

To further confirm the bolometric origin, the bolometric model described above has been used to predict the photoresponse characteristics. Figure 4.10 compares an experimental response with the response simulated for identical experimental conditions. The experimental response (also shown in Fig. 4.5) was obtained when illuminating a 240-nm thick film with CO₂ laser pulses. The incident energy density contained in each pulse was 15 mJ / cm². The far infrared reflectance of a comparable film was measured to be ~ 0.7 at temperatures near $T_{\rm c}$ [4.31]. Assuming a transmittance of 0.1, the net energy density delivered to the film was taken as 3 mJ / cm² in the modeling. The specific heat ($c = 0.9 \text{ J} / \text{cm}^3$.K) and thermal conductivity $(k = 10^{-2} \text{ W} / \text{cm.K})$ of the film were respectively extracted from measurements by Fisher et al. [4.32] and by Peacor and Uher [4.33]. The thermal diffusivity was taken as $D \sim k / c = 1.1 \ge 10^{-2} \text{ cm}^2 / \text{ s}$. The selected values of boundary resistance, $R_{bd} \sim 5 \ge 10^{-4} \text{ K.cm}^2 / \text{ W}$, and penetration depth, $\delta \sim 100$ nm, were in the same order of the values reported for YBaCuO films [4.20, 4.21]. It is seen in Fig. 4.10 that the experimental response, at T = 105 K, is in good agreement with the computed response, except that it decays more gradually in the time interval beyond $t = 0.5 \ \mu s$. The slower decay of the experimental response may be due to the fact that the substrate was not biased at T= 0 K and acted as a perfect heat sink as postulated in the modeling. The effect of bias temperature on the transient structure of the response was also examined using the bolometric model. Figure 4.11 shows the computed responses for different bias temperatures. This result confirms the experimental bolometric signature observed previously, that is, the time delay increases and the response magnitude decreases with decreasing bias temperatures.

Although the bolometric response was solely observed in the above experimental results, one still can not rule out the possibility of nonbolometric effects for different film structures and experimental conditions. The lack of evidences of nonbolometric response in the present study may be due to a number of possibilities. One possibility is that the recombination time of the photodissociated Cooper pairs is shorter than the data sampling time of the measuring oscilloscope (500 ps). It is noted, however, that most of the nonbolometric time constants reported for YBaCuO films are of nanosecond order (Table 4.2). Another possibility is the magnitude of the nonbolometric response is either too small to be detected or is short circuited by the superconducting bottom layer of the film. This possibility is based on the conjecture that the optical penetration depth is smaller than the film thickness. In this case, the photodissociation of Cooper pairs occurs only within the top layer of the film and only this portion is driven into the normal state. Therefore, the generated nonbolometric response would drop as soon as the current could divert into the deeper layer of the film that is superconducting. The optical penetration depth was measured for YBaCuO using a spectrophotometer and found to be ~ 120 nm and weakly dependent on wavelength [4.20]. Some effort has been spent on the synthesis of 100-nm thick PbBiSrCaCuO films during the thesis work. However, the resulted films showed a superconductivity too weak to be maintained when a current was supplied to the film, partly because the current density increased with decreasing film thickness.

4.9 Conclusions

The photoresponse of YBaCuO superconductor films has been observed and investigated by different groups. Numerous authors interpreted the response as solely bolometric in origin, whereas a comparable number associated the response with a nonbolometric origin. An examination of the reported nonbolometric response shows that it occurred mainly in thin epitaxial films and thick granular films. Conditional on the film structure, different physical mechanisms have been suggested to account for the nonbolometric response. These include photodissociation of Cooper pairs and vortex-antivortex pairs, photoinduced suppression of superconductivity, and photoenhanced flux creep.

This chapter reports on the first experimental study on the photoresponse of PbBiSrCaCuO films at below and around T_c . Both epitaxial and granular films with thicknesses of 200-250 nm were investigated. The optical measurements were performed at near infrared and far infrared wavelengths. In the transition region, the measured responses exhibited several bolometric signatures. Firstly, a good agreement was obtained between the temperature dependence of photoresponse and that of temperature derivative of film resistivity. Secondly, the recovery time of the response was many times that of the optical excitation. Thirdly, the linear increase of photoresponse with increasing supplied current was confirmed. At temperatures below T_c , a fast response appeared when the power density of optical excitation exceeded a certain threshold. However, the effect of bias temperature on the transient structure, magnitude, and time delay of the fast response showed that it is also bolometric in origin.

Chapter 4 – Photoresponse at superconducting temperatures

One approach to confirm the origin of the experimental response is to compare it with the prediction of a bolometric model. In this thesis work, a bolometric model has been developed using the solutions of the problem of linear heat flow in a solid bounded by a pair of parallel planes. For a given thermal excitation input, the temperature increase of the film could be computed as a function of space and time, that was then converted into photoresponse. Under the experimental conditions of this study, it was found that the experimental response is in good agreement with the simulated response. This agreement suggests that the model is suited for the simulation of bolometric photoresponses and for the validation of the film parameters used in the simulation.

In summary, it was shown for the first time that the photoresponse of epitaxial and granular PbBiSrCaCuO films is purely bolometric at superconducting temperatures and around T_c . During the experiments no evidence of nonbolometric response has been found. The absence of the nonbolometric response suggests the possibility that it is generated within the top layer of the film and is short circuited by the superconducting bottom layer. This possibility could be not verified because of the difficulty in obtaining ultra thin films with satisfactory superconducting properties.

<i>t</i> (nm)	λ (μm)	<i>P</i> (W)	<i>f</i> (Hz)	<i>D</i> * (cm. Hz ^{1/2} /W)	τ (ms)	Ref.
200	0.63	0.003	1	$1 \ge 10^{6}$	3300	4.11
300	0.63		10		0.055	4.12
350	0.63	0.003	725	$1 \ge 10^{8}$	1	4.9
350	10.6	0.04	725	$1 \ge 10^8$	1	4.9
800-2000	6		3.7	$8.9 \ge 10^5$	8.8	4.10
	8-14		50	$1.6 \ge 10^8$	16	4.13
50		2.5	pulsed		0.004	4.8
170		2.5	pulsed		0.022	4.8
320		2.5	pulsed		0.05	4.8

Table 4.1 – Measuring conditions and detectivity of the bolometricphotoresponse observed in YBaCuO films.

Table 4.2 – Measuring conditions and responsivity of the nonbolometric photoresponse observed in YBaCuO films.

