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Investigation on Fabrication Processes and Characteristics of BiSrCaCuO Films

Lixia Li

A thesis submitted to the Faculty of Graduate Studies and Research in partial fulfilment of the requirements for the degree of Doctor of Philosophy

> Department of Electrical Engineering McGill University Montreal, Canada April, 1996

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To the memory of my grandmother

Abstract

Superconducting thin films of BiSrCaCuO with a thickness from 0.4 to 1 μ m have been successfully fabricated on (100) oriented MgO substrates by CO₂ laser ablation and post annealing. Pb-doped BiSrCaCuO targets were prepared from oxide with different ratios of metals. Oxygen pressure during deposition was found to affect the composition of the asdeposited films. Although the substrate heating improved morphology of the films, it did not have a strong effect on the stoichiometry. Good quality superconducting films were produced after a two-step annealing with a controlled rate of temperature increase, which was determined by the chamber pressures used.

The onset critical temperature for the superconducting films was between 86 and 118 K, and the zero critical temperature was between 77 and 106 K. These critical temperatures are the highest ones obtained so far for BiSrCaCuO films prepared by the CO₂ laser ablation technique. The critical current density of the films was in the range of $10^2 \sim 10^3$ A/cm². The films were found to contain 2212 and 2223 superconducting phases, with a dominant 2223 phase. The composition was uniform along the films and the average ratio was close to that for the standard 110 K high-T_c phase.

The noise of the BiSrCaCuO films in normal state was inversely proportional to frequency and was at least 5 orders of magnitude larger than the noise of typical metals. In the superconducting state, the films showed a noise peak in the tail region of the superconducting transition. This noise peak also showed a 1/f variation at intermediate frequencies. The noise peak was maximum at a given current, and decreased with an increase in the external magnetic field. It is believed that this noise peak was caused by the vortex motion. Three peaks were observed in microwave-induced voltage versus temperature curves (microwave frequency = 10.28 GHz) for the BiSrCaCuO superconducting films. One of the peaks occurred at the midpoint of the superconducting transition, which was due to a bolometric effect. The other two peaks occurred at temperatures near the tail region of the transition and these were caused by a non-bolometric effect.

Résumé

Des couches minces supraconductrices de BiSrCaCuO ayant des épaisseurs de 0.4 à 1 m ont été déposés sur des substrats (100) de MgO en utilisant la technique d'ablation par laser CO₂ suivi par un recuit. Des cibles de BiSrCaCuO dopées au Pb ont été préparées à partir des oxydes correspondant avec les proportions atomiques adéquates des métaux. La stoéchiométrie des dépôts variait selon la pression d'oxygène utilisée pendant le dépôt. La morphologie des couches déposées a été améliorée en chauffant le substrat pendant le dépôt sans affecter, d'une façon significative, la stoéchiométrie des films. De plus, on a observé que la qualité des films de BiSrCaCuO peut être améliorées par un procédé de recuit en deux étapes, et ce en choisissant les taux de recuit appopriés correspondant à la pression à laquelle chaque film a été déposé.

La région de transition à la température critique des films supraconducteurs varie entre 86 K et 118 K, alors que la valeur de la température critique pour zéro résistance varie entre 77 K et 106 K. Les valeurs ainsi obtenues de température critique sont les plus élevées pour des films supraconducteurs de BiSrCaCuO déposés par ablation laser en utilisant un laser CO₂. La densité de courant critique des films varie entre $10^2 \sim 10^3$ A/cm². Les films sont formés d'un mélanges des phases supraconductrices 2212 et 2223, cette dernière étant la dominante. La composition des films s'est avérée uniforme avec en moyenne un rapport proche de la phase standard 2223 pour laquelle T_c = 110 K.

Le bruit dans l'état normal du film est inversement proportionnel à la fréquenec et est de 5 ordre de grandeurs plus élevé que le bruit mesuré pour des métaux typiques. Dans l'état supraconducteur, les films de BiSrCaCuO présentent un pic de bruit dans la région de la transition supraconductrice. Le bruit dans cet état suit une relation 1/f aux fréquences intermédiaires. Le pic du bruit présente un maximum à un certain courant de transport et diminue en augmentant le champ magnétique externe. Ce pic dans le bruit peut être du au déplacement du vertex.

Trois maximums ont été observé dans le voltage induit par les micro-ondes (10.28 GHz) en fonction de la température. Le pic détecté au centre de la région de transition est attribué à un effet bolométrique. Par contre, les deux autres pics qui apparaissent à une température proche de la queue de la région de transition, seraient dus à un effet non-bolométrique.

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Chapter 1

Introduction

One of the remarkable developments in science over last decade is the discovery of high critical temperature superconductors. A superconductor carries a current without resistance. A current flowing around a superconducting ring will remain indefinitely as long as the temperature is below the critical value. Superconductors have been used in many fields, from electrical wires, cables and high-field magnets to passive microwave devices (filter, antenna, and mixer), optical detectors and bolometers.

1.1 Historical Review

Many scientists have contributed to the development of the theory underlying superconductivity. Knowledge about superconductors, especially knowledge about high-Tc superconductors, is still increasing. This section gives a brief historical view on the development of superconductors and some breakthroughs made that clarify the theory of superconductivity. Methods used to prepare superconducting films, especially the laser ablation method, will then be briefly described.

1.1.1 Brief Review on the Discovery of Superconductors

Conventional superconductors, which are also called low-T_c superconductors (or low critical temperature superconductors), were first discovered by a Dutch physicist, Heike Kamerlingh Onnes, in 1911.^[1.20] In his lab in Leiden, Onnes found that the dc resistivity of a mercury sample suddenly become zero when the sample is cooled below 4.2 K. He named this new phenomenon as superconductivity. Following his discovery, superconductivity was found in many other metallic elements such as Al, Pb, and Nb. The materials with the superconductivity properties are called superconductors.

In 1933 Meissner and Ochsenfeld found that in the superconducting state a metal exhibits perfect diamagnetism, which is another distinct property of a superconductor^[1,25]. The magnetic flux is expelled from the interior of a superconductor that is cooled below the critical temperature in low external magnetic fields. This effect is also called the Meissner effect. Zero resistance and the Meissner effect are the two criteria for categorizing superconductors.

Two years after the discovery of the Meissner effect, F. London and H. London proposed a simple two-fluid model to explain the superconductivity phenomenon.^[1,16] In their model they assumed that of the total density of electrons, n, there is a fraction n_3 that behaves in an abnormal way and represents superconducting electrons. These electrons are not scattered by either impurities or phonons, and thus they do not contribute to resistivity. F. and H. London modified the Ohm's law while retained the Maxwell equations as formulated. They predicted the penetration depth λ , which is the characteristic length of penetration of the static magnetic flux into a superconductor, and derived a function of H(x) $= H(0)exp(-x/\lambda)$, where H(0) is applied magnetic field at the surface of the superconductor and H(x) is the magnetic field inside the superconductor at a distance x away from the surface. The static magnetic flux persists within a sheath of depth λ at the surface of the superconductor, and its magnitude decreases exponentially towards the core of the superconductor.

In 1950 V. Ginzburg and L. Landau^[1,18] proposed a macroscopic theory for superconductivity from which one can obtain an insight into the properties of the more interesting superconducting materials, the high-T_c superconductors. A. Abrikosov studied the behaviour of superconductors in an external magnetic field in 1957, and classified the superconductors as type-I and type-II superconductors. The difference between these two types of superconductors stems from the Meissner Effect. A type-I superconductor excludes a magnetic field until superconductivity is destroyed suddenly. The field then penetrates the material completely. A type-II superconductor excludes the magnetic field completely up to a field H_{el} . Above H_{el} the magnetic field is partially excluded, but the sample remains electrically superconductivity vanishes. The state in which a magnetic field exists between H_{el} and H_{e2} is called vortex state. Figure 1-1 shows curves of magnetization versus applied magnetic field for type-I and type-II superconductors. It should be noted that negative values of M in figure 1-1 corresponds to diamagnetism.

In 1957 J. Bardeen, L. Cooper and R. Schrieffer proposed a complete microscopic theory of superconductivity that is usually referred to as the BCS theory.^[1.17] Their theory suggested that there is an interaction between a gas of conduction electrons and elastic wave of the crystal lattice. In general, the electrons repel each other by the Coulomb force. However, in the case of a superconductor at sufficiently low temperatures there is a net attraction between two electrons that form the so-called Cooper pairs. All Cooper pairs move in a single coherent motion, and an individual pair cannot be scattered. The conclusions of BCS theory are summarized below.

(a) As a result of electron-lattice-electron interaction, the electrons remain in the ground state which is separated from excited states by an energy gap.

(b) Penetration depth and coherence length emerge as natural consequences of the BCS theory, as well as the Meissner Effect.

(c) For an elemental or alloy material with the electron density of orbitals $D(\epsilon_F)$ of one spin at the Fermi level and the electron-lattice interaction U, the superconducting transition temperature can be predicted from $T_c = 1.140 \exp[-1/UD(\epsilon_F)]$, where $UD(\epsilon_F) \ll 1$, and θ is the Debye temperature. The prediction suggests that a metal which has a higher resistivity at room temperature (thus a higher U) is more likely to be a superconductor at low temperatures.

(d) Magnetic flux through a superconducting ring is quantized and the effective unit of charge is 2e rather than e.

The BCS theory still provides the basis for the present understanding of superconductivity in conventional low-T_c materials, as well as the understanding of some properties in high-T_c oxides.

In 1962, after the announcement of the BCS theory, B. Josephson postulated that there would be fascinating quantum tunnelling effects in superconductor-insulatorsuperconductor sandwich structures.^[1,19] His predictions were confirmed within a year and the effects are now known as the Josephson effects. There are two kinds of Josephson effects: dc and ac Josephson effects. The dc effect is that direct superconducting current can flow through a tunnel junction without an applied voltage. The ac Josephson effect is that an alternating superconducting current can flow across a tunnel junction if a constant voltage is applied to the junction. The frequency of the alternating current is related to the applied voltage by $\omega = 2eV/\hbar$, where V is the applied voltage and \hbar is Plank's constant. Today, devices based on the Josephson effects are used in superconducting electronics.

Figure 1-2 displays the evolution of increase of critical temperatures of superconductors from 1911 to the present. It can be seen that several low-T_c superconductors

(conventional superconductors) are based on Nb-compounds. In 1986 G. Bednorz and K. A. Müller discovered superconductivity in cuprate oxides at IBM's Zurich laboratory^[1,21]. They found evidence of superconductivity in LaBaCuO ceramics at about 30 K. Following that, in February 1987 research groups coordinated by M. K. Wu and P. Chu discovered $Y_1Ba_2Cu_3O_7$ ceramics with transition temperature of $T_c = 92 \text{ K.}^{[1,22]}$ This is the most important discovery which captured the worldwide attention because it is the first time a superconductor with a transition temperature above the boiling temperature of liquid nitrogen had been found. Only one year later, BiSrCaCuO compounds, with transition temperatures up to 115 K, were discovered by Maeda et al ^[1,23] in Japan and the TIBaCaCuO compounds, with transition temperature up to the 125 K, were discovered by Herman and Sheng at the university of Arkansas.^[1,24] Very recently (September 1993), two research groups ^[1,10,1,11] reported that superconducting transition temperature can reach 153 K in the compound HgBa₂Ca₂Cu₃O₈₊₆ at a pressure of 150 kbar.

1.1.2 Development of Laser Ablation Technique

Many methods have been adopted to prepare bulk and thin film high- T_c superconductor samples. For the film deposition, techniques that have been used include coevaporation, ion beam sputtering, rf-sputtering, laser ablation, chemical vapour deposition (CVD), molecular beam epitaxy (MBE) and metalorganic chemical vapour deposition (MOCVD). Among these, laser ablation is considered to be one of the best methods. Since laser ablation has been used in this thesis work, a brief review on the development of this technique is presented as follows.

Conceptually and experimentally, laser ablation, or pulsed laser deposition (PLD) is extremely simple. It uses pulsed laser radiation to vaporize materials and to deposit films in a vacuum chamber. However, the beam-solid interaction that leads to evaporation/ablation is a very complex physical phenomenon. By choosing an appropriate laser, laser ablation can be used to deposit films of almost any material. The development of pulsed laser deposition technique can be roughly divided into four periods. During the first period (1965 - 1969),

Chapter 1 Introduction

Smith and Turner^[1,1] deposited thin films of a variety of semiconductors, dielectrics, chalcogenides, and organometallics using a ruby laser. Their early work established basic procedures for PLD technique. Following this, several research groups also deposited various thin films using CO₂ lasers and Nd:YAG glass lasers. Most of work during the period was aimed at testing laser ablation and did not attempt to improve film quality by optimizing substrate temperature and ambient conditions during deposition.

During the second period (1970-1979), Q-switch technique made very short optical pulses available. Lasers with a short pulse width resulted in higher peak powers, so that congruent evaporation was observed in many systems including low-temperature superconductors. A typical contribution was made by Gaponov and co-workers who carried out PLD in a reactive ambient.^[1,2-1,4] This period was marked with numerous studies in plume diagnosis. Most of the work focused on the characterization of the mass, charge distribution and kinetic energy content of the laser-induced plume.

During the third period (1980 - 1987), PLD technique was developed to deposit epitaxial semiconductor films with a quality comparable to films grown by MBE. With lasers having an excellent long-term stability available, the deposition of very thick (tens of microns) semiconductor layers became possible. FLD was also used to deposit oxide and other ceramic films with improved film crystallinity over e-beam deposited films.

Since 1987, the successful deposition of high-temperature superconductor films by laser ablation has accelerated the development in this field. The number of research groups working in this field has increased rapidly. PLD technique has the capability to preserve multicomponent system stoichiometry, to oxygenate films *in situ* by reactive deposition and to evaporate just about any material. Production-related issues such as uniform coverage over large areas and multilevel devices were also first studied during the period,

The application of laser ablation in high- T_c superconducting films was started from the YBaCuO compound^[1,5-1,8] because it is the first oxide compound found with transition temperature above 77 K. In situ laser ablation technique had been optimized with further experiments by adjusting laser energy, deposition angle and oxygen pressure. The deposition results of YBaCuO high-T_c films showed that quality of the films is superior and the critical current density is higher compared to the one deposited by other techniques. After the discovery of BiSrCaCuO high-T_c superconductor by Maeda et al, PLD technique was also adopted to deposit this material. Both *in situ* and *ex situ* laser ablations were used by several research groups. However, the quality of resulted films was not satisfactory. Further research work to improve film quality is still needed.