Film structure	<i>t</i> (nm)	λ (μm)	P _{peak} (W)	Pulse width (ns)	τ (ns)	Non- bolometric signature	Ref.
Granular	1000	500	100		20	с	4.18
Epitaxial	80	0.53	80	6	15	a, b	4.19
Epitaxial	40	1.06	0.08	200	1	a,b	4.14
Epitaxial	70	0.63		0.005	0.7	a	4.16
Epitaxial	20-80	0.66		0.0003	0.5	a,b	4.21
Epitaxial	250-					с	1 15
	600						4.10
Granular	250	0.58		8		Ċ	4.17

- (a) Time constant shorter than that expected from a bolometric mechanism.
- (b) Weak temperature dependence of photoresponse at below $T_{\rm c}$.
- (c) Significant deviation between photoresponse and temperature derivative of film resistivity.
Table 4.3 – Time constants of the incident CO_2 laser pulse and photoresponse of a PbBiSrCaCuO film. The laser pulse was recorded with a photon drag detector. The film was biased at T = 105 K with I =10 mA.

	CO ₂ laser pulse	Photoresponse
Rise time 10 - 90% (ns)	40	41
Fall time 100 - 36% (ns)	70	250
Pulse width 50% (ns)	85	210

Table 4.4 - Time constants of the incident Nd:YLF laser pulse and photoresponse of a PbBiSrCaCuO film. The laser pulse was recorded with an InGaAs detector. The film was biased at T = 105 K with I = 10mA.

	Nd:YLF laser pulse	Photoresponse
Rise time 10 - 90% (ns)	2	5
Fall time 100 - 36% (ns)	3	50
Pulse width 50% (ns)	3	28

 $Chapter \ 4 - Photoresponse \ at \ superconducting \ temperatures$



Fig. 4.1 - Principle of the bolometric mechanism that relies on the *R*-*T* characteristic of superconductor film. Upon absorption of radiation, the film temperature rises from *T* to $T + \Delta T$, resulting in an increase of the film resistance from *R* to $R + \Delta R$. When a dc current, *I*, is supplied to the film, a voltage $V = I \Delta R \approx I (dR/dT) \Delta T$ appears across the film.



Fig. 4.2 - Simplified thermal model of superconductor film.



Fig. 4.3 - Schematic diagram of the meanderline line structure in four terminal configuration.



Fig. 4.4 - Experimental setup for the measurement of photoresponse of PbBiSrCaCuO films. The pulsed laser source consisted of either a Q-switched solid state Nd:YLF laser (wavelength ~ 1.047 µm) or an experimental TEA CO₂ laser (wavelength ~ 10.6 µm).



Fig. 4.5 - Photoresponse of a PbBiSrCaCuO film to CO_2 laser pulse. The laser pulse, recorded using a photon drag Ge detector, is magnified by 100 times for visual aids. The thickness of the film is d = 240 nm. The film was biased near the midpoint of resistance transition, T = 105K, and was supplied with I = 10 mA. The recovery time of the photoresponse is about 3.5 times longer than that of the incident pulse.



Fig. 4.6 - Temperature dependence of the photoresponse and resistance of a PbBiSrCaCuO film. The thickness of the film is d = 240 nm. The film was illuminated by CO₂ laser pulses. The dc current supplied to the film was I = 10 mA. The solid line is provided as visual aids. The dependence of the photoresponse is analogous to that of the temperature derivative of the film resistance.



Figure 4.7 - Effect of bias temperature on the transient structure of photoresponse of a PbBiSrCaCuO film. The transient structure of the incident laser pulse is also shown for the purpose of comparison. The thickness of the film is d = 220 nm. The dc current supplied to the film was I = 1 mA during the optical measurement.



Fig. 4.8 - Time delays of the photoresponses measured at different bias temperatures on a PbBiSrCaCuO film. The film was illuminated by CO_2 laser pulses. The thickness of the film is d = 220 nm. The dc current supplied to the film was I = 1 mA during the optical measurement.



Fig. 4.9 - Temperature dependence of the photoresponse and resistance of a meanderline PbBiSrCaCuO film. The thickness of the film is d = 210 nm. The film was illuminated by Nd:YLF laser pulses. The dc current supplied to the film was I = 10 mA. The solid line is provided as visual aids. The dependence of the photoresponse is analogous to that of the temperature derivative of the film resistance.



Fig. 4.10 – Computed bolometric photoresponse of a PbBiSrCaCuO film to CO₂ laser pulse. The experimental photoresponse is also shown for the purpose of comparison. The power and energy densities of the incident pulse were respectively 54 kW / cm² and 15 mJ / cm². The thickness of the film is d = 240 nm. The film was biased near the midpoint of resistance transition, T = 105 K, and was supplied with I = 10 mA.



Fig. 4.11 – Computed bolometric photoresponses of a PbBiSrCaCuO film to CO_2 laser pulse for different bias temperatures. Similarly to the behavior of experimental responses, the computed responses vary in magnitude and time delay with bias temperature. The thickness of the film is d = 240 nm. The film was supplied with I = 10 mA during the optical measurement.

Chapter 5. Photoresponse of PbBiSrCaCuO films at normal state temperatures

5.1 Introduction

As stated before, one of the main objectives of this thesis is to study the photoresponse of the PbBiSrCaCuO films. In Chapter 4, results from the studies at temperatures in the vicinity of T_c have been presented. In this chapter, the study is extended to temperatures beyond T_c .

The photoresponse of high T_c films in normal state has received little attention. So far, the bolometric mechanism is believed to be exclusively responsible of photoresponses in current biased normal state films. Given the inherently small temperature coefficients of resistance of the films at temperatures above T_c , there has been little interest shown in the bolometric response of those films [5.1]. Brocklesby *et al.* [5.2] were among a few groups who extended their investigation on the photoresponse to temperatures above T_c . They attributed the observed photoresponse of YBaCuO films to the bolometric mechanism alone as it follows the temperature derivative of film resistance. Braginski *and al.* [5.3] also reached the same conclusion when performing laser pulse excitation on YBaCuO films over a broad range of temperatures.

The study presented in this chapter was motivated by the observation of an anomalous nonbolometric photoresponse in normal state PbBiSrCaCuO films [5.4, 5.5]. The objective of this study is to determine the characteristics and origin of the observed photoresponse. Section 5.2 presents details of the experimental approaches to this purpose. The experimental evidence of the nonbolometric photoresponse is presented in section 5.3. Sections 5.4 and 5.5 describe the experiments and results on the characteristics of the photoresponse. In section 5.6, a model is proposed for the PbBiSrCaCuO film in order to explain the origin of the observed photoresponse. The consistency between this model and the experimental results is discussed in section 5.7.

5.2 Experimental details

The PbBiSrCaCuO films investigated were prepared on monocrystalline substrates of MgO and LaAlO₃ by magnetron rf sputtering. The film thickness was in the range from 20 to 1000 nm. The details on the synthesis and properties of these films were presented in Chapters 2 and 3. For the most part of the work, substrates with the (100) orientation were used for film growth. In addition, certain samples were prepared on the substrates cut with surface normal at an angle, θ , to the (100) orientation. These substrates were supplied by Target Materials Inc., with θ ranging from 5 to 20 degs. The latter samples were intended for use in the study on the effects of film orientation. If the films grown on these substrates conserved the *c*-axis orientation normal to the (100) plane, their structure would consist of CuO planes coherently inclined by θ with respect to the substrate surface (Fig. 5.1).

Figure 5.2 shows a schematic diagram of the experimental setup for the photoresponse measurements. Because this setup is similar to the one described previously in Chapter 4, only a brief account is

provided here. The setup was intended for photoresponse measurements in the temperature range from T_c to 300 K. In the low temperature experiments, the film was anchored thermally to the cold head of the Gifford-McMahon closed cycle cryocooler with KRS-5 infrared window. This cryocooler provided a stability of better than 0.3 mK in the experimental temperature range. When required, a low noise current source (Keithley 224) was used to supply dc currents of up to several mA to the film. Upon illumination, the voltage generated across the film was recorded with a digital storage oscilloscope (HP 54542A) or a lock-in amplifier (EG&G 5316A), via a high impedance amplifier (gain ~ 30 dB). The size and intensity of the laser beam incident on the film were adjusted by means of a set of optical attenuators, focal lenses, and diaphragms.

Two infrared lasers were used as the main light sources in the experiments. A Q-switched solid state Nd:YLF laser (Lightwave Electronics 110) supplied either cw light (400 mW) or pulsed light (175 μ J) at the wavelength of 1.047 μ m. The intensity and transient characteristic of the light output were monitored respectively with a power meter (Scientech 365) and an InGaAs photodetector. The cw light could mechanically be modulated by means of a chopper. The second light source consisted of a pulsed CO₂ laser (25 mJ) operating at the wavelength of 10.6 μ m. A photon drag Ge detector (Rofin 7441) was used to characterize the CO₂ laser pulse.

5.3 Observation of nonbolometric photoresponse

In a first series of experiments, the photoresponse of PbBiSrCaCuO films was measured at room temperature. Upon laser

illumination and in the presence of a current, I, supplied to the film, a voltage, V_t , appeared across the film. The temperature dependence of V_t was found to follow approximately that of a bolometric photoresponse. This result was predictable because the film exhibited a finite temperature coefficient of resistance at room temperatures. Unexpectedly however, these experiments revealed also the presence of a nonbolometric photoresponse.

Experimental evidence of the nonbolometric photoresponse was seen when measurement was performed in the absence of a supplied current, *i.e.* with I = 0. Figure 5.3 shows the voltage signal recorded at room temperature from an electrically unbiased film. In this experiment, the film was shined with the cw Nd:YLF laser beam modulated at 30 Hz. The voltage signal disappeared when the laser beam was disrupted or blocked from the film. Considering that a bolometric photoresponse could no longer be present for I = 0, the observed voltage, v, must purely be nonbolometric. Preliminary data showed that the nonbolometric responsivity was in the range of 1-100 μ V/W. This magnitude decreased by a factor of 2 when a resistor of resistance R was connected in parallel with the film resistance R, indicating a true current flow.

5.4 Characteristics of nonbolometric photoresponse

To better discern the origin of the observed nonbolometric photoresponse, further investigations were carried out on the characteristics of the latter. In these investigations, the films were at room temperatures and electrically unbiased unless stated otherwise. The experimental details and results are presented as follows. Chapter 5 – Photoresponse at normal state temperatures

The thermocouple effect due to laser heating of the electrodes was first investigated as a possible nonbolometric mechanism behind the observed photoresponse. In this conjecture, the voltage v could be the result of the differential temperature between the two electrodes. The method devised to verify this consisted in examining whether or not, upon laser scanning of the film area between the electrodes, a polarity reversal of v would occur. The laser scanning was performed by moving the film behind a fixed diaphragm using a micrometer manipulator (Newport 462). The diaphragm served as a mask limiting the illuminated area to a spot of 1.2-mm diameter. Prior to scanning, the Nd:YLF laser fluence was measured to be ~ 0.2 W / cm² with a power meter placed behind the diaphragm. One possible source of errors in this type of experiment is irregularities in the spatial distribution of laser power. In such case, the power entering the diaphragm would change by a large amount if the incident beam was slightly deviated. To confirm whether the power distribution was free of irregularities, the incident beam was characterized using an electronic laser beam profiler (Spiricon). Figure 5.4 reveals a nearly rectangular cross-sectional profile of the laser power, according to which power variation across the diaphragm (1.2 mm) was less than 10% compared to that in the central part of the beam. It follows that errors due to slight deviations of the beam between measurements could be neglected. Figure 5.5 displays the responsivities measured for a laser spot at different positions along a PbBiSrCaCuO film. The polarity of v is seen to remain unchanged as the beam scanned between electrodes, excluding the possibility that v was due to a differential temperature. Another fact lending support to this conclusion is that responsivity decreased by ~ 2.5 times when the beam was directed at each electrode. Results similar to the above could be

reproduced when scanning other films with either a cw or pulsed laser beam.

During the experiment it was noted that the polarity of vreversed when the positions of the electrodes were inverted. In addition, significant changes in responsivity was seen when measurement was taken from different pairs of electrodes on the same film. These observations suggested that v could be derived from a fixed electric field in the film plane. To verify this, the spatial distribution of v in the film plane was measured. As illustrated in the inset of Fig. 5.6, a series of Ag electrodes was formed in the circumferential area of ~ 8.5-mm diameter on the film. A diaphragm placed in front of the film limited the optical access to an area of ~ 7-mm diameter inside the circle of electrodes. This area was shined with CO_2 laser pulses of ~ 80 kW / cm² intensity. The use of such a large intensity was desirable in this experiment as it allowed for measurement of small responsivities. In Fig. 5.6, the peak voltages measured across diametrically facing electrodes are plotted as a function of the angle α between the line connecting measuring electrodes and an arbitrary axis. The experimental data show that v varies sinusoidally with α , thus suggesting the presence of an electric field, E, with a component in the illuminated film area. The direction of E is fixed with respect to the film plane.

On the basis of the angular dependence of v, a four-point method was devised to determine more rapidly the direction of E in the film plane. This method consisted of measuring the voltage v_1 across a first pair of electrodes along an arbitrary axis, and v_2 across a second pair of electrodes along the normal to that axis. Let ϕ be the angle between E

and the axis of the first pair of electrodes, it follows that $v_1 \propto \cos \phi$ and $v_2 \propto \cos (\phi + \pi/2)$. Therefore, the value of ϕ can be derived from:

$$\tan\phi = -v_2 / v_1 \tag{5.1}$$

Once the direction of E determined, the field distribution along this direction was examined. For this purpose, a number of films were patterned into 1 x 7 mm² striplines in the field direction. The lithography and etching processes used for the patterning of PbBiSrCaCuO films were similar to the ones described in Chapter 4. Figure 5.7 shows the pattern of the stripline and a series of equally distant contacts along its length. This pattern was intended for the measurement of v on different segments of the stripline. Using a set of masks with varying slit widths, the segment areas between electrodes i and j, A_{ij} , were successively exposed to identical fluences (~ 0.41 W/cm²) of cw Nd:YLF laser. Table 5.1a shows the nonbolometric voltages recorded on these areas. Neglecting errors due to diffraction at the slit, it is seen that a linear relation:

$$v\left(\Sigma A_{ij}\right) = \Sigma v\left(A_{ij}\right) \tag{5.2}$$

could be corroborated. The linear increase of v with increasing length of stripline suggested a uniform distribution of E. It could also be confirmed that E was created solely in the illuminated part of the stripline. As evidenced in Table 5.1b, upon illumination of the segment between electrodes 1 and 4, the voltage measured on this segment was equal to the voltage measured on longer segments, *i.e.* between electrodes 1 and 6, 1 and 9, and 1 and 12. Finally, the measurement

performed on striplines of larger widths confirmed a rather weak dependence of v on line width.