1.2 High Critical Temperature Superconductors

Higher transition temperature, higher critical field, mixed state, longer penetration length and shorter coherence length is what distinguishes high- T_e superconductors from conventional superconductors. The physical properties of high- T_e superconductors are not very well described with the theories used to describe conventional superconductors. However, the high- T_e superconductors and the conventional low- T_e superconductors have some common characteristics such as paired carriers and energy gap. The theoretical explanation for the behaviour of high- T_e superconductors is still being formulated. In this section, the structure, electrical and magnetic properties of high- T_e superconductors will be introduced briefly. Special emphasis will be given on the BiSrCaCuO compound.

1.2.1 Structure

Most of the high- T_c superconducting oxides discovered so far are cuprate compounds. One inherent characteristic of high- T_c superconducting oxides is the presence of the CuO₂ layers which govern most of the electrical properties. Unlike normal oxides which are insulating materials, the high- T_c superconducting oxides exhibit metallic behaviour at room temperature. Conductivity of high- T_c superconducting oxide is mainly due to the CuO₂ planes. The conductivity in the direction perpendicular to CuO₂ planes is lower. BiSrCaCuO compound has a pseudotetragonal structure. The general formula is Bi₂Sr₂Ca_{n-1}Cu_nO_y with n = 1, 2, and 3. The difference among the three phases is in the number of CuO₂-Ca-CuO₂ slabs. Figure 1-3 shows the structures of these phases. There is no CuO₂-Ca-CuO₂ slab in the n=1 phase. The crystal lattice constant of Bi₂Sr₂CuO_{8+y} (2201 phase) is a = 5.39 Å and c = 24.6 Å. One slab of CuO₂-Ca-CuO₂ exists in the Bi₂Sr₂CaCu₂O₈₊₁₀ phase and two slabs of CuO₂-Ca-CuO₂ are found in the Bi₂Sr₂Ca₂Cu₃O_{10+y} phase. The lattice constant *a* of the 2212 and 2223 phases is the same as the lattice constant of the 2201 phase (*a* = 5.39 Å); however, the lattice constant *c* increases to 30.6 Å and 37.1 Å respectively^[1.9]. The superconducting properties of these phases depend on the CuO₂-Ca-CuO₂ slabs.

The transition temperatures of the 2201, 2212, and 2223 phases are 10 K, 85 K, and 110 K, respectively. In the BiSrCaCuO structure, the Bi-O layer can be considered as a "charge reservoir". The Bi-O layer is needed to transfer the charge into CuO₂ layers. The structure is therefore also described as "CuO₂-Ca-CuO₂ slabs separated by a charge reservoir". An addition of oxygen or a deficiency of Bi creates holes in the Bi-O layer. To maintain the charge balance, electrons are removed from the CuO₂ planes, leaving holes in the planes to form "Cooper pairs" at temperatures below the superconductor transition temperature.

1.2.2 Physical Properties

When compared with conventional superconductors, high- T_c superconducting oxides have many new features. One of these new features is a high anisotropy of conductivity caused by structural anisotropy. The anisotropic properties are more pronounced in the BiSrCaCuO compound than in the YBaCuO compound. Conductivity of superconducting oxide perpendicular to the *c* axis is much higher than along *c* axis. This difference of conductivity between the orientation perpendicular to the *c* axis and parallel to the *c* axis is about 5 orders of magnitude in the BiSrCaCuO compound. Hall effect measurements show that most of the high- T_c superconducting oxides are p-type. The carriers in the oxides are holes which are located in CuO₂ planes. Comparing to a normal metal, the typical carrier concentration of these holes is pretty low (about 10^{21} cm⁻³). However, if one assumes that the holes are mostly in the CuO₂ planes, the carrier concentration of the superconducting oxides is close to that of copper.

Energy gaps (2Δ) , coherence lengths (ξ) and penetration depths (λ) in high-T_c superconducting oxides all differ from the counterparts in conventional superconductors. The energy gap is equal to the energy needed to break a Cooper pair. The energy gaps in high-T_c superconductors are anisotropic, and are larger along the orientation perpendicular to the *c* axis. The coherence length is a measure of the distance over which the gap can vary. The coherence lengths of high-T_c superconductors are extremely short, about 10 Å or less. The coherence lengths are also anisotropic, and with larger values in the direction perpendicular to the *c* axis. The thickness of the region of a superconductor through which the supercurrent flows is called the penetration depth of the magnetic field. It is one of the quantities that characterize the superconductor. In type-II high-T_c superconducting oxides, the penetration depths are anisotropic with larger values in the direction perpendicular to the *c* axis. Table 1-1 lists some of physical parameters for the three high-T_c superconducting oxides.

Table 1-1. Critical Temperature, Estimated Penetration Depth λ , Coherence Length ξ , and the Upper Critical Field B_a of Three High-T_c Superconductor Oxides

Compound	T _c (K)	$\lambda_{c}(\dot{A})^{T}$	$\lambda_{ab}(\dot{A})^{ab}$	$\xi_{ab}(\dot{A})^{**}$	ξ _c (Å) [*]	$B_{c2,ab}(T)^{**}$	$B_{c2c}(T)$
La _{2-x} Sr _x Cu ₄	38	800	4000	35	7	80	15
Y ₁ Ba ₂ Cu ₃ O ₇	92	1500	6000	15	4	150	40
Bi.Sr.Ca.Cu.O.	110	2000	10000	13	2	250	30

* λ_c , ξ_c , and B_{c2c} : parallel to c axis.

** λ_{ab} , ξ_{ab} , and $B_{c2,ab}$: perpendicular to c axis.

As shown in Table 1-1, the critical magnetic fields are quite anisotropic. The critical values are much larger when the magnetic field is applied parallel to the *ab* planes ($B_{c2,ab}$) than when it is applied perpendicular to the planes ($B_{c2,c}$). This is a consequence of the anisotropy of the structures, particularly the anisotropy of the transport properties. Because the conductivity is larger along the *ab* plane, a magnetic field applied parallel to the planes will not be very effective in destroying superconductivity within the planes.

Another feature of high-T_c superconductors is that the resistive transition becomes broader and broader under an increasing magnetic field. This is quite different from that exhibited by a conventional superconductor in which the resistive transition shifts to lower temperatures with increasing magnet field. The broader resistive transition is due to the existence of a mixed state in the high-T_c superconductor. In the mixed state, magnetic flux can partially penetrate the superconductor, and is usually pinned by some defects. Since high-T_c superconductors have short coherence length, the energy involved in thermal fluctuation $(\mu_0 H_c^2 \xi^3)$ is small. Therefore, the flux inside the pinning centre is easy to overcome the barrier and driven by the Lorentz force. Dissipation then arises due to the movement of the flux, resulting in a broader resistive transition region.

Two important properties of high- T_c superconductors are the critical current and its dependence on the magnetic field. The critical current of a high- T_c superconductor is relatively low compared to that of a conventional superconductor. This is because many small grains exist in the material. The intergrain regions behave like weak links or Josephson junctions. The critical current of a Josephson junction or a weak link is very low. Thus, with an applied current, these superconducting links are more easy to be destroyed and result in a high resistivity. Low values of the critical current of a high- T_c superconducting oxide reflect the low value of the critical current of the intergrain regions. Moreover, since the critical current of a Josephson junction is also very sensitive to magnetic field, the critical current of a high- T_c superconductor decreases quickly under a magnetic field.

1.3 Motivation

Although bulk high- T_c superconductors have a variety of applications, the materials in a thin film form are more important. This is because thin films can be processed into different structures for various electronic devices. They can also be combined with other materials to form multilayer structures. There are three main categories of applications for high- T_c superconducting thin films. One is for passive microwave components like filters, antennas, and components like bolometers and optical detectors. Another is for semiconductor-superconductor hybrid devices^[1,12] or chip interconnects. Yet another application is for superconductor-insulator-superconductor (SIS) and superconductor normal metal- superconductor (SNS) 'sandwich' structures for tunnel junctions and weak link devices. For electronic applications of the high- T_c superconducting films, it is required to deposit high quality films using an efficient method. This method should be relatively simple and ideally should yield films with composition exactly the same as that of the target.

The superconducting compound BiSrCaCuO was selected as the material for the present study due to several reasons. One of the reasons to study this superconductor is due to the relatively high resistive transition temperature (110 K), which is higher than the transition temperature of YBaCuO superconducting compound (92 K). Although Tl-compounds (such as TlCaBaCuO and TlSrCaCuO) have even higher stable resistive transition temperatures, they contain the extremely toxic element thallium. Another reason to study BiSrCaCuO compound is that unlike YBaCuO compound, which has been successfully deposited, patterned, and used for various applications, the development of BiSrCaCuO compound is less advanced. For instance, only very limited work has been reported on the deposition of BiSrCaCuO films with laser ablation technology. Thus, it is important to investigate BiSrCaCuO films through growth, patterning, characterization and device applications.

 CO_2 laser ablation was used in this project to deposit BiSrCaCuO films. As described above, laser ablation is a very powerful technique for the deposition of high-T_c superconducting films. Theoretical analysis suggests that the short wavelength laser ablation, which is often performed by excimer lasers, would produce high quality films with appropriate stoichiometry and good morphology. However, excimer lasers are costly and their deposition rates are relatively low. Low deposition rates of excimer lasers are caused by low output and high absorption of photons at target surface due to short wavelength. Thus, only a very thin target surface layer interacts with photons during the deposition using these excimer lasers. Conversely, extremely high power laser pulses can be obtained from a CO_2 laser. The radiation emitted by a CO_2 laser is in the infrared region (10.6 μ m). Relatively low absorption of low energy photons allows a relatively thick layer target surface to be ablated during the CO_2 pulse laser deposition. Thus, the deposition rate of CO_2 laser ablation is expected to be higher compared to that of excimer lasers. Using the CO_2 laser with a high output, the deposition of films with larger areas, which are required for many electronic applications, should be possible.

The drawbacks of long wavelength laser ablation, such as non-stoichiometry films forming from the stoichiometric target and high absorption of laser pulse by the plasma produced near the target surface, may be overcome by choosing an appropriate ratio of target elements and appropriate width of lase pulse. This may also be overcome by applying substrate heating during film deposition. By adjustment of deposition conditions using CO_2 laser ablation, it is hoped BiSrCaCuO films with a better quality can be developed.

Very few publications are involved in the deposition of high-T_c superconducting films by CO₂ laser ablation. YBaCuO superconducting thin films with a sharp resistive transition have been obtained using CO₂ laser ablation,^[1,13] and a comparison of the quality between the YBaCuO films prepared by the short wavelength laser and CO₂ laser was reported by Dyer er al.^[1,14] Meskoob et al ^[1,15] first reported deposition of BiSrCaCuO films by CO₂ laser ablation using a laser source with a pulse width of 1 ms. In their experiments, BiSrCaCuO superconducting films with a zero resistance T_c of 78 K were obtained after an annealing at

Chapter 1 Introduction

868 °C for 3 hours. However, no sign of resistive transition corresponding to the 110 K high- T_c phase (2223) was seen. Thus, one of the objectives of the present work is to establish CO₂ laser deposition conditions which can produce BiSrCaCuO superconducting films with an zero resistance temperature near 110 K. The results on the deposition and characterization of BiSrCaCuO are described in chapter 4.

For optoelectronic applications, the noise characteristics of high-T_c superconducting films are extremely important. For instance, noise can affect the operation of bolometers, infrared detectors and dc superconducting quantum interference devices (SQUID). Considerable attention has be paid by researchers in this field. However, most of the work on noise study is in the YBaCuO compound. In this thesis, the experimental noise behaviour of BiSrCaCuO superconducting films deposited by laser ablation and rf-sputtering is specially investigated. Efforts have been made to identify the origin of noise in BiSrCaCuO films both in superconducting and normal states so that a better understanding of noise mechanisms can be procured. Results obtained on the noise study are presented in chapter 5.

In chapter 6 the thesis, results on investigation of microwave response of BiSrCaCuO superconducting films are presented. The microwave measurements were made on rf-sputtered BiSrCaCuO films instead of the laser ablated ones. This investigation is essential if BiSrCaCuO films are to be used for infrared and microwave detector applications. Superconducting bridge devices are specially fabricated to detect microwave signals. The mechanism related to microwave response is studied and the results obtained will be given.



(b**)**

Figure 1-1 (a) Magnetization versus applied magnetic field for a type-I superconductor.
(b) Magnetization versus applied magnetic field for a type-II superconductor.



Figure 1-2 The evolution of critical temperature since the discovery of superconductivity.

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Figure 1-3 The crystal structures of $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ with n = 1, 2, and 3.

Chapter 2

Apparatus

The laser ablation method has been adopted in the present work to deposit BiSrCaCuO films. The facility necessary for producing BiSrCaCuO superconducting films can be divided into three parts. The first part is the CO_2 pulsed laser which is used as a radiation source, the second part is the equipment for the deposition, and the third part is the equipment for the annealing. The main apparatus used for characterization of the films is a cryostat, which can cool down samples to a desired temperature. This chapter begins with an overview of the principles and operation of the CO_2 pulsed laser used. The set up of the vacuum system and the design of deposition chamber are next described in detail. Following this, the structure of furnace is introduced as well as the design of the step motor controller. Finally, the operating principles of the cryostat are presented.

2.1 CO₂ Laser

A Lumonics transversely excited atmospheric (TEA) pressure carbon dioxide (CO₂) pulsed laser was used in the deposition of the BiSrCaCuO films. The CO₂ pulsed laser emits light at a wavelength of 10.6 μ m in the far infrared region of the electromagnetic spectrum. The lasing medium is a mixture of carbon dioxide, nitrogen, and helium. Excitation of the carbon dioxide is achieved by increasing the vibrational energy of the molecules. The actual pumping is achieved by a dc electrical discharge. During the operation, only a small percentage of the carbon dioxide molecules is excited directly by the electrical discharge, and most of the electrical energy is absorbed by nitrogen molecules. The vast majority of carbon dioxide molecules achieve excitation by colliding with the nitrogen molecules, which transfer their added vibration energy, as shown in figure 2-1. This transfer is extremely efficient and energy selective because nitrogen is a dimer with one vibrational mode and only one excitation state. The nitrogen excited state is very close to the required excitation state of the carbon dioxide (state 001).

Once excitation is achieved in the CO_2 molecule, the electrons can release energy through collisions with other CO_2 molecules still in the ground state. These collisions lower the excited electrons to intermediate energy states 100, 020 and 010. Of these energy changes, only the transformation of electrons from state 001 to state 100 releases energy in the form of 10.6 µm laser light. The remaining energy between the intermediate states and the ground state is lost through kinetic energy transfer, which generates heat instead of light. In CO_2 molecules, the rate of energy release in the form of heat is much lower than energy release in the form of light. Therefore, the introduction of helium, which has a very high thermal diffusivity, into the lasing gas mixture can aid in the energy release through heating, and achieve a higher efficiency.