It was found in the above experiments that v remained unchanged when the laser source was rotated around the beam axis. This finding showed that the induced field was independent of light polarization. To verify whether the field was induced optically or thermally, the Nd:YLF laser was replaced by a blackbody (Infrared Systems 11-210) as the radiation source. The blackbody temperature was adjusted to $\sim 1000 \text{ }^{\circ}\text{C}$ so that the peak of the spectral radiance (~ $2.3 \,\mu\text{m}$) shifted towards the laser wavelength. The radiation power incident on the film was modulated at 30 Hz and monitored with a power meter. The experimental results produced the evidence that an electric field was also created upon thermal heating of the film. The responsivity obtained with the blackbody was comparable with that obtained with the cw Nd:YLF laser source. It was also found that a dc field could be maintained in the absence of laser beam modulation. Because of the relatively low responsivity of the film, this was more obvious with laser heating instead of blackbody heating.

5.5 Temperature dependent characteristics

It has been established in the previous section that an electric field could be induced in the film plane upon illumination of PbBiSrCaCuO films. As an attempt to discern the origin of this field, its dependence on the film temperature was investigated. To avoid excessive laser heating that could alter the bias temperature of the film during the measurement, the film was shined with low levels of modulated cw laser power ($P \sim 240$ mW). Figure 5.8 shows the typical

temperature dependence of the nonbolometric voltage of a 1-µm thick film. When T was reduced from 300 K to 160 K, v, which was negative, decreased continuously towards zero. When T was reduced further, the polarity of v changed and the magnitude of v started to increase. The voltage reached a maximum near the onset $T_{\rm c}$ (~ 110 K), then decreased to the noise level with decreasing temperature. At temperatures below $T_{\rm c}$ (~ 90 K), v could no longer be detected, implying that the nonbolometric voltage occurs only in normal state films. For the purpose of comparison, the temperature dependent characteristics were also measured when the film was supplied with a dc bias current (I = 0.5 mA). The plots of the photoresponse obtained in the presence of a bias current, $V_{\rm t}$, and of the film resistance, R, are shown in Fig. 5.8. It is seen that the temperature dependence of V_t follows approximately that of dR/dT, indicating that V_t is predominantly bolometric in origin. On the other hand, the nonbolometric origin of v is further evidenced as its temperature dependence clearly differs from that of dR/dT.

In the experiments where the film was current biased, it was noted that the magnitude of V_t changed when I was inverted. Figure 5.9 clearly shows the dissimilarity between the photoresponse signals V_t (I) and V_t (-I), both recorded for I = 0.5 mA and identical intensity (~ 50 kW/cm²) of CO₂ laser pulse. This result suggests the presence of a current independent component in the overall voltage, in addition to the bolometric component. Assuming that v is the sole component that is current independent, the overall voltage can be expressed as:

$$V_{\rm t} = RI + V + v, \tag{5.3}$$

where V is the bolometric component:

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$$V = I \left(\frac{dR}{dT} \right) \Delta T, \tag{5.4}$$

and ΔT is the temperature increase in the film due to radiation heating. Measuring the ac components of V_t with and without current inversion, *i.e.* neglecting the dc component *RI*, *v* and *V* could be computed as:

$$v = [V_{\rm t} (I) + V_{\rm t} (-I)] / 2, \tag{5.5}$$

$$V = [V_t (I) - V_t (-I)] / 2.$$
(5.6)

To verify the conjecture expressed in Eq. 5.3, the transient characteristic of v was computed from experimental data of V_t (I) and V_t (-I) using Eq. 5.5. After this, the computed characteristic was compared with the one experimentally recorded in the absence of a bias current. Figure 5.9 confirms the agreement between these characteristics and validates Eq. 5.3, that is, v (t) and V (t) superimpose linearly. Another remarkable feature is the polarity reversal observed in both the computed and measured signals of v at T= 120 K. Referring to Fig. 5.8 where the polarity reversal was established to occur near T = 160 K, it is believed that the film temperature could have attained this value after a short period of intense heating by a strong laser pulse (~ 50 kW/cm²). This phase reversal provides valuable information on the evolution of the film temperature under laser heating.

Figure 5.10 shows the effect of the bias temperature of the film on transient structures of nonbolometric voltage. It is seen that the polarity reversal in the signal v(t) at T = 120 K disappears at T = 160

K. This fact is consistent with the temperature dependence of v as shown in Fig. 5.8. In effect, because the bias temperature is the lowest film temperature during laser heating, polarity reversal occurs only when the film is biased at below 160 K. It is also seen in Fig. 5.10 that the amplitude of v (t) increases with increasing bias temperature. Again, this result can be explained by the temperature dependence of v. Regardless of the bias temperature, when the film is exposed to identical laser energies the resulting temperature increases are the same. Hence, the highest temperature of the film when biased at T =160 K exceeded the one when biased at T = 120 K, resulting in a larger signal of v.

Considering the thermal origin of v, it is instructive to further confirm its nonbolometric origin. One possibility is to verify whether the transient v(t) follows the temperature change $\Delta T(t)$ of the film, as does the bolometric V(t), or behaves differently. The voltage V(t) can be derived from Eq. 5.6, in which the signals $V_t(I)$ and $V_t(-I)$ were measured at T = 160 K with I = 0.5 mA, and is plotted in Fig. 5.10. Also shown in Fig. 5.10 is the result with CO₂ laser pulse illuminating the film, as recorded with a Ge photon drag detector. Here, it is seen that the time constant of V(t) is significantly longer than that of v(t), also taken at T = 160 K. After the completion of the laser pulse, vdisappears while V continues to decay. The half-amplitude fall times of v and V were measured to be 120 and 1220 ns respectively. The observed difference in time constant confirms that v(t) is nonbolometric as it is unrelated to the temperature change $\Delta T(t)$ of the film.

5.6 Thermoelectric response

The experimental results obtained so far indicate that the observed voltage is thermal nonbolometric in origin. Among the possible thermal nonbolometric mechanisms, pyroelectricity, piezoelectricity, and thermoelectricity have been considered. The first two were excluded on account of the experimental results. Pyroelectrics generate an electric charge in response uniquely to a change in temperature. Pyroelectricity is excluded because a dc voltage could be maintained across the film when the latter was shined with a cw source, *i.e* held at steady temperatures. Piezoelectricity is excluded on the basis that the nonbolometric voltage was independent of light polarization. The remaining possibility, thermoelectricity, is examined in the following.