The properties of a carbon dioxide laser are primarily determined by the method of gas flow. The flow method determines how fast the post-stimulation carbon dioxide gas can
be removed from the optical cavity so that new carbon dioxide gas in a ground state can be introduced for excitation and stimulation. The CO_2 laser used in the experiments was a transverse flow laser, in which the gas mixture of helium, nitrogen and carbon dioxide flowed perpendicularly to the optical cavity axis. The gas flow was maintained by a blower and it was cooled by a heat exchanger. The ratio of carbon dioxide, nitrogen and helium was adjusted to 0.6: 0.8: 4. The electrodes were arranged on either side of the cavity and the voltage required to maintain high current discharge was about 37~40 kV. Output rate of laser pulses was controlled by a pulse generator. A typical pulse rate was 2 - 4 Hz during the deposition.

Laser pulse energy was measured using a BNC 7441 photon drag detector and a digitizing oscilloscope. The detection process of the photon drag detector is based on unequal charge (electrons and holes) distribution which is produced by the laser irradiation. Figure 2-2 displays a measured CO₂ laser pulse. Using a calibration of 0.24 V/MW for 1 M Ω match, the CO₂ laser pulse power was calculated. The average peak power was about 179 kW and pulse width was about 200 nsec. The CO₂ pulsed laser was focused by a germanium (Ge) lens, which was mounted on the wall of the deposition chamber. The laser beam had an area of 1 mm² after the focus, and the laser energy density at the focus point was about 3.6 J/cm².

2.2 Deposition System

The deposition system included a vacuum system and a deposition chamber. The vacuum system was used to evacuate the deposition chamber and to provide an enviorment where a long mean free path of particles during the deposition could be insured because of low pressure. In order to obtain an appropriate oxygen content in the films, oxygen gas was introduced into the chamber for reaction. The deposition chamber consisted of a base plate, a top cover and a cylinder. There were two holes in the cylinder wall for housing a transparent window to introduce laser beam, and a rotating shaft to hold a BiSrCaCuO target. Figure 2-3 shows a schematic diagram of the deposition system.

2.2.1 Vacuum System

The vacuum system used consisted of a small diffusion pump (with a height of 5 inches and a diameter of 1.5 inches) and a Model E2M8 Edwards rotary vacuum pump to evacuate the deposition chamber. The rotary pump contained an eccentrically mounted rotor with spring-loaded vanes. During rotation the vanes slid in and out within the cylindrical interior of the pump, enabling a quantity of gas to be confined, compressed, and discharged through an exhaust valve into the atmosphere. The rotary pump could pump the deposition chamber to a pressure of $1 \times 10^{-2} \sim 3 \times 10^{-2}$ torr. Below these pressures the rotary pump was inefficient.

The operation of the diffusion pump is achieved through the action of a fluid medium that is boiled and vaporized in a jet assembly. As the oil vapour stream emerges from the top no zles, it collides with and imparts momentum to residual gas molecules present in the pump throat. These molecules are thus driven toward the bottom of the pump and compressed at the exit side where they are exhausted. A region of reduced gas pressure in the vicinity of the jet is produced, and more molecules from the high vacuum side move into this zone, where the process is repeated. The diffusion pump could reduce the chamber pressure to 6×10^{-6} torr through an overnight pumping. Since a resistive heater was used to heat up the diffusion oil, water cooling was needed to avoid overheating.

The operation of the vacuum system is as follows: (a) Close the roughing valve and air admittance valve "1, open the backing valve and turn on the diffusion pump and rotary pump. Wait 20 minutes to allow the pressure of the diffusion pump to reach around 10^{-2} torr. (b) Close the backing valve and air admittance valve "2, open the roughing valve and let rotary pump to pump the deposition chamber until the pressure of deposition chamber reaches 10^{-2} torr. (c) Close roughing valve and open backing valve. Wait for $1 \sim 2$ minutes and lift the valve between the diffusion pump and the deposition chamber. After $10 \sim 12$ hours, the base pressure of the deposition chamber drops to $10^{-6} \sim 10^{-5}$ torr. Oxygen gas is then introduced into the deposition chamber through a needle valve until a desired pressure is reached. The

oxygen pressure is monitored by a Varian 801 vacuum gauge $(1 \times 10^{-3} \text{ torr} \sim \text{ atmosphere})$ and a Pennig Alcatel FA101 high vacuum gauge $(7.5 \times 10^{-8} \text{ torr} \sim 7.5 \times 10^{-3} \text{ torr})$.

2.2.2 Deposition Chamber

The deposition chamber used was specially designed and manufactured for the CO_2 laser ablation. It contained an aluminum cylinder with a height of 30 cm and a diameter of 25 cm, an aluminum top cover and a base plate. Two holes were machined into the wall of the cylinder with an angle of 135° between their central axes. One hole was for a germanium window, and the other hole was for a rotating shaft used to hold and rotate the target holder. An adaptor in the centre of the top cover was used for the high vacuum gauge. There were four adaptors in the base plate for connecting to a common ground, a thermocouple, a power supply of the substrate heater and the Varian vacuum gauge. As shown in figure 2-3, substrates were placed on a substrate holder parallel to the target with an adjustable distance of 1 to 6 cm. In some cases, a substrate heater was used to raise the temperature of the substrates. The substrate heater, located just behind the substrate holder, consisted of a graphite frame and a nickel wire wound resistor. If the substrate heater was used during the film deposition, the substrate heating, the substrates were mounted on the substrate holder with a double sided Scotch tape.

The incident CO₂ laser beam was focused by a Ge lens with a diameter of 20 mm. The diameter of the incident laser beam was 15 mm, and the area of the beam after focusing was 1 mm². The target was placed near the laser focus point and rotated by an ac motor. The laser beam was incident at an angle of 45 ° with respect to the target surface. This arrangement can allow most of the material to be deposited on substrates since the angular distribution of the emitted material from the target is given by a function of $cos^8\theta$ (θ is the angle between incident beam and emitted material)^[21, 2.2]. No intentional cooling was applied to the target due to the low laser pulse rate (2 Hz).

2.3 Annealing System

The annealing system consisted of a furnace, a stepping motor and gas supplies. Figure 2-4 is a diagram for the annealing system.

2.3.1 Furnace

A Thermco Mini-Brute diffusion furnace was used for the annealing of the asdeposited BiSrCaCuO films. The furnace is able to reach a maximum operating temperature of 1400 °C within 75 minutes from the room temperature, and cool down from 1200 °C to 500 °C with a linear program rate of at least 3 °C per minute. The furnace temperature can remain stable within $\pm 1/4$ °C over long term operation. The temperature controller of the furnace employs master-slave control system. It is a differential system in which the central (master) zone temperature is monitored by a thermocouple and compared with a precise reference voltage. The two end (slave) zones compare their respective thermocouple outputs with a reference thermocouple located in the central zone. Therefore, the temperatures of the end zones track the temperature setting of the master central zone, allowing an accurate flat zone temperature profile to be achieved.

The temperature dial of the centre zone can be set between 0 to 1000 corresponding to a real temperature range of 400 °C to 1400 °C. The maximum temperature difference between the central zone and end zone is ± 50 °C. An end zone dial setting of 500 causes the end zone and central zone temperatures to be equal. An offset temperature, X, of the end zone from the central zone can be achieved by setting the end zone dial to (500+10X).

2.3.2 Stepping Motor Controller

In order to control the temperature setting of the furnace to the desired increase or decrease rates, a stepping motor controller circuit was specially designed. The circuit

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consisted of three integrated circuit chips: SGSL297, SGSL298N and NE555. Figure 2-5 shows the schematic diagram of the circuit.

The L297 stepping motor controller IC can generate four-phase drive signals. It only requires three input signals: clock, direction and mode. The "Clock" input signal comes from the output of the oscillator NE555. The oscillator controls the speed of the stepping motor. An active low pulse on this input advances the motor by one increment. The step occurs on the rising edge of this input signal. The direction of the stepping motor is governed by a "CW/CCW" input signal. An active high signal of "CW/CCW" results in clockwise rotation of the motor, and an active low signal causes counterclockwise rotation of the motor. The direction of the motor rotation also depends on connection of windings. If the "Control " signal is set to active high, the chopper acts on phase lines of A, B, C, and D.

A L298N high voltage, high current (up to 4 A) dual full-bridge driver is integrated so as to accept standard TTL logic levels and drive inductive loads like stepping motors and relays. The four input signals of the chip are connected to the four phase lines (A, B, C, and D) of L297. The four output signals of the chip are linked directly to the windings of the stepping motor.

NE555 IC chip is capable of producing accurate time delays or oscillation. When the NE555 IC chip is used as an oscillator, the free running frequency and the duty cycle are both accurately controlled by two external resistors (R_A and R_B) and one capacitor (C_i), with relations of $f = 1.443 / (R_A + 2R_B)C_i$, $T_i = 0.693 (R_A + R_B)C_i$, and $T_2 = 0.693R_BC_i$. Here, f is the pulse frequency, T_i is the pulse width and T_2 is the pulse interval. The maximum frequency of generated pulse is 500 kHz. The output of NE555 is connected to the "Clock" of the stepping motor controller, L297, and controls the motor speed.

2.4 Cryostat

The cryostat is an important part for characterizing the superconductors. The DL4960

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liquid nitrogen cryostat, which is a part of the Bio Rad DLTS (deep level transition spectroscopy) system, was used to characterize the BiSrCaCuO superconducting films. A schematic diagram of the cryostat is shown in figure 2-6.

The samples were cooled by pumping liquid nitrogen through the base of the sample stage using a liquid nitrogen pump in a 30 litre Dewar. When the pump is running at speeds of around 4000 rpm, it lifts liquid nitrogen from the bottom of the Dewar to the outlet port. At lower rotational speeds the pump delivers only cold nitrogen gas. The capacity of the heater attached to the sample stage is about 30 W. The temperature control parameters are set on the temperature programmer unit. A feedback loop automatically controls the heating element output and the liquid nitrogen flow. A window on the top of the cryostat allows the sample to be illuminated.

2.5 Summary

In this chapter, the facilities used in the present work have been described. The function of three parts of the facilities which were used to produce and characterize the BiSrCaCuO films has been detailed. A TEA CO₂ pulse laser with a power of 179 kW, a pulse rate of $2 \sim 4$ Hz and a wavelength of 10.6 µm was used as a source for the laser ablation. The deposition was achieved by a vacuum system and a deposition chamber. The vacuum system had a ability to reach 6×10^{-6} torr using a rotary pump and a diffusion pump. Specially designed and manufactured deposition chamber can insure deposition to be carried out at a given oxygen pressure and a given substrate temperature. Annealing system which consisted of a furnace and a stepping motor controller was critical for producing BiSrCaCuO superconducting films. The furnace with a master-slave thermocouple system can be operated at a temperature range between 400 and 1400 °C. The stepping motor controller was made for adjusting the increasing or decreasing rate of the furnace temperature. For the characterization of the films, a liquid nitrogen cryostat with a nominal cooling temperature low to 77 K was adopted.







200 ns/div.

Figure 2-2

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45[°]

To Motor

BiSrCaCuO Target

Figure 2-3 A schematic diagram of the deposition system.

CO₂ Laser







Figure 2-5 The circuit of stepping motor controller





Chapter 3

Principles of Laser Ablation and Characterization

3.1 Laser Ablation

In laser ablation matter is ejected from a target by the interaction of an intense laser pulsed beam with the material on the target surface. Laser ablation includes the removal of atoms and molecules or layers of these species, and is associated with macroscopic effects such as cratering and plasma emission.

There are two major processes for material removal from a solid surface by laser ablation. (1) At the time that a laser pulse hits a target, photons are absorbed by the surface, forming a molten layer that vaporizes. (2) The vaporization process generates recoil pressure on the liquid layer and expels the molten material. Therefore, the removed material by the laser pluses is a combination of vapour and liquid.

More specifically, the interaction between a high power pulsed laser with a superconductor target can be viewed in several stages as shown in figure 3-1. First of all, incident photons are absorbed by the target and cause surface heating. The amount of increase in the surface temperature depends on the optical penetration depth of the material , the thermal diffusivity of the target and the rate at which energy is applied in the system. At laser power levels of $10^7 \sim 10^8$ W/cm² (1.79 × 10⁷ W/cm² in the present work), surface heating is followed by target material melting and evaporation. Material is then removed in this stage. It has been reported that the amount of material removed varies linearly with laser energy density above a threshold energy density.^[3,1]

The material from the target contains many species: such as ions, electrons, neutral atoms and molecules that are dissociated from the target. Continued interaction of the radiation field with the ejected material results in dissociation of the molecular species or aggregates desorbed from the target. An expanding plasma is then formed above the surface of the target, in a form of plume, due to photoionization of these ejected material. The formed plasma absorbs the laser radiation before laser pluses reach the target. The absorbtion is caused by inelastic free electron scattering (or inverse bremsstrahlung), and it results in more heating of the plasma and regulates further interaction between the laser radiation and the target.^[3.2]

The plume of ejected material from the target is cone-shaped and has a highly forward peaked mass distribution. The mass distribution can be described by cos^n (θ) with 8 < n < 12, where θ is measured with respect to the target normal.^[3,3] Compared to the mass distribution of a purely thermal evaporation characterized by cos (θ), laser ablation is more directional and has a more limited deposition area.

The characteristics and quality of thin films produced by pulsed laser ablation (PLD) depend mainly on the interaction of the laser radiation with the target material. The nature of the laser-target interaction relies on (a) the thermodynamical properties of the target, (b) the optical properties of the target, (c) the laser wavelength, and (d) the laser pulse power and its duration. For metallic and small band gap materials, the thermal diffusion distance is long compared to the optical absorption distance. The electronic structure of the target is not important since the high electric fields generated by the laser result in dielectric breakdown. This is because all the material absorbs a significant fraction of the radiation, resulting in surface heating. Under these conditions, the surface temperature can exceed the melting temperature of a ceramic material (melting point of BiSrCaCuO is about 860 °C).

Optical properties of BiSrCaCuO target has been studied in this work by measuring the absorbance spectra of the as-deposited BiSrCaCuO films which had a stoichiometry close to the target. The measurements were carried out using a monochrometer. Both as-deposited BiSrCaCuO films on MgO substrates and MgO substrates were measured, so that the absorbance of the BiSrCaCuO films could be derived. The absorbance is calculated by $log_{10}(I_0/I)$, where I_0 is incident radiation and I is transmitted radiation. Figure 3-2 shows results obtained from one of the samples. The wavelength of the spectrometer is scanned from 1.4 µm to 12 µm. Since the MgO substrate is transparent in the 2.8 µm to 10 µm wavelength range, only data within that wavelength range is meaningful to the absorbance of the BiSrCaCuO material. The absorbance of BiSrCaCuO target decreases when the wavelength is increased. At the wavelength of 10.6 µm, which is the wavelength of the CO₂ laser beam, the value of absorbance is very low.