One of the basic thermoelectric effects is the Seebeck effect. This effect is illustrated using an open circuit shown in Fig. 5.11. The two sections of the circuit are made of different conductors with thermopower S_a and S_b . When a temperature gradient $T_1 - T_2$, where $T_1 > T_2$, is applied to the circuit, a voltage v_{ab} is generated. The voltage polarity is the one shown in the figure if $S_a > S_b$. This voltage, known as the Seebeck voltage, depends on the temperature gradient and not on the shape or dimensions of the conductors. Another well established experimental result of the Seebeck effect is that it does not occur in superconductors at temperatures below T_c . The fact that the nonbolometric voltage could be observed only at normal state temperatures appears to support the Seebeck effect possibility.

To explain the observed voltage as a direct result of the Seebeck effect, a model is proposed in Fig. 5.12 for the PbBiSrCaCuO film. Here, the film consists of layers with the thermopower S_a sandwiched between CuO layers with a different thermopower, S_b . These layers are parallel and believed to form a tilt angle, θ , to the substrate surface in a natural way due to surface defects and misalignments in substrate cutting. Such a structure can be seen as the equivalent of a number of thermocouples connected in series, n, along the length of the film, l. Upon laser heating of the film, the temperature gradient ΔT in the individual thermocouples results in Seebeck voltages that add up to a transverse component [5.6]:

$$v = n \left(S_{\rm a} - S_{\rm b} \right) \Delta T \tag{5.7}$$

where, according to the geometry shown in Fig. 5.12:

$$n = l / x_0 \tag{5.8}$$

Considering the relation between x_0 and the spacing, c, between adjacent CuO layers:

$$c = x_0 \sin\theta \tag{5.9}$$

One obtains:

$$n = l \sin\theta / c \tag{5.10}$$

On the other hand, the temperature gradient in each individual thermocouple can be expressed as:

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$$\Delta T = (T_1 - T_2) y_0 / d \tag{5.11}$$

where T_1 and T_2 are respectively the temperature at the top and bottom of the film, d is the film thickness, and:

$$y_0 = c \cos\theta \tag{5.12}$$

Introducing Eqs. 5.10 through 5.12 in Eq. 5.7, the latter becomes:

$$v = (S_a - S_b) (T_1 - T_2) (l \sin\theta \cos\theta / d)$$
(5.13)

This equation provides insight as to the dependence of the transverse Seebeck voltage on thermopower difference, temperature gradient along film thickness, tilt angle, and the film's length-to-thickness ratio. These relations will be verified against experimental data in order to confirm the proposed thermoelectric mechanism.

5.7 Discussion

The dependence of the Seebeck voltage on the film geometry, as suggested by Eq. 5.13, is consistent with the previous findings. The experimental observation reported in section 5.4 shows effectively that v increases linearly with the length while varies slightly with the width of the film stripline. In order to verify whether v depends on the tilt angle, several films were prepared under identical conditions on MgO substrates cut with surface normal at an angle, θ , to the (100) orientation. Using a cw Nd:YLF laser modulated at 30 Hz as the heat source, the nonbolometric responsivity, r, was measured upon these films along the field direction. In Fig. 5.13, r is shown for a range of values of θ between 0 and 20 deg (it is believed that the film grown on the substrate with $\theta = 0$ forms a finite tilt angle to the substrate surface due to surface defects). It is seen that *r* generally increases with increasing tilt angle for θ of up to 15 deg. The increase rate varies from one sample to another, possibly due to nonuniformity in the film growth. Despite this variation, the ratio of *r* between the most sensitive film with $\theta = 10$ deg and the least sensitive film with $\theta = 5$ deg remains close to the ratio predicted by Eq. 5.13. As θ was increased to 20 deg, *r* decreased drastically. It is believed that the films grown on the substrates cut with a too large angle may be disordered and consist of areas with different crystalline orientations, thereby resulting in mutually cancelling photoresponses.

Equation 5.13 provides insight as to the temperature dependence of v as described in section 5.5. According to this equation, the temperature characteristic of v is related mainly with that of thermopower difference, ΔS . Although v depends equally on the temperature gradient which varies with thermal constants of PbBiSrCaCuO, the temperature dependence of these constants is relatively small at normal state temperatures. Conversely, the temperature dependence of ΔS can be inferred from the experimental v (T). If ΔS (T) follows the behavior predicted for the thermopower of PbBiSrCaCuO, the temperature or v is indirectly confirmed.

By rearranging Eq. 5.13, the temperature dependence of ΔS can be expressed as:

$$\Delta S (T) = \left[d / l \sin\theta \cos\theta \left(T_1 - T_2 \right) \right] v (T)$$
(5.14)

For a typical film with $d = 1 \mu m$, l = 1 mm, and $\theta = 5 \deg$, $\Delta S(T)$ can be computed from the data of v(T) shown in Fig. 5.8. In this computation, the temperature gradient was taken as ~ 1 mK according to results from the heat transfer model (section 4.6) for low levels of cw laser power ($P \sim 240 \text{ mW}$). The resulting $\Delta S(T)$ characteristic, as shown in Fig. 5.14, was compared with those obtained in the previous work. Xin *et al.* [5.7] investigated the temperature characteristic of thermopower of Tl₂Ba₂Ca₂Cu₃O_y crystals. These authors found that the conventional characteristic for metals cannot account for the experimental data obtained for high T_c superconductors. On the other hand, they found a better agreement with a two-band model proposed for the thermopower of Tl₂Ba₂Ca₂Cu₃O_y, where one band is formed by the CuO planes and the other by TlO. This model is described by the following temperature dependence of thermopower:

$$S(T) = AT + (B + CT) \exp[-E_g/2kT]$$
(5.15)

where A, B, C are the material parameters, k is the Boltzmann's constant, and E_g is the energy gap of the semiconductorlike band structure of TIO layers. Later on, Awana *et al.* [5.8] carried out a similar investigation on 2223 phase PbBiSrCaCuO crystals and confirmed that Eq. 5.15 described consistently their measured values of S (T). In this thesis work, it is found that the temperature characteristic of ΔS is also in good agreement with the two-band model. As shown in Fig. 5.14, the experimental data were fitted with:

$$\Delta S(T) = S_{a} - S_{b} = AT + (B + CT) \exp[-E_{g}/2kT] - S_{b}$$
(5.16)

where S_b is assumed to be a constant. The best agreement was found for $E_g \sim 35$ meV [5.9], that is consistent with the value reported for PbBiSrCaCuO in other work [5.8]. Therefore, the ΔS (*T*) characteristic, as derived from v (*T*), is consistent with the two-band model predicted for high- T_c superconductors. In addition, its magnitude (~ 2 μ V / K) is close to that measured on PbBiSrCaCuO crystals [5.8, 5.10, 5.11].