W. Kautek et al^[3,4] measured the absorbance of YBaCuO compound in the 0.2 μ m to 1.0 μ m wavelength range and they obtained a similar relationship between absorbance and wavelength. The shorter the wavelength is, the higher is the absorption. Hence, long wavelength laser beams (e.g.: CO₂ laser) can penetrate the target surface more deeply than the short wavelength lasers (e.g.: excimer lasers). Furthermore, the short wavelength radiation can interact with a lesser volume of material from the target surface and result in

more efficient coupling of the optical energy to the target. Long wavelength radiation causes more thermal-like heating of the target material. With the long wavelength radiation, differences in the equilibrium vapour pressures of the target constituents are more likely to affect the composition of the laser produced vapour and lead to the production of nonstoichiometric films. Thus, in order to obtain appropriate BiSrCaCuO film stoichiometry by CO, laser ablation, the composition of the BiSrCaCuO target should be carefully adjusted.

The absorption coefficient of the plasma formed near the target surface is also wavelength dependent.^[3,3] It is given by the following equation

$$\alpha = 3.69 \times 10^8 Z^3 n_i^2 / T^{0.5} \gamma^3 [1 - \exp(-h\gamma/KT)]$$
(3.1)

Where γ is the laser frequency in Hz, n_i is the plasma density in cm⁻³, T is the plasma temperature in K, and Z is the average charge in coulomb. Low energy photons (from IR or CO₂ laser) are absorbed significantly by plasma formed near the surface of the target. This results in large attenuation of the laser power. A short wavelength laser beam (UV laser with high energy photons) can easily go through the plasma cloud and reach the target due to lower absorption of the plasma.

Both laser pulse power and pulse duration affect the growth of the films. If low pulse power is used, the growth rate of films will be reduced or films may not grow at all. However, too high a pulse power will suppress the growth rate of the films due to the inverse Bremsstrahlung effect near the surface of the target,^[3,4-3,6] which is caused by laser induced plasma. This phenomenon is more serious when a long wavelength laser is used in ablation since the power threshold for plasma formation is inversely proportional to $1/\lambda^2$, and absorption of photons by the plasma is proportional to λ^3 . However, for long wavelength CO₂ laser, plasma-caused power attenuation can be overcome by its very high output power. Similarly, for long pulse duration, the initial part of the laser pulse rapidly heats up a thin layer of the target surface and produces a plasma cloud. The continuing laser radiation heats the plasma to a high temperature. If the plasma density reaches a sufficiently high value, the plasma becomes opaque and laser-target interaction stops. However, for a sufficiently long pulse width, the laser can interact again with the target after the formed plasma expands away from the target and the electron density decreases.

 CO_2 pulsed laser ablation has been shown theoretically to reach the saturation growth rate more easier than short wavelength excimer lasers, and nonstoichiometric films would be produced from stoichiometric target. On the other hand, the CO_2 laser has higher pulse power than excimer lasers. After a final focusing, the energy density at the target can be much higher than that of excimer lasers. The actual mass removal rate by a CO_2 pulse laser has been measured by Dyer et al^[3,6] and the value found was significantly higher than that reported for excimer laser ablation. Furthermore, if long duration pulse is used (200 nsec in the present experiments), the drawback of long wavelength laser ablation can be reduced. By properly adjusting the target composition, films with desired constituents and a relatively large area are possible to be obtained by the CO_2 laser ablation.

3.2 Electrical Characterization

Since the discovery of superconductivity, there have been many measurements made to characterize superconducting materials. These measurements were part of attempts to understand the nature of the superconducting state and utilize the unique properties that had been discovered. These measurements involve the critical temperature (T_c) , the critical current density (J_c) , and the critical magnetic field (B).

For a material to be considered as a superconductor, it has to exhibit two distinctive properties. (1) A: It temperatures below a critical temperature, T_c , the resistivity must be zero. However, if one passes a current higher than the critical current density J_c through a superconductor, superconductivity disappears. (2) There should be no magnetic induction inside a superconductor when it is cooled to a temperature below T_c in a weak external magnetic field. The magnetic flux is expelled from the interior of the superconductor. This effect is also called the Meissner-Ochsenfeld effect. However, if the external magnetic field exceeds the critical field, superconductivity of the material vanishes.

3.2.1 DC Resistance

The critical temperature is one of the anomalous parameters in a superconductor, at which the resistance of a material begins to decrease drastically and eventually vanish. There are two ways to determine the critical temperature of a superconductor. One is to measure the change of resistance with temperature, and the other is to measure the change of susceptibility with temperature.

The resistance measurement requires a sample to have at least four contacts, as shown in figure 3-3. The two outermost contacts are for the dc current source and the two inner ones are used to detect the voltage and thus the resistance of the sample. Before the measurement, it should be made sure that the contact resistance of the samples are low enough and ohmic so that they do not rectify the current. A resistor in series with the sample is often introduced to monitor the current through the sample. A small current is passed through the sample, and the voltage across the sample as well as the series resistor is measured as a function of temperature. Once reaching the superconducting transition, the voltage across the inner contacts decreases to the noise level of the voltmeter and the current of the sample remains constant.

Several points should be considered when doing resistance measurements. (1) The resistive transition is not a bulk measurement. If only a single superconducting filament is connected to voltage probes, the resistance measurement will show the same result as that for a bulk superconductor. Therefore, it is necessary to carry out the measurements with different combinations of the probes. (2) A crack developed inside the sample sometimes causes the voltage to go to zero but the current to remain constant. The remedy for this is also to permute the voltage and current probes, and repeat the measurement. (3) A true zero resistance is never actually found because of limitation in the sensitivity of the voltmeter. For a resistance measurement to be conclusive, the measured resistivity in the sample must be

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much less than that of copper at the same temperature. The measured resistance must not change over a certain range of current.

3.2.2 AC Susceptibility

A mutual inductance technique can be used to measure ac susceptibility for determining the critical temperature, as shown in figure 3-4. The sample is put inside or beside a coil (coil 1 in figure 3-4) to which it is very closely coupled. A second coil (coil 2) is wound in a direction opposite to the first one and connected in series with the first coil. The second coil does not contain a sample in it. Therefore, the second coil can be used to make the differential measurement, so that any background temperature dependencies in the coil are cancelled out. Both the sample and the coils are thermally anchored to a stage the temperature of which can be varied to a value below the critical temperature of the sample. A low-frequency ac signal is applied to the primary coil. The ac voltage across the secondary coils is monitored by a lock-in amplifier.

When the sample is in the normal state, the skin depth is typically nuch larger than the sample dimensions. The eddy current losses in the sample contribute to the resistive part of the coil's effective impedance, but the inductive part of the impedance is only slightly changed from the value of which no sample is contained in the coil. When the sample becomes superconducting, due to Meissner effect, the ac field is excluded from the interior by superconducting shielding currents that counter the applied field. The change in the field profile has a very significant effect on the inductance of the coil which contains the sample. Thus, a significant change in the out of phase component of the voltage across the coils can be observed. The amplitude of the resistive or in phase component of the voltage across the coils also decreases because the fields only exist in the penetration depth of the superconducting sample surface and the currents in the superconducting sample are much less loss than that in the normal state sample. In most instances, the inductive changes are larger than the resistive effects, as such the out-of-phase component can be monitored to detect the superconducting transition. There is a potential pitfall with this method. If the superconducting material forms a shell around the sample and the sample is non superconducting, then the signal would be the same as if the sample were completely superconducting. A test for this is to divide the sample into increasingly smaller pieces and measure each sub-sample. The inductive signal should be proportional to the volume of the sample if the sample is a bulk superconductor.

3.2.3 Critical Current Density

Critical current density is the maximum current density that a superconducting film can carry without dissipation. In general, there are two contributions to the current flowing on the surface of a superconductor. One current is called "transport" current which is passing through a superconducting film from some external source such as a battery. This current transports charges in and out of the film. If the superconducting film is in an applied magnetic field, "screening" currents circulate so as to cancel the flux inside the material. These "screening" currents are superimposed on the "transport" current, and at any point, the current density J can be considered to be the sum of a component J_i due to the "transport" current and a component J_{R} which arises from the "screening" currents. Superconductivity will break down if the magnitude of the total current density J at any point exceeds the critical current density J_c , at which the total magnetic field strength, due to "transport" current and the applied magnetic field, exceeds the critical field H_c . Therefore, the stronger the applied magnetic field, the smaller this critical current density will be. If there is no applied magnetic field, the only magnetic field will be that generated by the "transport" current. In this case, the critical current will be the current which generates the critical magnetic field H_c at the surface of the material.

In high- T_c superconductors, under an external magnetic field between the lower critical field H_{cl} and the upper critical field H_{c2} , a mixed state exists where partial magnetic flux can penetrate the material in the form of tiny microscopic filaments called "vortices". A superconductor in the mixed state has zero resistance and its properties depend on the microstructure and pinning effectiveness. Pinning centres usually are inhomogeneities or defects in the material. They are the sites where vortices are energetically favourable to locate. The definition of critical current density in a high- T_c superconductor does not suggest the onset of finite resistivity but rather it indicates some threshold value at which the material begins to behave as one with joule losses.

There are mainly two methods to measure the critical current density. One is based on electrical properties, the other is based on the hysteresis of magnetization. The criterion related to electrical properties is $J = E/\rho$, where J is the current density, E is the electric field and ρ is the resistivity. If one chooses an electric field criterion of 1 μ V/mm, the value of current per unit cross-sectional area through the superconductor that causes this value of the electric field between the voltage probes is called the critical current density J_c . A power law between current and voltage ($V = I^n$) should be checked near the threshold region during the determination of the critical current density. If n is larger than 20, then the critical current density deduced is not very dependent on the electric field criterion. If n is between 1 and 5, then a lower field criterion is needed.

Another method of determining the critical current density is to measure the hysteresis of the magnetization curve of a superconductor. Because of the pinning effect in superconducting materials, current can flow in the mixed state without dissipation. If a superconductor is exposed to a changing external magnetic field, "screening" current up to a critical current will prevent the corresponding change of the magnetic field inside the material. Therefore, a different magnetization will be expected for increasing or decreasing magnetic field. Figure 3-5 show a magnetization curve for a high-T_c superconductor at a magnetic field which first increases from 0 to H_{c2} , and then decreases from H_{c2} to 0. It can be seen that the magnetization curve is irreversible. The irreversible variation in magnetization at a certain magnetic field is related to critical current density at that field. The critical current density can be calculated with the Bean model,^[3,7] which is $J_c (Am^{-2}) = 2 \Delta M/d$, where d is the thickness of the sample. ΔM is the difference between the magnetization measured in increasing and decreasing fields (M1 - M1).

3.2.4 Critical Magnetic Field

Another important parameter of a superconductor is the value of the upper critical field H_{c2} . Two methods are used to determine the critical field. The first one, which has been successfully used for conventional superconductors, is based on resistance measurements in different applied magnetic fields. The second method, which is more suitable for high-T_c superconductors, is based on the measurements of change of magnetization with temperature.

With the resistive method, the resistance of the superconductor as a function of temperature in a constant magnetic field is measured. In this case the critical temperature is defined by the midpoint of the transition curve. By carrying out the measurements in different magnetic fields, a relationship between the critical temperature and the applied field, or equivalently, critical field versus temperature can be obtained. For high-T_c superconductors, the resistive method does not work since the resistive transition becomes broad and asymmetric in a magnetic field. Even at very low current, the low density of pinning sites and the small pinning potential barrier due to the short coherence length can make the effects of flux creep and flux motion serious. Therefore, the midpoint of the resistive transition is no longer associated with the upper critical field.

The magnetization measurement is carried out in a constant magnetic field. It relies on the fact that the upper critical field is the field at which the diamagnetic moment vanishes at a temperature, T. The magnetization is measured as a function of temperature when the temperature is decreased from a value well above the critical temperature. At relatively high magnetic fields, the magnetization of the sample in the normal state is constant and starts to decrease linearly as soon as superconductivity appears in the sample at a temperature below $T_c(H)$. The intersection of the linear magnetization and the normal state magnetization gives $T_c(H)$, and thus determining the critical field at a certain temperature.

3.3 Crystalline Structure Analysis

There are several ways to characterize the crystalline and morphological structure of a material. In this work, the three methods employed to study material structure are scanning electron microscopy (SEM), electron probe microanalysis (EPMA) and X-ray diffraction. The topography and morphology of a superconducting film can be studied by SEM. Information on the structures and phases of the superconducting film can be obtained through X-ray diffraction patterns, and the composition of the superconducting films can be analyzed using EPMA.

3.3.1 Scanning Electron Microscopy

SEM is the most widely employed instrument for thin film characterization. A schematic diagram of a typical SEM is shown in figure 3-6. Electrons thermionically emitted from a tungsten or LaB₆ cathode filament are drawn to an anode. They are focused by two successive condenser lenses into a beam with a very fine diameter (~ 50 Å). The electron beam is deflected either linearly or in raster fashion over a rectangular area of the sample surface by a pair of scanning coils located beside the objective lens. The focused electron beam of the SEM has an energy ranging from a few thousand to 50 keV. The image of the sample is obtained by detecting secondary electrons or backscattered electrons emitted from the sample.

When an electron beam impinges on the sample, the primary electrons decelerate and transfer their energy to other atomic electrons and to the lattice. The interaction between the incident electron beam and electrons (or lattice) of the material results in a distribution of electrons that leave the sample with the energy spectrum shown schematically in figure 3-7. The most common imaging mode relies on the detection of secondary electrons. Secondary electrons have low energy and come from a subsurface depth no thicker than several angstroms. This signal is captured by a detector consisting of a scintillator-photomultiplier

combination. The output of the detector is used to modulate the intensity of a CRT, which is rastered in synchronism with the raster-scanned primary beam. Sloping surfaces produce more secondary electrons than flat surfaces because the portion of the interaction volume projected on the emission region is larger.

The image of the sample can also be obtained by detecting the backscattered electrons. The backscattered electrons have higher energy and are elastically scattered. Essentially, they possess an energy comparable to the energy of incident electrons. Since the probability of backscattering increases with the atomic number Z of the sample material, a useful contrast can be developed between regions of the sample with large difference in atomic number Z. However, the escape depth for high-energy backscattered electrons is much greater than the depth for low-energy secondary electrons. Topological contrast in the images is lower. All of the SEM images in the present experiments are obtained by detecting the secondary electrons emitted from the samples.

3.3.2 Electron Probe X-ray Microanalysis

Electron probe X-ray microanalysis (EPMA) can identify elements by detecting the wavelength of X-rays emitted from the sample. Characteristic X-rays are excited from the area of the sample being probed when an electron beam impinges on that area. The energy of emitted X-ray is determined by the energy difference between the levels which are involved in the electron transition. Since each atom in the periodic table exhibits a unique set of levels (K, L, M shells), the emitted X-rays related to these special shells can be unambiguously identified. In the real case, the emitted X-rays are diffracted from single crystals with known interplanar spacings. Based on Bragg's law, each characteristic wavelength diffracts constructively at different corresponding angles. The angles can be measured by a goniometer-detector with very high precision. As the detector assembly rotates, the X-ray peak is swept as a function of angle. The amount of an element is proportional to the height of its X-ray peak.