One characteristic of the Seebeck response that is different from the thermal bolometric response is that it depends on the temperature gradient between the surface and bottom of the film, rather than the average temperature increase of the film. In this case, the time constant associated with the temperature gradient is determined by the diffusion time for heat propagation through the film:

$$\tau \sim d^2 \,/\, D \tag{5.16}$$

To confirm the Seebeck origin of the photoresponse, τ was computed using the thermal diffusivity constant $D \sim 2 \ge 10-3 \text{ cm}^2/\text{s}$ for room temperature BiPbSrCaCuO [5.12], and then compared with that obtained experimentally. In Table 5.2, the computed time constant is compared with the fall time (from 90% to 10% of signal amplitude) of the transient response of the film to a Nd:YLF laser pulse. Good agreement between the computed and measured time constants was obtained over an extended range of film thickness, corroborating the suggestion that the photoresponse is thermoelectric in origin. The discrepancy on the 20-nm thick sample may be due to the fact that the measured fall time was limited by that of the incident excitation; using a picosecond InGaAs detector, the fall time of the Nd:YLF laser pulse was measured to be ~ 7 ns.

5.8 Conclusions

The attention of previous studies on photoresponse of superconductor films were drawn commonly towards the temperature ranges below or around T_c . In this chapter, photoresponse was studied specifically at temperatures beyond T_c . In this temperature range, the existence of a nonbolometric photoresponse of PbBiSrCaCuO films was evidenced for the first time. A series of experiments have been carried out to investigate the nonbolometric characteristics and origin. The experimental results confirmed the following:

- (i) At $T > T_c$, a nonbolometric component, v, and a bolometric component, V, of the photoresponse coexist when the illuminated film is electrically biased. Their signals superimpose linearly and can be extracted from the photoresponses of the film with forward and reverse bias currents.
- (ii) v also manifests itself as the photoresponse of electrically unbiased films. It is obtained when the film is illuminated with either blackbody radiation or laser beam, thereby confirming its thermal origin. The time constant of v corresponds with the diffusion time for heat propagation across the film, that is shorter than the bolometric time constant of V. The temperature dependence of v differs also from that of V.
- (iii) It is excluded that v is generated by the differential temperature induced between electrodes by laser illumination. Rather, v is found to be associated with a fixed electric field thermally induced in the film plane.
- (iv) v is independent of light polarization, excluding piezoelectricity
 as a possible nonbolometric mechanism. Further, a dc voltage is

maintained across the film when cw radiation is supplied to the film, excluding pyroelectricity as the other mechanism.

The above findings pointed to the thermoelectric Seebeck effect as the nonbolometric mechanism. This conjecture was confirmed from the results of a model proposed for the PbBiSrCaCuO film. The film was depicted as a number of parallel layers having different thermopowers and forming a tilt angle to the substrate surface. Such a structure can be seen as the equivalent of a number of thermocouples connected in series along the length of the film. Upon laser heating of the film, the temperature gradient in the individual thermocouples results in Seebeck voltages that add up to the transverse component v. The dependence of v on the film geometry, measured experimentally, was consistent with the one predicted by the model. Further evidence of the thermoelectric origin was obtained as the temperature dependence of the measured thermopower corresponds with that theoretically predicted for PbBiSrCaCuO. **Table 5.1** - Nonbolometric photoresponses measured between electrodes *i* and *j* of a 7-mm PbBiSrCaCuO stripline (pattern shown in Fig. 5.7) when: (*a*) the stripline areas A_{ij} were shined by modulated cw Nd:YLF laser beam via slits of different sizes; and (*b*) only the stripline area A_{14} was shined. The incident laser beam had a diameter of ~ 1 cm and a fluence of 0.41 W/cm².

i-j	1-4	4-8	8-12	1-12
$A (cm^2)$	0.0190	0.0255	0.0255	0.07
p (W/cm ²)	0.41	0.41	0.41	0.41
<i>υ</i> (μV)	0.47	0.63	0.64	1.75

i-j	1-4	1-6	1-9	1-12
$A (\mathrm{cm}^2)$	0.0190			
p (W/cm ²)	0.41	0.41	0.41	0.41
υ (μV)	0.47	0.47	0.47	0.47

1a.

1b.

Table 5.2 - Computed and measured time constants of thethermoelectric response for different thicknesses of BiPbSrCaCuOfilms.

	Thickness (nm)	Computed τ (ns)	Fall time (ns)
PbBiSrCaCuO film	n 20	2	8
	50	13	12
	100	50	55
	150	113	115
	300	450	430
	430	925	890
Laser pulse			7



Fig. 5.1 - Cross sectional schematic of the film grown on a substrate cut with surface normal, n, at an angle, θ , to the (100) orientation. The film structure consists of CuO planes inclined by θ with respect to the substrate surface.



Fig. 5.2 - Schematic diagram of the measuring circuit for the determination of the photoresponse of PbBiSrCaCuO films. Incident light is obtained from either Nd:YLF or CO₂ laser source at wavelengths of 1.05 and 10.6 μm . The size and intensity of laser beam on the film are adjusted using a set of attenuator, focal lens, and diaphragm.



Fig. 5.3 - Evidence of the nonbolometric photoresponse that appears across a PbBiSrCaCuO film at room temperature, in the absence of bias current. The film was shined with a cw Nd:YLF laser beam modulated at ~ 30 Hz. The photoresponse disappeared when the laser beam was suppressed.



Fig. 5.4 - Cross-sectional profile of the Nd:YLF laser beam incident onto the PbBiSrCaCuO film.



Fig. 5.5 - Responsivities obtained on a PbBiSrCaCuO film as a Nd:YLF cw laser beam scanned between electrodes. The film was shined with a beam of 10 mm size through a diaphragm of ~ 1.2 mm. The power and modulation frequency of the incident beam were respectively 150 mW and 30 Hz. The open squares show the positions of the electrodes on the film.



Fig. 5.6 - Peak voltages measured across diametrically facing electrodes as a function of the angle formed between the line connecting the measuring electrodes and an arbitrary axis. The solid line depicts the sinusoidal variation of the voltage. The inset diagram shows the schematic arrangement of the electrodes on the film. The film was illuminated with CO_2 laser pulses of ~ 80 kW / cm² density through a slit of 7-mm diameter.


Fig. 5.7 - Schematic diagram of the stripline film (shown in gray) with a series of equally distant electrodes along its length. The electrode arrangement allows for measurement of the photoresponse across different segments of the stripline.



Fig. 5.8 - Temperature dependence of R, V_t , and v of a PbBiSrCaCuO film; V_t as shown is multiplied by a factor of 50 for visual aids. The film was illuminated by a modulated cw Nd:YLF laser beam in the low power mode to avoid film heating.



Fig. 5.9 - Transient structures of the computed and measured nonbolometric voltages, v_{comp} and v, of a PbBiSrCaCuO film. Both are multiplied by a factor of 10 for visual aids. The film was held at T =120 K and was illuminated by a CO₂ laser pulse. Also shown are the photoresponses V_t (I) and V_t (-I) of the film measured with I = 1 mA. The nonbolometric voltage v_{comp} was computed as $[V_t$ (I) + V_t (-I)] / 2.



Fig. 5.10 - Transient structures of the nonbolometric voltages, v, measured at T = 120 K and 160 K, and the bolometric voltage, V, computed for T = 160 K. The bolometric voltage was computed as $[V_t$ $(I) - V_t (-I)] / 2$ where $V_t (I)$ and $V_t (-I)$ were experimentally obtained with I = 0.5 mA. Also shown is the transient structure of the CO₂ laser pulse illuminating the film as recorded with a Ge photon drag detector.



Fig. 5.11 - Basic thermoelectric circuit illustrating the Seebeck effect. The two sections of the circuit are made of different conductors with thermopower S_a and S_b . When a temperature gradient $T_1 - T_2$, where $T_1 > T_2$, is applied to the circuit, a voltage v_{ab} is generated with the polarity shown if $S_a > S_b$.



Fig. 5.12 - Illustration of a model for the PbBiSrCaCuO film. The film structure consists of CuO planes inclined by θ with respect to the substrate surface. This results in thermocouples connected in series along the film. Temperature gradients in the thermocouples lead to a transverse Seebeck voltage.



Fig. 5.13 - Nonbolometric voltages measured on PbBiSrCaCuO films on MgO substrates as a function of angle θ . The substrates were cut with surface normal at the angle θ to the (100) orientation.



Fig. 5.14 - Temperature dependence of the thermopower difference $\Delta S = S_a - S_b$ of a PbBiSrCaCuO film. The solid line represents the theoretical $\Delta S = AT + (B+CT)\exp[-E_g/2kT] - S_b$ derived from the two-band model in which A, B, C, and S_b are constants and $E_g = 35$ meV.

The discovery of cuprate superconductors has relieved the stringent cryogenic requirement of conventional superconductors. As a result, renewed interests were sparked in applications previously hindered by the low temperature requirement. In recent years, much effort has been devoted to thin film processes of cuprate superconductors for fundamental studies and various electronic applications. Of these superconductors, BiSrCaCuO is quite attractive in that it exhibits the highest known T_c among compounds that are free of toxic elements. However, this compound is known to be challenging to grow high quality films in single phase because it contains a large number of elements and has a multiphase characteristic. Because of the difficulty in obtaining quality specimens of BiSrCaCuO films, there has been relatively few studies on their optical and electronic properties. This is in sharp contrast with the extensive investigation on compounds that are available more readily in thin film form, such as YBaCuO.

This thesis work focuses on two objectives. The first objective is to devise a process for the growth of single phase, high quality BiSrCaCuO superconductor films. The second objective is to identify the physical mechanisms behind the infrared photoresponse of superconducting and normal state films. These two objectives have been met. For each objective, the main results and contributions to the current knowledge will be outlined.

6.1 Thin film synthesis of PbBiSrCaCuO superconductors

Prior to the thesis work, there was scarcely any report of BiSrCaCuO superconductor films with single crystal quality. Thin films of Bi₂Sr₂Ca_{n-1}Cu_nO_y may be synthesized in at least two superconducting phases which differ mainly in the number of CuO₂ planes between Bi₂O₂ along the *c*-axis. These phases are commonly referred to by their cation ratios as 2212 with n = 2 and $T_c \sim 80$ K, and 2223 with n = 3 and $T_c \sim 110$ K. One problem commonly encountered in the film synthesis was that the low $T_{\rm c} 2212$ phase tends to develop more rapidly, impeding the growth of the desired high $T_{\rm c}$ 2223 phase. As an attempt to promote the growth of the 2223 phase, the effect of Pb doping has been investigated by a number of authors, including the present study. Typically, the film synthesis consisted of two steps. Firstly, PbBiSrCaCuO films are grown on unheated substrates by means of various deposition techniques. Secondly, the as-deposited films are heat treated in O₂ or in air for a period from 20 to 50 hrs. Although the addition of Pb enhanced the growth of the 2223 phase, most resulting films retained the 2212 phase and remained heterogeneous. It was found that the composition of metal constituents of the film varied with annealing time. This suggested that the difficulty in compensating adequately elemental losses in such a long heat treatment contributed to the low yield of single phase 2223 films. Furthermore, a long heat treatment is undesirable for practical applications.

The possibility that superconducting PbBiSrCaCuO films could be obtained from a much shorter heat treatment emerged from the findings of Tanaka *et al.* [6.1]. During the investigation of BiSrCaCuO

films containing co-deposited PbO layers, these authors found that films with 2223 dominant multiphases could be developed after just one hour of annealing. Following this report, there has been no other work supporting their results. More importantly, it remained questionable whether the single high T_c 2223 phase could be segregated after a short heat treatment. One important achievement of this thesis work is the first demonstration that it is possible to achieve single phase 2223 films with a heat treatment as short as one hour. This evidence was obtained through control of film stoichiometry and phase formation. Details are as follows.

One advantage of the short annealing is that the elemental losses are less important during the treatment. As a result, it was the stoichiometry of the as-deposited film that received particular attention in this work. The choice of magnetron sputtering over other deposition techniques was motivated essentially by the ease of stoichiometry control over a large film area. Unlike the multi-target approach used by Tanaka, single target magnetron sputtering has been selected to reduce the number of process variables. On the other hand, in order to obtain the desired film stoichiometry from single target sputtering, the ability to control the cation ratio of the multicomponent target becomes critical. This is increasingly important as the content of Pb in the film appears to be a variable determining the crystalline structure formed during the heat treatment. Because of the lack of commercial PbBiSrCaCuO sputter targets, a process had to be devised to prepare targets with suitable cation ratio and sufficient Pb content. This was achieved using a blending of precursor powders, followed by solid state reactions and pressing of the reacted powder compound. Experimental conditions were determined for each step,

which resulted in high quality sputter targets for magnetron sources. The compositional analysis of the sputtered films suggested that the target was composed of Pb:Bi:Sr:Ca:Cu:O ~ 1:2:2:2:3 with low carbon content.

Several effects of the sputter deposition that had not been reported elsewhere were observed. For instance, surface profiling over a film length of 12 cm showed the evidence of a decrease of film thickness around the discharge center. This depletion was found to be consistent with the structure zone model of sputtered films, in which an increase in film density at the center area could be predicted. Beside film densification, it is believed that the decrease of film thickness was also a result of film erosion due to the bombardment of the growing film by energetic ions. The composition of the sputtered films was examined at different locations on the substrate. The EPMA data revealed a significant loss of Pb had occurred during the target sintering and film deposition. The deviation of film composition from nominal composition of the target was found to increase with increasing distance between the film and the discharge center.