3.3.3 X-ray Diffraction

X-ray diffraction is a very important experimental technique that has been used to address all issues related to crystal structure (lattice constants and geometry), identification of unknown materials, orientation of single crystals and preferred orientation of polycrystals, defects and stresses. When performing X-ray diffraction measurements on thin films one problem should be noticed. The X-ray can penetrate the thin films due to great penetrating ability. As such the scattered X-ray signals may consist of both thin film and substrate components.

Figure 3-8 displays the Seeman-Bohlin diffraction geometry, where f is the effective location of X-ray source, γ is incident angle and θ is Bragg angle. In order to make the film appear to be thicker to the beam than it actually is, the grazing angle of incidence γ should be small. Usually, a Cu K α X-ray is used as an incident source. Seeman-Bohlin diffraction geometry is employed with the focal point of the X-ray source, measured film and X-ray detector slit all located on the circumference of one great circle. Each of the diffracted peaks, which are produced in accordance with Bragg's law of $2dsin\theta = n\lambda$ (λ is the wavelength of Cu K α), is detected at different angles when the X-ray detector moves along the circumference.













A schematic diagram of standard four probe resistance measurement.

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Figure 3-4

A schematic diagram of a mutual inductance technique for measuring the critical temperature.











A schemetic diagram of the scanning electron microscope.





(b)



(c)

Figure 3-7 (a) Electron and photon signals emanating from teardrop-shaped interaction volume during electron-beam impingement on specimen surface. (b) Energy spectrum of electrons emitted from specimen surface.
(c) Effect of surface topography on electron emission.



Figure 3-8 X-ray diffraction geometry.

Chapter 4

Fabrication and Characterization of BiSrCaCuO Films

The objectives of research work to be described in this chapter are as follows. (1) To fabricate superconducting thin films of BiSrCaCuO by CO_2 laser ablation. (2) To study effects of substrate heating on the morphology and composition of the deposited BiSrCaCuO films. (3) To study effects of oxygen partial pressure on the film composition. (4) To establish heat treatment conditions for the CO_2 laser-ablated BiSrCaCuO films. Results on noise measurements and microwave response in the BiSrCaCuO films will be described in subsequent chapters.

4.1 Deposition of BiSrCaCuO Films

The discovery of superconductivity in BiSrCaCuO compounds by Maeda et al.^[1.23] has galvanized research activity. Deposition of BiSrCaCuO films has been carried out by various methods, such as magnetron sputtering,^[4,2,4,3] coevaporation,^[4,4,4,5] ion-beam

sputtering,^[4,6] electron-beam evaporation^[4,3] and laser ablation^[4,7-4,15]. Among these deposition techniques, the laser ablation technique is considered to be one of the best methods of obtaining superconducting films with a high current density and controlled stoichiometry. Both *in situ* and *ex situ* laser ablation have been utilized by researchers.^[4,7-4,15] In situ deposition can be used to obtain films with better morphology, however, the values of zero resistance T_c of the superconducting films are relatively low. Although the morphology of films is not as good as that of the films deposited with the *in situ* method, higher zero resistance T_c can be achieved by the *ex situ* method if appropriate post-annealing treatment is carried out.^[4,16, 4,17] Most of the laser sources used for high- T_c film deposition emit in the 0.193 to 1.06 µm short wavelength range because radiation at these wavelengths can be highly absorbed by the target surface.

Even though the technique has not been well developed, laser ablation using a long wavelength CO_2 pulsed laser is of special interest due to high pulse energy and relatively low equipment cost, which are beneficial for large area film processing. There are only few publications in the deposition of high-T_e superconducting films using CO_2 laser ablation. Most of these publications are on YBCO superconducting films. In order to obtain good quality superconducting films with a proper stoichiometry, deposition parameters such as substrate temperature, target composition and chamber pressure should be determined. So far no detailed research has been reported in this field, specially on BiSrCaCuO compounds. Therefore, it is very important to investigate deposition conditions for BiSrCaCuO films using CO_2 laser ablation. This chapter presents the research work done on the deposition of BiSrCaCuO films using a TEA CO₂ pulsed laser with a wavelength of 10.6 µm. Specific efforts will be put on target preparation, oxygca pressure of deposition chamber, substrate heating and conditions for post-deposition heat treatment.

4.1.1 Substrate

The selection of a substrate is of primary importance on producing good quality films. Several parameters should be considered when choosing a substrate. First of all, the

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requirements for small lattice mismatch and thermal expansion coefficient are critical. Low dielectric constant and good mechanical properties of substrates are also important if superconducting films are to be used in microwave applications. Of course, the cost of the substrate also plays a role in the selection. Many substrates such as CaNdAlO₄, NdGaO₃, LaGaO₃, SrTiO₃ LaAlO₃, MgO and YSZ (yttrium stabilized zirconia) can be chosen for the deposition of high-T_e superconductors. CaNdAlO₄ and NdGaO₃ were reported to have a small lattice mismatch with YBCO and have low dielectric losses. LaGaO₃ exhibits a favourable thermal expansion coefficient and lower dielectric constant. However, these substrates are very expensive. SrTiO₃ and LaAlO₃ also have a small lattice mismatch with BiSrCaCuO and have been successfully used, particularly those for passive microwave devices. Compared to the above substrates, MgO (~ 21% mismatch with BiSrCaCuO) and YSZ are the cheapest and have the largest lattice mismatch with BiSrCaCuO. However good deposition results of BiSrCaCuO on MgO substrates have been disclosed in many articles. It is clear that in the long run it will be necessary to use cheaper substrates.

Crystalline MgO has the same structure as sodium chloride. As shown in figure 4-1, this structure can be described as a face-centred cubic lattice with a basis consisting of an Mg ion at 0 and an O ion at the centre of the conventional cubic cell, (a/2)(X+Y+Z). The crystal lattice constant, a, of MgO is 4.21 Å.

Since the lattice constants of the Bi₂Sr₂Ca_{n-1}Cu_nO_y structure are a = 5.39 Å and c = 24.6, 30.6 and 37.1 Å corresponding to n = 1, 2, and 3, the lattice mismatch between the MgO and the BiSrCaCuO (x-y plane) is about 21.9%. The large lattice mismatch seems to affect epitaxial growth of superconducting films and result in films with a low critical current density. However, good lattice matching between the BiSrCaCuO compound and the substrates would favour and enhance the growth of the 85 K phases, and make their transformation into the 110 K phase difficult.^[4,18] Conversely, substrates like MgO with a relatively large lattice mismatch with BiSrCaCuO facilitates the transformation of the 85 K phase to the 110 K phase by providing an additional freedom in x-y plane during the film growth on the MgO surface. Experimental results of BiSrCaCuO films on MgO substrates
have been reported by several researchers, showing higher zero resistance T_c but lower critical current density compared to the BiSrCaCuO films grown on substrates with small

lattice mismatch.

The deposition of BiSrCaCuO films described in this chapter was made on cleaved and polished (100) MgO substrates. The surface of cleaved MgO substrates contain many shallow steps. An effort was made to etch away these steps in diluted HNO₃ solution. However, no significant improvement in electric properties was observed on BiSrCaCuO films which were deposited on etched MgO substrates instead of non-etched ones. In this thesis, cleaved MgO substrates refer to cleaved MgO substrates without etching. The polished (100) MgO substrates were supplied by Superconductive Components Inc.. Dimensions of the polished MgO substrates are $10 \times 10 \times 0.5$ mm³.

4.1.2 Target Preparation

The targets used for the deposition of BiSrCaCuO films were prepared by mixing powders of Bi₂O₃, SrCO₃, CaCO₃, CuO and PbO of a certain ratio. The Pb was introduced into the target in a form of PbO to enhance the formation of BiSrCaCuO films with 2223 high-T_c superconducting phase.^[4,18-4,21] Three targets with different elemental ratios were made. The procedure of making a target is given below. First, powders of Bi₂O₃, SrCO₃, CaCO₃ and CuO are mixed thoroughly and pressed to form a pellet at a high pressure. The pellet is then sintered in atmosphere at a temperature of 790 ~ 860 °C for a period of 3 ~ 14 hours. During the sintering process, the pellet is partially melted. After the first sintering, the pellet is pulled out of the furnace and cooled down in air. Following the cooling, the pellet is reground and mixed thoroughly with the PbO powder. A new pellet is then pressed and this pellet is subsequently sintered at 800 ~ 866 °C for a given period of time. An additional annealing is carried out at 700 °C for 1 hour on target B6. The final targets prepared using the above procedure had a thickness of 4.5 mm and a diameter of 20 mm. The targets had a dark colour and they were amorphous with a density of about 6.4 g/cm³.

Target	Bi: Pb: Sr: Ca: Cu	First Step Sintering	Second Step Sintering
Number		Temperature	Temperature
Bl	2:0.6:2:2:3	830 °C, 3.5 h	866 °C, 3 h
B6	2 : 2.5 : 2 : 2.15 :3.3	860 °C, 14 h	842 °C, 0.25 h + 700 °C, 1 h
B7	2:2:2:2:3	790 °C, 13 h	800 °C, 11 h

 Table 4-1. Preparation Conditions of the Three Targets

Table 4-1 presents the nominal compositions and preparation conditions for three targets. Except for the difference in heat treatment conditions, the main difference between target B1 and target B7 is the Pb content. More Pb was added to target B7 than target B1. Therefore, the Pb content in BiSrCaCuO films deposited using the target B7 is higher than the films deposited using the target B1. It has generally been believed that Pb would help to produce BiSrCaCuO superconducting films with a larger portion of 110 K high-T_c phase (2223 phase). Experimental results revealed that Bi₂Sr₂CuO (2201 phase) and some intermediate phases including Ca₂CuO, CuO and Ca₂PbO₄ were first formed at around 650 °C, but these phases began to decay as the Bi₂Sr₂CaCu₂O₈ (2212 phase) grew in at about 800 °C.^[4,21] These residual phases together with the 2212 phase were further reduced as the Bi₂Sr₂Ca₂Cu₂O₁₀ (2223 phase) crystallized at around 840°C. The transformation mechanisms can be described by the following equation:

$$2Bi_2Sr_2CuO_6 + Ca_2CuO_3 + CuO - 2Bi_2Sr_2CaCu_2O_8$$

$$(4.1)$$

$$Ca_2PbO_4$$

$$2Bi_2Sr_2CaCu_2O_8 + Ca_2CuO_3 + CuO \rightarrow 2Bi_2Sr_2Ca_2Cu_3O_{10}$$
(4.2)

The presence of Ca_2PbO_4 in the mixture produced a lead-rich liquid phase and increased interdiffusion among the 2212 phase, the Ca_2CuO_3 and the CuO beyond that of solid-state diffusion. CaO from decomposition of Ca_2PbO_4 further reacted with CuO to form Ca_2CuO_3 and accelerated the formation of the 2223 phase. On the other hand, Pb-doping probably can partially lower the melting point of the BiSrCaCuO films. During the annealing of BiSrCaCuO films at a given temperature, the Pb-rich films could be partially melted due to the lower melting point. The partial melting / sintering treatment effectively enhanced the growth rate of the 2223 high-T_e superconducting phase.^[4,22]

Compared to the target B1 and the target B7, the target B6 has higher contents of Ca and Cu. One reason for adding more Ca and Cu to this target is to compensate the lack of Ca and Cu in the as-deposited films using the target B1 and B7. Since long wavelength CO₂ laser beam would be absorbed in a relatively thick layer of target surface, evaporation mechanism was present during the film deposition. The melting points and vaporization points of Ca and Cu at the deposition pressure are higher compared to the other elements, resulting in the lack of Ca and Cu. On the other hand, based on the formation mechanism of the BiSrCaCuO superconducting films, it can be seen that during the annealing, both Ca- and Cu-rich films can produce more intermediate phases such as Ca_2CuO_3 , CuO and Ca_2PbO_4 , and enhance the transformation of BiSrCaCuO from the 2201 phase to the 2212 phase and finally to the 2223 phase.

It was observed in the experiments that the BiSrCaCuO films deposited using the target B6 can be converted relatively easily into superconducting films with high resistive transition temperatures after annealing. In fact, most of the BiSrCaCuO superconducting films discussed in this thesis were deposited using the target B6. most of the BiSrCaCuO films fabricated using the target B1 and B7 had low-T_c values and hence, were not selected for further investigation.

4.1.3 Deposition Conditions

Deposition of BiSrCaCuO films using CO_2 pulsed laser ablation consists of two steps. The first step is the ablation of the target and the second step involves the subsequent growth of the BiSrCaCuO films from the material ejected from the target. Various deposition

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parameters affect the two-step process. Some of these, the laser beam parameters (beam wavelength, power density, pulse duration and repetition rate) and the target parameters (composition, density and texture) directly control the ablation process. Other parameters such as substrate temperature and the oxygen partial pressure in the deposition chamber govern the growth of the BiSrCaCuO films. The substrate temperature influences the surface mobility and sticking coefficient of the ablated species, and the oxygen pressure in the deposition chamber determines the composition of the films through certain chemical effects.

A CO₂ pulsed laser was adopted in this work for the deposition of the BiSrCaCuO films because of its special properties mentioned previously. The laser pulse had a width of $200 \sim 250$ nsec. The laser energy density in the ablated target was 3.6 J/cm² after focusing. The repetition rate of the CO₂ pulsed laser was up to 6 Hz which was controlled by controlling trigger pulses. Usually, a repetition rate of 2 Hz was used in the deposition because this was the most stable rate that could be achieved by this CO₂ pulsed laser. The area of the laser beam near the focus point was estimated using carbon-coated paper to be about 1 mm².

As described in the previous section, the target B6 used in the film deposition had a composition of Bi : Pb : Sr : Ca : Cu = 2 : 2.5 : 2 : 2.15 : 3.3. The density of the target was calculated based on the weight and volume, yielding a value of 6.36 g/cm³. During the deposition, MgO substrates were placed parallel to the target. Distance between substrates and target was set carefully since it could affect the quality of the as-deposited films. Too large a distance between the substrates and the target could reduce the growth rate of the BiSrCaCuO films, however, too small a distance could result in non-uniform deposition and a rough surface morphology. It was reported that the optimum target-substrate distance for deposition occurred at the plume range, L_p , which is defined as the distance from the target at which the pressure of the ablated plume of materials falls to that of the background gas.^[4,23] For the deposition of BiSrCaCuO films in this work, the distance between the substrates and the target was selected experimentally to be between 2 mm and 5 mm.