After the magnetron sputter deposition, the films underwent a short heat treatment in an apparatus set up for precision annealing. The effects of annealing conditions on the formation of superconducting phases in the film were systematically studied. This study has revealed for the first time important information on the kinetics of the phase formation. It was found that the films preannealed in O_2 at relatively low temperatures (810 to 830 °C) had initially a semiconductive structure. During the 20 min preannealing, a solid state reaction occurred, resulting in a transition towards a

superconductive structure in the film. At the end of the preannealing period, the low T_c 2212 phase was formed readily. During the subsequent treatment in air, a gradual structural transition from the 2212 phase to 2223 phase occurred as the annealing temperature and duration were increased. Experimental evidences of the phase transition were first obtained from measurements of the XRD spectra. These evidences could subsequently be confirmed by the *R*-*T* and χ -*T* characteristics and elemental compositions of the treated films. For all films, the superconducting phases as revealed by the *R*-*T* and χ -*T* characteristics are precisely consistent with the phases identified in the XRD spectra. Under specific conditions, nearly single 2223 phase was achieved in the films treated for 40 min in air. These films, homogeneous and highly oriented, exhibit a $T_{\rm c} \sim 107$ K and a $J_{\rm c}$ exceeding 8x10³ A / cm². The uniform superconductivity achieved over a large film area was corroborated by the weak dependence of $T_{\rm c}$ on magnetic field intensity. These results were reproducible for at least three different substrate materials, MgO, LaAlO₃ and SrTiO₃. The treatments of shorter duration or at lower temperatures resulted in heterogeneous films with mixed 2212 and 2223 phases, in which a superconducting percolation path could be established at temperatures as high as 100 K. The evolution of film compositions with annealing time suggested that Pb is a precursor of the reactions accounting for the rapid phase transition. It was seen that concentrations of individual metals varied appreciably with annealing time throughout the 20 min of preannealing and the first 10 min of annealing. Coincidently in this period, the concentration of Pb decreased steadily. This correlation suggests the role of Pb as a precursor of the solid state reactions occurred in this period. By the end of this period, the XRD spectra shows that the volume fraction of the 2223 phase in the film

became substantial. Following this, a much slower decrease in the Pb concentration was observed as the transition from the 2212 to 2223 phase completed. After 40 min of annealing, a small but detectable amount of Pb remained in the nearly single phase film. This result is consistent with the observation that the reduction of Pb concentration to essentially zero results in a halt in the 2212-to-2223 transition.

6.2 Photoresponse of PbBiSrCaCuO films

Prior to this thesis work, there has been practically no study on the photoresponse of PbBiSrCaCuO films. Attention was rather focused on the photoresponse of YBaCuO films as these films were available more readily and their properties were better understood. At superconducting temperatures, numerous authors interpreted the response observed by them as solely bolometric in origin, whereas a comparable number associated the response with a nonbolometric origin. Conditional on the film structure, different physical mechanisms have been suggested to account for the nonbolometric response. These include photodissociation of Cooper pairs and vortexantivortex pairs, photoinduced suppression of superconductivity, and photoenhanced flux creep. The photoresponse at normal state temperatures has received little attention. The bolometric mechanism was believed to be exclusively responsible of photoresponses in normal state films. Given the inherently small temperature coefficients of resistance at temperatures above $T_{\rm c}$, there has been little interest shown in the bolometric response of these films.

In this thesis work, the photoresponse of PbBiSrCaCuO films was investigated at temperatures below, around, and above T_c . The

results obtained provide a better understanding of the response mechanisms and their relation with the film structures in these temperature ranges. It was shown that the photoresponse of epitaxial and granular films is purely bolometric at superconducting temperatures and around T_c . During the experiments no evidence of nonbolometric response has been found. Beyond T_c , the existence of a nonbolometric component in the photoresponse has been found. Results of a series of experiments pointed to the thermoelectric Seebeck effect as the nonbolometric mechanism. The details are as follows.

The photoresponses of both epitaxial and granular films with thicknesses of 200 - 250 nm were investigated. The optical measurements were performed at near infrared and far infrared wavelengths. In the transition region, the measured responses exhibited several bolometric signatures. Firstly, a good agreement was obtained between the temperature dependence of photoresponse and that of temperature derivative of film resistivity. Secondly, the recovery time of the response was many times that of the optical excitation. Thirdly, the linear increase of photoresponse with increasing supplied current was confirmed. At temperatures below T_c , a fast response appeared when the power density of optical excitation exceeded a certain threshold. However, the effect of bias temperature on the transient structure, magnitude, and time delay of the fast response showed that it is also bolometric in origin.

One approach to confirm the origin of the experimental response is to compare it with the prediction of a bolometric model. In this thesis work, a bolometric model has been developed using the solutions

of the problem of linear heat flow in a solid bounded by a pair of parallel planes. For a given thermal excitation input, the temperature increase of the film could be computed as a function of space and time, which was then converted in photoresponse. Under the experimental conditions of this study, it was found that the experimental response is in good agreement with the simulated response.

At temperatures beyond T_c , the occurrence of a nonbolometric component in the photoresponse was evidenced for the first time. A series of experiments was performed in order to investigate the nonbolometric characteristics and origin. The experimental results confirmed the following:

- (i) At $T > T_c$, a nonbolometric component, v, and a bolometric component, V, coexist in the photoresponse when the illuminated film is electrically biased. Their signals superimpose linearly and can be isolated through numerical treatment of photoresponses with forward and reverse bias currents.
- (ii) v manifests also itself as the photoresponse of electrically unbiased films. It is obtained when the film is illuminated with either blackbody radiation or laser beam, thereby confirming its thermal origin. The time constant of vcorresponds with the diffusion time for heat propagation across the film, that is shorter than the bolometric time constant of V. The temperature dependence of v differs also from that of V.
- (iii) It is excluded that v is generated by the differential temperature induced between electrodes by laser

illumination. Rather, v is found to be associated with a fixed electric field thermally induced in the film plane.

 (iv) v is independent of light polarization, excluding piezoelectricity as a possible nonbolometric mechanism.
 Further, a dc voltage is maintained across the film when cw radiation is supplied to the film, excluding pyroelectricity as the other mechanism.

The above findings pointed to the thermoelectric Seebeck effect as the nonbolometric mechanism. This conjecture was confirmed from the results of a model proposed for the PbBiSrCaCuO film. The film was depicted as a number of parallel layers having different thermopowers and forming a tilt angle to the substrate surface. Such a structure can be seen as the equivalent of a number of thermocouples connected in series along the length of the film. Upon laser heating of the film, the temperature gradient in the individual thermocouples results in Seebeck voltages that add up to the transverse component v. The dependence of v on the film geometry, measured experimentally, was consistent with the one predicted by the model. Further evidence of the thermoelectric origin was obtained as the temperature dependence of the measured thermopower corresponds with that theoretically predicted for PbBiSrCaCuO.

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Chapter 6

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