Once the materials are ejected from the target surface, they form a plume which expands towards the substrate. The interactions between the ejected materials and the molecules (O_2) in the chamber are quite important. The number and nature of these molecules largely determine the energy and the chemical state of the species that arrive at the substrate surface. The presence of oxygen in the deposition chamber increases the probability of incorporation of oxygen atoms in the films. Experimental data revealed that the partial pressure of oxygen in the chamber determines the stoichiometry of the BiSrCaCuO films^[4,17]. Furthermore, the presence of oxygen produces films with more uniform spatial distributions of thickness and elemental composition. This is because the uniformity of films is related to the scattering of the ejected species induced by collisions between the species and oxygen molecules. The spatial uniformity improves with the increase of oxygen pressure, however the deposition rate decreases with the increase of oxygen pressure.

A number of deposition runs of BiSrCaCuO films have been carried out at various oxygen pressures. The oxygen used was supplied by a high purity oxygen source and the oxygen pressure in the deposition chamber was controlled to a range between 6×10^{-6} torr and 10^{-1} torr by a needle valve connected to the chamber. A chamber pressure less than 6×10^{-6} torr was not used because of the limitation of pumping capacity. Oxygen pressure larger than 10^{-1} torr often produced BiSrCaCuO films with a rough surface. The composition of BiSrCaCuO films at different oxygen pressures has been determined by electron probe microanalysis (EPMA) and the results will be presented in section 4.3. Moreover, it was found that the oxygen pressure in the deposition chamber dramatically affected the formation of the superconducting phase during the heat treatment, and thus the superconducting transition temperature. Detailed information about this will be further described in section 4.2. Table 4-2 lists the deposition conditions for some of the experiments carried out for studying the effects of oxygen pressure and substrate temperature.

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Number of Run	Oxygen Pressure (torr)	Substrate Temperature	
B6W*	7.5×10 ⁻⁴ ~7.5×10 ⁻³	room temperature	
B6X	(51~81)×10 ⁻³	room temperature	
B6Y	(6~8)×10 ⁻²	380~401.5□C	
B6Z	(7~8)×10 ⁻²	389~391□C	
B6A'	(5~6)×10 ⁻²	474~477□C	
B6B'	(6~9)×10 ⁻²	502□C	
B6C'	(5.5~7)×10 ⁻²	496□C	
B6D'	(5.5~6.5)×10 ⁻²	554.5□C	
B6E'	(6~10)×10 ⁻²	493□C	
B6F	(7~9)×10 ⁻²	510.5□C	
B6G'	(6~10)×10 ⁻²	506□C	
В6Н	(7.5~9.5)×10 ⁻²	524□C	
B6T	(3~4.5)×10 ⁻²	521~527□C	
ВбЈ	(3~9)×10 ⁻²	531□C	
B6K'	(5~7.5)×10 ⁻²	532~535□C	
B6L'	(6~10)×10 ⁻²	600~620□C	
B6M'	(5~9)×10 ⁻²	room temperature	
B6N	(3~10)×10 ⁻²	room temperature	
B6O'	(3~10)×10 ⁻²	100m temperature	
B6P'	(4~7.5)×10 ⁻²	room temperature	
B6Q'	6.5×10 ⁻²	room temperature	
B6R'	5×10 ⁻²	room temperature	
B6-1	(8~10)×10 ⁻²	room temperature	
B6-2	(2~2.5)×10 ⁻²	room temperature	

Table 4-2. Deposition Conditions of BiSrCaCuO Films Using CO₂ Laser Ablation

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B6-3	(3.5~4)×10 ⁻² room temperature		
B6-4	5.5×10 ⁻²	room temperature	
B6-5	3.75×10 ⁻⁵	room temperature	
B6-6	(0.9~1.13)×10 ⁻⁴	room temperature	
B6-7	9×10 ⁻⁶	room temperature	
B6-8	(1.17~1.5)×10 ⁻³	room temperature	
B6-9	(4.5~5.25)×10 ⁻⁴	room temperature	
B6-10	(1~1.1)×10 ⁻¹	room temperature	
B6-11	8×10 ⁻²	room temperature	
B6-12	(1.98~2.02)×10 ⁻¹	room temperature	
B6-13	2.5×10 ⁻¹	room temperature	
B6-14	(5.7~6.2)×10 ⁻²	153~157°C	
B6-15	(5.8~6.5)×10 ⁻²	294°C	

* Typical length of the samples = 1 cm, typical width of the samples = 0.35 cm.

As mentioned before, the substrate temperature played a major role in the deposition of the BiSrCaCuO films. This is because both the sticking coefficient and the nucleation of the species on the substrate can be affected by the temperature. The substrate temperature was controlled by adjusting power applied to a nickel ribbon which was wound around a piece of ceramic located behind the substrates. A specially designed graphite holder was used to support the heater in order to obtain a uniform heat distribution. The substrates, which were mounted on the surface of the graphite holder, had a temperature that varied from 100 °C to 600 °C.

The substrate temperature was monitored by a 60 Ω iron constantan thermocouple installed on the substrate holder. Higher substrate temperatures were not applied because of the limitation of the chamber cooling system and the low melting point and vaporization point of Pb at the deposition pressure. It was found that the morphology of BiSrCaCuO films deposited on the heated substrates was better than that of films deposited on un-heated substrates. Specifically, the density of small particles on the films deposited at a high temperature was less. This was caused by a diffusion effect on the films.

Figure 4-2 shows two scanning electron microscopy (SEM) pictures for two films deposited at the same oxygen pressure $(5 \sim 6 \times 10^{-2} \text{ torr})$ at two different temperatures. One of the films was deposited on a heated substrate (496 °C) and the other film was deposited on a substrate without heating. It is seen that the density of particles on the surface of as-deposited films without substrate heating is larger. These particles are by-products of the laser ablation. The fact that laser ablation produces films with fine particles is well known. However, the diameter of particles in the films deposited using long wavelength (10.6 μ m) laser ablation is larger. This is because that the absorption of photons by the target is dependent on wavelength. The shorter the wavelength, the greater the absorption rate. Therefore, long wavelength CO₂ laser beam can penetrate into the deep region of the target and sputter out larger particles to the substrates.

4.1.4. Heat Treatment

Since the *ex-situ* deposition method has been adopted in this work, heat treatment of the deposited films is a required step in obtaining superconducting films. The temperature and duration of heat treatment are critical for the formation of the superconducting phases. When the temperature of heat treatment is below 650 °C, no superconducting phase will form. Above 650 °C, a low-T_c phase (10 K) begins to form and treatsforms into a 80 K high-T_c phase at a temperature of about 800 °C. Further increase of the temperature will finally produce a 110 K superconducting phase. Compared to the 10 K and 85 K superconducting phases, the 110 K high-T_c phase is relatively unstable. Only those films treated at temperatures within a very narrow temperature range for a specific period of time can develop relatively large amounts of 110 K high-T_c phase.

In addition, rates of increase and decrease of temperature during the heating and cooling steps also affect the formation of the 2223 high-T_c phase. The value just below

melting point of the BiSrCaCuO films was found to be the best temperature for forming the high- T_c phase. Since the melting points of the deposited films are sensitive to the composition of the films, the best temperature for forming a superconducting film with a high resistance transition temperature varies from film to film. Good quality films with a high T_c value can be produced only when the conditions of deposition and heat treatment are strictly controlled.

A two-step heat treatment was used for the present experiments. The purpose of using this two-step heat treatment was to avoid the evaporation of films that occurs during a conventional one-step heat treatment. It has been observed that the BiSrCaCuO films can evaporate completely after the one-step treatment. The two-step treatment was carried out in the following manner. As-deposited BiSrCaCuO films located inside a small quartz tube (12 mm in diameter) were pushed into the centre of the furnace tube (set at 400 °C) at a rate of 0.67 cm/min. through a distance of one meter. When the films reached the centre of the furnace, the temperature of the furnace was increased at a rate of 3 ~ 5 °C/min.. The rate of temperature increase was controlled by a stepping motor. The stepping motor was stopped when the temperature of the furnace was 800 °C for the first heat treatment. The first step took between 10 and 40 minutes. Following the first step, the temperature of the furnace was increased further at the same rate until it reached a value between 840 °C and 860 °C for second heat treatment step. The duration of the second heat treatment step varied from 20 to 60 minutes, depending upon the thickness of the BiSrCaCuO films. After the two-step heat treatment, the furnace was switched off and the films were kept inside the furnace until the temperature of the furnace decreased to 500 °C. The small quartz tube containing the films was finally pulled out of the furnace in three or four steps.

During the process of the heat treatment, either dry air or a mixture of dry air and pure oxygen was allowed to flow through the furnace tube. The flow rate was monitored by a Matheson 602 E300 flowmeter. The typical flow rate at 1 atm was about 30 cc/min.. It was found the presence of water vapour enhanced film quality. Therefore, the oxygen gas or dry air was allowed to pass through a glass jar containing DI water before entering the furnace tube. It was also found experimentally that oxygen gas increased the melting point of the BiSrCaCuO films. This is probably because of the reaction between the O atoms and the asdeposited films. A change in the composition of the BiSrCaCuO films resulted in a change in the melting point of the films. Thus, the heat treatment temperature had to be selected by considering the flowing rate of O_2 in the furnace.

After the above described treatment, the thickness of the as-treated BiSrCaCuO films was measured by Dek Tek profiler. The results obtained were compared with those measured before the treatment. The thickness value of as-deposited films was normally between 0.8 μ m and 1.5 μ m and the thickness of as-treated films ranged from 0.4 μ m to 1.0 μ m.

4.2 Electrical Characterization of BiSrCaCuO Films

The fabricated BiSrCaCuO films were characterized to determine the critical temperature and critical current density. The critical temperature and critical current density were measured using a four probe method.

4.2.1 Critical Temperature

Critical temperature, T_c , is one of the most important characteristics in superconducting materials. It defines the phase boundary between the normal conducting and the superconducting states. Two critical temperatures can be defined for a superconductor. One is the onset T_c and the other is zero resistance T_c . The onset T_c is defined as the temperature just above the start of the resistance transition. It has a value between the temperatures at which the resistance decreases to one-half and one-third of its normal conducting value. Zero resistance T_c is the temperature at which the resistance of material reaches zero. There are two methods for determining the critical temperatures. One of the methods is to measure the change of resistance with the shange of the temperature. The other is to measure the change of magnetic susceptibility when the temperature is varied. For a superconducting thin film with a small thickness, the resistance measurement is the preferred method. This is because signal from the magnetic susceptibility measurement may be small due to the small volume of the thin film material.

Before doing the resistance measurements, four contacts were made on each film by evaporating high purity silver (59's) through an aluminum mask. The resistance of contacts was determined from a plot of total resistance versus distance between contacts. The total resistance between any two contacts can be expressed as

$$R_T = \frac{\rho_x d}{Z} + 2R_c \tag{4.3}$$

where, ρ_s is the sheet resistance of BiSrCaCuO, *d* is the spacing between the two contacts, *Z* is the width of the contacts and R_c is the contact resistance. Figure 4-3 shows plots of total resistance versus distance between the contacts for two BiSrCaCuO films before and after a 10 minute annealing at 90 °C. The contact resistance can be deduced from the intercept of the R_T axis. It can been seen from figure 4-3 that the contact resistance increases after the contacts are subjected to the annealing. The contact resistance is about $10^{-2} \sim 10^{-1} \Omega$ -cm² before and is about $10^{-1} \sim 1 \Omega$ -cm² after the annealing. Therefore, annealing process was not applied after the formation of contacts in all subsequent experiments.

During the resistance measurements, the BiSrCaCuO sample was mounted on a metal stage inside a cryostat. An electrical insulator (mica) and thermal conduction paste were applied between the sample and the stage. A 100 Ω platinum resistance thermometer was attached directly to the stage for temperature measurement. A heater was installed against the underside of the stage for temperature control. At first the cryostat was evacuated to a pressure of 10⁻³ torr in order to remove moisture which might interfere with the measurement and reduce heat loss from the sample. The temperature of the cryostat was then controlled by pumping liquid nitrogen into or applying heat to the cryostat. Electrical connections were made to the film by Au pressure contacts. A dc current (4 ~ 20 μ A) was applied to the two outer contacts of the sample. The corresponding voltage of two inner contacts was measured by a Hewlett Packard 3478A multimeter.

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The resistance of a typical BiSrCaCuO film decreases linearly with the decrease of the temperature. At a temperature around 100 ~ 120 K, the resistance of the film begins decreasing abruptly and reaches the noise value of the multimeter at a temperature of $80 \sim$ 106 K (see figure 4-4). Between room temperature and the temperature before superconducting transition, the steady decline of the film resistance with the decrease of the temperature can be explained by the reduction of the collision of electrons with lattice phonons. This is similar to that in a normal metal. Below the superconducting transition, the decrease of resistance has to be interpreted by the microscopic BCS theory. An intuitive and brief description of the phenomenon is given below. Unlike a normal metal which has the electrical resistance due to the interaction of the electrons with the crystal lattice vibration, the interaction between electrons and the crystal lattice in a superconducting material at low temperatures is minimized leading to an absence of resistance. At temperatures below the critical value, T_{c.zero}, of a superconductor, a conduction electron of a given momentum and spin can weakly couple with another electron of the opposite momentum and spin to form a pair (Cooper pair) through a medium of the lattice. The paired electrons have a zero net momentum and are in a bound state. Hence, they cannot be scattered and have no contribution to the electrical resistance of the material.

Figure 4-4 (a) and (b) show plots of resistance versus temperature for four of the BiSrCaCuO superconducting films studied. In figure 4-4 (a), the resistance of the samples is seem to decrease linearly with the decrease of temperature from room value to 112 K. Further decrease in the temperature results in a sharp reduction of the resistance. This sharp reduction region is the superconducting transition region of the BiSrCaCuO films. The resistance of sample B6S4 reaches zero at a temperature of 106 K and the resistance of sample B6K12 becomes zero at a temperature of 98.5 K. The transition width, which is the temperature difference between the onset T_c and zero resistance T_c is about 6 K and 10 K for the two samples, suggesting a domination of the 2223 phase (110 K) in the films.

In figure 4-4 (b), although sample B6-10-1 has a high onset T_{c} , the transition is wide and the resistance does not reach zero until T = 80 K. This fact suggests that the film consists

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of a mixture of the 2212 (85 K) and 2223 phases. The low onset T_c (89 K) and zero T_c (80 K) of sample B6A'1 suggests that the 2212 phase is dominant in this film. Measurements similar to the ones described above are also made for all of the post-annealed samples. It was found that superconducting transition temperature was sensitive to oxygen pressure in the deposition chamber and to heat treatment temperature (the investigated samples were listed in table 4-2). When the films were treated under optimum conditions, onset T_c would range between 105 and 112 K and zero T_c would range between 81 and 106 K. These critical temperatures are the highest ones ever achieved in the BiSrCaCuO films deposited by CO₂ laser ablation.

As mentioned before, it is crucial to have a proper oxygen pressure in the deposition chamber if BiSrCaCuO films with high critical temperature are to be obtained. The amount of oxygen incorporated to the films is directly related to the formation of the CuO planes in the BiSrCaCuO structure. The number of the CuO planes in the BiSrCaCuO structure determines the electrical properties of the films, such as critical temperature and critical current density. Critical temperature of the films deposited at various oxygen pressures at room temperature was measured. Figure 4-5 shows the relationship between oxygen pressure (in the 10⁻⁴ to 10⁻¹ torr range) and critical temperature for several BiSrCaCuO superconducting films. The films used were prepared under the same conditions except the oxygen pressure. T_{onset} refers to the temperature at which the resistance transition begins and $T_{2\pi0}$ is the temperature at which resistance of the films just reaches zero. It is evident that the highest T_{zero} occurred on samples prepared at an oxygen pressure of $5 \times 10^{-2} \sim 8 \times 10^{-2}$ torr. The width of the resistance transition was narrow near this range of oxygen pressure. Beyond this oxygen pressure range, samples with low critical temperatures and wide resistance transition were usually obtained. The above results thus confirm that an oxygen pressure between 5×10^{-2} and 8×10^{-2} torr is required to form the 2223 phase in the BiSrCaCuO films.

For the BiSrCaCuO films deposited at the same oxygen pressure, the electrical properties of the resulted superconducting films were found to vary with the annealing temperature. If the annealing temperature was too low, phase transformation could not complete within a given annealing time, films dominated by the low-T_c phase were produced. Conversely, if the annealing temperature was too high, the BiSrCaCuO films would partially evaporate. The structure would decompose to low-T_c phases, resulting in films with a low critical temperature. Table 4-3 lists results of eight samples, which were all deposited at an oxygen of $7 \sim 8 \times 10^{-2}$ torr but with different heat treatment temperatures for the second step. It can be seen that the optimum temperature for the second heat treatment step is about 850 °C. For the samples treated at 840 °C and below (results not shown), zero resistance occurred at temperatures below 77 K. The transition temperature corresponding to the low-T_c (2212) phase was generally observed in the films deposited at $7 \sim 8 \times 10^{-2}$ torr and subsequently heat treated at temperatures above 858 °C.

Sample	Oxygen	Treatment Ter	mperature (°C)	Onset T _c	Zero T _c
Number	Pressure (torr)	First Step [*]	Second Step ^b	(K)	(K)
B6M9	$(7 \sim 8) \times 10^{-2}$	800	840	86.0	< 77
B6-11-1	$(7 \sim 8) \times 10^{-2}$	800	842	92.5	79.3
B6M3	(7~8)×10 ⁻²	800	850	101.0	94.7
B6M7	$(7 \sim 8) \times 10^{-2}$	800	850	117.0	92.1
B6M 10	(7~8)×10 ⁻²	800	852	118.0	84.5
B6Q10	$(7 \sim 8) \times 10^{-2}$	800	854	112.5	78.1
B6Q15	$(7 \sim 8) \times 10^{-2}$	800	856	115.5	79.0
B6M1	$(7 \sim 8) \times 10^{-2}$	800	858	105.0	< 77

Table 4-3. Critical Temperatures of BiSrCaCuO Films with Different Second Step Heat Treatments

a. Time for the first heat treatment step is 30 minutes.

b. Time for the second heat treatment step is 30 ~ 40 minutes.

4.2.2 Critical Current Density

Critical current density is the maximum current density a superconducting film can carry. The value often depends on the microstructure of superconducting films. There are two methods to determine the critical current density of the superconducting films. One is to observe the change in resistance when the electric field (applied current) in the films is increased. The other is to obtain the critical current density from a magnetization measurement by utilizing the hysteresis in the magnetization curves (the critical state model).^[4,1] Due to a limitation of availability of magnetization measurement equipment, the critical current density for all of the samples in this work was measured by the resistance method.

Sample Number	Critical Current Density (A/cm ²)	
B6S2	3.43×10^{3}	
B6S1	1.52×10^{3}	
B6K12	3.34 × 10 ²	
B6M3	1.28×10^{3}	
B6-7-2	3.34×10^{2}	
B6-10-2	8.57×10^{2}	
B6R10	1.39×10^{3}	
B6-8-1	4.29×10^{2}	

 Table 4-4. Critical Current Densities of BiSrCaCuO Films at 77 K

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The measurements were normally carried out on the superconducting BiSrCaCuO films (without patterning and etching) at 77 K. The four-point probe method was used to measure the change in voltage with the increase of current. The critical current density is taken as the current density when the electric field from the voltage measurements is

1 μ V/mm. Table 4-4 lists some of results for the BiSrCaCuO superconducting films deposited by CO₂ laser ablation. The values of critical current density are in the order of $10^2 \sim 10^3$ A/cm² at 77 K. For films with larger grain sizes and relatively high critical temperatures, the critical current densities were found to be greater. For those films with a high density of microparticles critical current densities were low.

The critical current densities of BiSrCaCuO superconducting films also depend on temperature and magnetic field. The relationship between temperature and critical current density is simpler than that between magnetic field and critical current density. Specifically, the critical current density was inversely related to temperature. The relation between magnetic field and critical current density varies with temperature^[4,24,4,25]. In the present work, the effects of temperature and magnetic field on the critical current densities of the BiSrCaCuO films were only studied in the temperature range from 77 K to the critical temperatures. The effects of temperature and magnetic field at lower temperatures were not examined due to the limitation of the cooling system. During the experiments, the magnetic field was applied perpendicular to the current direction. Figure 4-6 gives tw- curves, showing variation of critical current density with temperature for one of superconducting BiSrCaCuO films. One of the curves is for the measurement without magnetic field and the other at 200 gauss.

It is noticed that the critical current density decreases with the increase of temperature for both B = 0 and B = 200 gauss. As the temperature is increased, the number of quasiparticles in the superconductor increases. The transport of these quasiparticles can cause dissipation, and reduce the critical current density. On the other hand, if the high-T_c films are considered to contain many Josephson junctions, the increase in temperature may also cause a decrease in the critical current density of Josephson junctions. Hence, the critical current density of the high-T_c superconducting films would decrease. Figure 4-6 also shows that the critical current density of a film in an external magnetic field is lower than that without the field. The magnetic field, which is perpendicular to the film surface, creates more flux vortices and greater fraction of material in the normal state, thus reducing the critical current density.

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The relationship between J_c and T can be described by the following equation: $J_c = (1-T/T_c)^n$. From the values of J_c at different temperatures, the value of n was found to be 2.57. This value is larger than the value n=2 predicted by Deutshcher and Müller.^[4,26] In their work, a power law dependence of critical current density on temperature was deduced assuming that the critical current density was determined purely by Josephson tunnelling at the grain boundaries of the high-T_c oxide.

4.3 Crystalline Structure of BiSrCaCuO Films

The crystalline structure of the laser-ablated BiSrCaCuO films was investigated using X-ray diffraction (XRD), scanning electron microscopy (SEM) and electron probe X-ray microanalysis (EPMA). As mentioned before, X-ray diffraction can provide useful information for determination of lattice constants and various phases (2201, 2212 and 2223) present in the BiSrCaCuO films. In addition to XRD, SEM was used to examine the morphology, thickness and the grain size of the films. The composition and compositional uniformity of the BiSrCaCuO films before and after treatment were determined by EPMA.

4.3.1 Results From X-ray Diffraction

X-ray diffraction using Cu Ka radiation was performed on both as-deposited and heat treated BiSrCaCuO films. Figure 4-7 presents three X-ray diffraction patterns. One is the pattern for the background, which is the glass plate used as a holder for the measured samples. The other two patterns are for as-deposited BiSrCaCuO films with and without substrate heating. It is obvious that there are no additional peaks in the as-deposited samples except for the background noise. The above results thus confirm that the as-deposited films are amorphous, even though they were deposited on heated MgO substrates.

After the heat treatment at a high temperature of 800 ~ 860 °C, semiconducting, low- T_c superconducting and high- T_c superconducting phases appeared. Figure 4-8 shows results for four heat-treated BiSrCaCuO films. All of these films were deposited at an oxygen

pressure of $7 \sim 8 \times 10^{-2}$ torr, and rate of increase of the heat treatment temperature was 5 °C/min. For all these samples, the temperature and duration of the first heat treatment step was 800°C and 30 minutes, respectively. The second heat treatment step was carried out at different temperatures but for a same period of time.

In figure 4-8, H, L, and X represent peaks corresponding to superconducting phases of 110 K, 85 K and 10 K respectively. The ratio of peak height, H0010/(H0010+L008), was used to determine the portion of the 110 K high-T, phase. This is because the peaks of H0010 and L008 were two of the most active and clear peaks in the films studied. It is seen in figure 4-8 (a) that the Ca₂PbO₄ and Ca₂CuO semiconducting phases and a small portion of the low-T_c phase (10 K) exist in the film treated at 815 °C. The value of H0010/(H0010+L008) is less than 0.08 at this treatment temperature. For the film treated at 835 °C [figure 4-8 (b)], the semiconducting phases and the 10 K low-T_c phase disappear. The ratio of H0010/(H0010+L008) increases to 0.33. Hence, this sample is still dominated by the 85 K low-T_c (2212) phase. As the second heat treatment step temperature is increased to 850 °C [figure 4-8 (c)], the ratio of H0010/(H0010+L008) rises to 0.62, indicating that a dominant high-T_c phase (110 K) in the film. When the heat creatment temperature further increases to 860 °C, as shown in figure 4-8 (d), the ratio of H0010/(H0010+L008) decreases to 0.46 and the low-T_c superconducting phase (85 K) is dominant again. MgO peaks in the above X-ray patterns were caused by the substrates since the BiSrCaCuO films were thin so that part of the Cu K α X-ray can penetrate the films and reach the substrates. Ag peaks in the patterns came from the contacts which were used for the electrical measurements.

Examination same as the one described above was also performed on other as-treated films. It was noticed that second heat treatment step at a temperature below 820 °C produced films with semiconducting phases (Ca₂PbO₄ and Ca₂CuO). For the films treated at temperatures between 825 and 840 °C, both low-T_c and high-T_c superconducting phases were present, with a dominant low-T_c phase (2212). At a temperature of 840 ~ 850 °C, the high-T_c superconducting phase (2223) was dominant. Further increase of temperature for the second heat treatment step resulted in a reduction of the high-T_c phase and an increase in the low-T_c

semiconducting phases due to the decomposition of the 2223 high-T_c superconducting phase.

Furthermore, it was found in the present work that different heat treatment procedures were required for films deposited at different oxygen pressures in order to obtain better quality. For the films deposited at an oxygen pressure of about $1 \sim 1.5 \times 10^{-1}$ torr and below 1×10^{-3} torr, large rate of temperature increase (about $20 \sim 60$ °C/min.) was required for the heating process. However, for those deposited at an oxygen pressure of $3 \sim 8 \times 10^{-2}$ torr, better film properties were found after a heat treatment with a slow increase of temperature (about $3 \sim 5$ °C/min.). The requirement of different rates of increase of temperature is still not well understood. It may be related to the amount of oxygen incorporated in the films during the deposition. Figure 4-9 shows a comparison of the X-ray diffraction patterns for three samples. These three samples were treated using the same process (rate of temperature increase is 5 °C/min) except the oxygen pressure. One was deposited at an oxygen pressure of $7 \sim 8 \times 10^{-2}$ torr (sample B6M3), another one was deposited at $1.15 < 10^{-1}$ torr (sample B6K3) and the last at 1×10^{-3} torr (sample B6H8).

It can be observed in figure 4-9 that both the 2212 (L) and the dominant 2223 (H) superconducting phases exist in the film deposited at $7 \sim 8 \times 10^{-2}$ torr. However, the films deposited at 1.15×10^{-1} torr or at 1×10^{-3} torr show a dominant 2212 low-T_c phase. In addition, weak semiconducting phases, such as Ca₂PbO₄ and Ca₂CuO, can be identified from the X-ray patterns.

4.3.2 Pesults from Scanning Electron Microscopy

The morphology of the BiSrCaCuO superconducting films was studied by a JEOL-6100 SEM. Images were obtained by detecting the secondary electrons emitted from the BiSrCaCuO films while an electron beam impinged on the surface of the films. The thickness of the films could also be determined from the SEM photographs of the film cross section. Before examining under the SEM, as-deposited BiSrCaCuO films must be coated with carbon so that electrons are able to discharge on the surface of the films. This process is not necessary for superconducting films because these films are good conductors at room temperature. If SEM pictures are to be taken of the cross section of the films, carbon coating is also required because MgO substrates are insulators. Figure 4-10 displays two SEM photographs of typical superconducting BiSrCaCuO films with high critical temperatures. Figure 4-10 (a) shows a film with a large grain size. It seems that the film has melted during the heat treatment process. Figure 4-10 (b) shows another film with a smaller grain size compared to the film in figure 4-10 (a). For this film, the surface is more uniform. From critical current density measurements, it was found that the value was higher for the film in figure 4-10 (b) than that in figure 4-10 (a). In these two BiSrCaCuO films, some small particles with a diameter of $1 \sim 2 \mu m$ are also present.

The thickness of the superconducting BiSrCaCuO films was also examined by SEM. Figure 4-11 shows a SEM picture of a BiSrCaCuO film cross section. The thickness of the film is about $0.4 \sim 0.5 \mu m$, which is thinner than the as-deposited films. The reduction in film thickness was caused by the heat treatment. Partial evaporation occurred during the melting process and phase transformation.

4.3.3 Results from Electron Probe X-ray Microanalysis

The composition of BiSrCaCuO films before and after treatment can be determined by electron probe X-ray microanalysis (EPMA). While electrons are impinging on the surface of a film, the analysis of the resulting X-ray can identify elements and determine their concentrations. The compositional uniformity can be obtained by carrying out EPMA at several points along the film. In order to determine the effect of the oxygen pressure during the deposition on the composition of as-deposited films, EPMA was carried out on several samples prepared at different oxygen pressures. In addition, the effect of substrate temperature on the film composition was investigated by performing EPMA on several films deposited at different temperatures. Figure 4-12 presents variation of composition with distance obtained from EPMA data for two as-deposited samples prepared at room temperature. During the deposition, oxygen pressure was 8×10^{-2} torr for one sample (B6SG) and was $4.5 \sim 5.3 \times 10^{-4}$ torr for the other (B6-9). The horizonal axes in figure 4-12 represent the distance from one edge of the films. The vertical axes are the normalized atomic concentration assuming Cu + Pb + Bi + Sr + Ca = 1.

It can be seen that distribution of each element is almost constant over the distance along the films. The ratio of Bi : Pb : Sr : Ca: Cu is about 3 : 3 : 1 : 0.9 : 2.1 for the film B6SG and about 2.7 : 2.7 : 1 : 1 : 2.6 for the film B6-9. Compared to the composition of the sintered target (B6), which was Bi : Pb : Sr : Ca : Cu = 1.73 : 2.16 : 1.51 : 1.92 : 2.70, the deposition rate of Bi and Pb was higher than Sr, Ca and Cu, especially at higher oxygen pressures. Since an evaporation mechanism was involved during the long wavelength CO₂ pulsed laser ablation, and since the melting points and vaporization points of Bi and Pb are lower than that of Sr, Ca and Cu, more Bi and Pb were deposited onto the MgO substrates.

Figure 4-13 shows EPMA result for a superconducting film after heat treatment (B6S2). The film has a uniform elemental distribution with a ratio of Bi : Pb : Sr : Ca : Cu ≈ 2.38 : 0.07 : 2.07 : 2.57 : 2.92. Pb was almost completely evaporated during the heat treatment after the phase transformation. There was also a large loss in Bi during the heat treatment. Compared to the standard ratio of 2223 high-T_c phase, it is evident that in figure 4-13 stoichiometry deviation exists in film B6S2. Film B6S2 was polycrystalline and contained a mixture of low-T_c and high-T_c phases.

The relationship between the oxygen pressure in the deposition chamber and the composition in the as-deposited films shown in the above experiments is quite complicated. Therefore, EPMA was further carried out on other films deposited at various oxygen pressures from 10⁻⁵ torr to 10⁻¹ torr. Figure 4-14 reveals the measurement results for films deposited at room temperature but with very different oxygen pressure. It is noticed that the change of Sr and Ca with oxygen pressure is opposite to the change of Bi and Pb with oxygen

pressure. With an oxygen pressure of 3×10^{-4} torr to 2×10^{-2} torr, the variation of the film composition with pressure is less than that in the two extreme regions. Large variation occurs at oxygen pressures below 10^{-4} torr and above 2×10^{-2} torr.

As mentioned above, substrate heating can improve the sticking coefficient and enhance the diffusion of deposited species. The effect of substrate temperature on the composition of the as-deposited films is also very important and should be investigated thoroughly. It is for this reason that EPMA was performed on BiSrCaCuO films deposited on MgO substrates subjected to various temperatures. Figure 4-15 presents the results for a series of films deposited at an oxygen pressure of $7 \sim 8 \times 10^{-2}$ torr and at different substrate temperatures. The distribution of the elements (Bi, Pb, Sr, Ca and Cu) did not change a lot from room temperature to a temperature of 600 °C, except for the temperature 475 °C at which Bi amount was too low compared to the value at other temperatures. Substrate temperature higher than 600 °C didn't apply because of low melting point of Pb and the limitation of cooling system in the deposition chamber. It is thus concluded that substrate temperature did not have a strong effect on composition, at least up to 600 °C, despite the fact that it did improve morphology and sticking coefficient of the films.

4.4 Conclusions

In this chapter, the formation of different phases of BiSrC. CuO films deposited using a TEA CO₂ pulsed laser has been studied. MgO substrates with (100) orientation were selected because of the low cost of these substrates and because of the reasonable crystal lattice mismatch between the substrates and the BiSrCaCuO films. Amorphous targets were prepared by sintering a mixture of Bi₂O₃, SrCO₃, CaCO₃ PbO and CuO powders at above 800 °C. Two parameters were found to be important for the film deposition, one was oxygen pressure and the other was substrate temperature. The oxygen pressure affected the composition of the as-deposited films. The variation in Bi and Pb contents of the as-deposited films with the change in the oxygen pressure during the deposition was opposite to that for Sr and Ca. On the other hand, substrate heating did not have a strong effect on the composition of the films, although their surface morphology was improved by the substrate heating. Observation under SEM revealed that the as-deposited films were uniform. In addition, some micro-particles were found on the as-deposited films. This phenomenon is similar to the one reported by other researchers on the films deposited by lasers having a short wavelength. However, the size of these particles in the films deposited by the CO_2 laser were larger. Moreover, it was found that the number and size of these micro-particles can be reduced by substrate heating which enhanced the diffusion of ejected species on the surfaces of the films.

Heat treatment has been found to be a critical step for obtaining BiSrCaCuO superconducting films. Several key points for the heat treatment should be noticed . (1) A two-step heat treatment should be used instead of conventional one-step heat treatment in order to prevent evaporation of the films. (2) Different rates of temperature increase should be applied to the films deposited at different oxygen pressures so that good quality films can be obtained. (3) Temperature of the second heat treatment step should be carefully chosen since it is crucial to the formation of 110 K high-T_c phase. The optimum temperature of second heat treatment step was about 850°C for the films deposited at 7 ~ 8 × 10⁻² torr of oxygen. In addition, water vapour was found to be important. The content of water vapour was controlled by allowing oxygen or dry air to pass through a bubbler before being introduced to the furnace tube.

Electrical properties of the obtained BiSrCaCuO superconducting films were determined by measuring both critical temperature and critical current density. The dc four probe method was used to measure the critical temperature. It was observed that the onset critical temperature of the films occurred between 86 K and 118 K, and zero resistance critical temperature occurred between 77 K and 106 K. These critical temperatures are the highest values reported so far in the BiSrCaCuO superconducting films deposited by CO_2 laser ablation. The critical current density was also measured by the four-point probe method. A criterion of 1 μ V/mm was used in determining the critical current density. The average

critical current density obtained was in the order of $10^2 \sim 10^3$ A/cm². Furthermore, it was observed that the critical current density of the BiSrCaCuO superconducting films decreased with the increase of temperature, and reached zero at the zero critical temperature of the films. The critical current density of the films was also found to decrease when the magnitude of the external magnetic field applied increased, due to an increase of flux vortices in the films.

The crystalline structure of BiSrCaCuO films was examined using XRD, SEM and EPMA. Results from the XRD study showed that a mixture of 2212 and 2223 phases was present in most of BiSrCaCuO superconducting films, with the c-axis perpendicular to the surface of the films. For the superconducting films with high critical temperatures, XRD patterns showed a dominant 2223 high-T_c phase. Even in the best quality film, XRD pattern still showed a polycrystalline structure rather than a pure monocrystalline structure. The morphology of superconducting films was studied by SEM where large grains parallel to the film surface were observed. The thickness of the superconducting films observed under SEM was about 0.4 μ m to 1.0 μ m. EPMA study was performed on as-deposited and annealed BiSrCaCuO films. It was observed that both as-deposited and annealed films have uniform distribution of composition. Although it was found by EPMA that the as-deposited films were rich in Bi and Pb due to high evaporation rates of Bi and Pb, the ratio of 2 : 2 : 2 : 3. The slight deviation in the ratio indicated that more than one high-T_c phase was in the films.



Figure 4-1 The unit cell of MgO crystal.

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(a)



SEM photographs of as-deposited BiSrCaCuO films: Figure 4-2 (a) with substrate heating (496 °C), (b) without substrate heating.

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(b)



Figure 4-3 Plots of resistance versus contact spacing for two BiSrCaCuO superconducting films, showing lower contact resistance in the film without post annealing.





Resistance characteristics of two BiSrCaCuO superconducting films with dominant 2223 phases.





Resistance characteristics of two BiSrCaCuO superconducting films with dominant 2212 phases.





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Relative Intensity





Figure 4-7 (b) X

X-ray diffraction pattern of an as-deposited BiSrCaCuO film on a heated MgO substrate.







X-ray diffraction pattern of an as-deposited BiSrCaCuO film on an un-heated MgO substrate.

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Relative Intensity

600 L008 H0012 L0010 500 Second heat treatment : 835 °C **Relative Intensity** 400 L0012 MgO H0010 300 H0014 200 Н Å 100 0 30 40 20 10 20 ÷. 5

Figure 4-8 (b)

X-ray diffraction pattern of a BiSrCaCuO superconducting film annealed at 835 °C.

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Figure 4-8 (c) X-ray diffraction pattern of a BiSrCaCuO superconducting film annealed at 850 °C.



Relative Intensity

X-ray diffraction pattern of a BiSrCaCuO superconducting film annealed at 860 °C.



Figure 4-9

X-ray diffraction patterns for three BiSrCaCuO samples fabricated with same heat treatment procedures but at different deposition pressures:
(a) at 7 ~ 8 × 10⁻² torr, (b) at 1.15 × 10⁻¹ torr, and (c) at 1 × 10⁻³ torr.



(a)



Figure 4-10 SEM photographs of BiSrCaCuO superconducting films: (a) with large grains. (b) with small grains.

(b)











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Figure 4-14 EPMA results for BiSrCaCuO films deposited at different oxygen pressures.



Figure 4-15 EPMA results for BiSrCaCuO films deposited at different substrate temperatures.

Chapter 5

Noise Characteristics of BiSrCaCuO Films

5.1 Introduction

The investigation of noise characteristics in high-T_c superconductors is important since it affects many potential applications such as infrared detectors and dc superconducting quantum interference devices (SQUID). Considerable attention has been paid by researchers in this field.^[5,1-5,13] There are two anomalous phenomena in the noise behaviour of high-T_c superconductors. One of the phenomena is the extremely large noise in the normal state. This large noise is difficult to be explained by either the universal conductance fluctuation model^[5,14] or the local interference model.^[5,15,5,16] The other phenomenon is a noise peak near resistive transition temperature of superconductors, T_c . The enhancement of the noise near superconducting transition temperature varied for different materials and different structures (single crystal, thin film). Therefore, different noise mechanisms have been suggested by different researchers. These noise mechanisms include thermal fluctuation mechanism.^[5,17-5,20] and the mechanism related to effect of superconducting fluctuation.^[5,21,5,22]

Thermal noise in a resistive material is caused by the random motion of free electrons. Two approaches have been used to explain thermal noise in metals. One is an empirical formula proposed by Hooge and Hoppenbrouwers.^[5,23] The other is a model proposed by Voss and Clark.^[5,24] Hooge and Hoppenbrouwers found that the noise power spectrum for metals at room temperature could be expressed by the empirical formula $P_v(f)/V^2 \approx 2 \times 10^{-3}$ $N_c f$, where V is the rms voltage across the sample, N_c is the number of charge carriers in the sample and f is the frequency. The dependence of the noise on the voltage is universally found in resistive materials. It is considered as arising from resistance fluctuations that generate a fluctuating voltage in the presence of a constant current. The noise power described by Hooge's formula is also proportional to 1/f. Thus the noise is also called Flicker noise.

Voss and Clarke suggested another origin for 1/f noise in metal films. They suggested that the noise is caused by temperature fluctuations that modulate the sample resistance and generate voltage fluctuations in the presence of a steady current, *I*. Based on Voss and Clarke's model, the empirical inclusion of an explicit 1/f dependence and appropriate normalization lead to $P_v(f)/V^2 \approx \beta^2 k_B T^2/C_v[3+2ln(l/w)]f$, where *l* is the length and *w* is the width of the measured film. This empirical formula was also used by Clarke and Hsiang to analyse 1/f noise of the low-T_e superconductor material Sn near its superconducting transition.^[5,25] Clarke and Hsiang found that the magnitude of the noise measured agreed well with the noise calculated using this empirical formula. After the discovery of high-T_e superconductors, many researchers tried to use Voss and Clark's model to explain the noise behaviour of high-T_e superconducting materials. Some of these researchers obtained very satisfactory results.^[5,17-5,20]

In addition to the thermal fluctuation mechanism, several other causes and models have been suggested to explain the experimental results of the spectral power density of voltage noise in high-T_c materials. These include the fluctuation effects of vortexantivortex,^[5,3] spontaneous generation and dissociation of fluctuational Cooper pairs,^[5,21,5,22] potential fluctuations in the grain boundary regions of superconductor (modeled as metalinsulator-metal junctions),^[5,8] flux hopping and thermally activated flux creep in the superconductor lattice structure.^[5,17]

Most of research on the noise properties of high-T_c superconductors was carried out in the YBCO compound. Several researchers also studied the noise behaviour in BiSrCaCuO compound.^[5,1-5,7] Maeda et al studied the noise behaviour in their BiSrCaCuO single crystals, polycrystals and thin films with 2212 superconducting phase.^[5,1,5,2] They found that the noise power spectral density reached a peak near the resistive transition in thin films, in polycrystals and even in single crystals, suggesting a common feature of the noise peak in BiSrCaCuO. Han et al measured the noise power spectral density of single crystal BiSrCaCuO exposed to different external magnetic fields and different applied currents.^[5,3,5,4] They also found an enhancement of the noise power spectral density near the resistive transition. In addition, they observed an unusual frequency dependence of the noise power spectral density on the external magnetic field. They suggested that the large noise near the transition region was the result of the fluctuation effect of the vortex-antivortex pairs.

Measurements of the resistance noise in thick films of BiSrCaCuO (granular superconductors) were carried out by Aponte et al.^[5,5,5,7] They measured the power spectral density (P_*/V^2) of the resistance noise in these granular superconductors in the proximity of the superconducting transition as a function of the current for a fixed temperature and as a function of the temperature at a fixed current. Aponte et al found that the magnitude of noise power spectral density increased as the resistance of a sample approached zero and that it was zero below the transition. They believed the results obtained were consistent with percolation models of normal-superconductor composites. Another group, R. W. Zindler et al, also investigated the 1/f noise of BiSrCaCuO thin films in the high-T_e superconducting transition

region.^[5,6] Their results were similar to those reported by Han et al.^[5,3,3,4] They suggested that thermal fluctuation was the main source of the excess 1/f noise detected in the lower temperature region of the transition.

The causes of the noise in the BiSrCaCuO superconductors are still in controversy. It is thus necessary to carry out more research on this compound prepared by different methods. This chapter presents results of noise studied on BiSrCaCuO thin films with 2223 dominant superconducting phases. The studied BiSrCaCuO thin films were fabricated by CO₂ laser ablation or rf-sputtering. The noise measurements were made on thin films both in normal state and superconducting state. The noise of BiSrCaCuO films at room temperature was obtained and compared with the noise of normal metals using Hooge's empirical formula and room temperature Voss and Clark's model. The noise power spectral density near the superconducting transition was compared to the value predicted by Voss-Clarke's thermal fluctuation and vortex motion models. Furthermore, the noise values measured on BiSrCaCuO films with different grain sizes and defects were compared. Finally, attempts were made to determine the possible origins of the excess noise near the resistive transition region of BiSrCaCuO films.^[5,28,5,29]

5.2 Noise Power Spectral Density

There are several types of noise, such as thermal noise, shot noise, and flicker noise. Thermal noise is related to temperature and is generated in active or passive devices having a resistive component. Shot noise is a result of random variation in a dc level and is generated only in active components. Flicker noise is inversely proportional to frequency. Whatever the noise is, the noise is considered as voltage fluctuation with time, v(t). If one examines the frequency characteristic of this noise (using a Fourier transform), the noise can be shown to consist of a group of frequency components. These frequency components may differ in amplitude and show a frequency spectrum. The height or magnitude of this spectrum is called the spectral density. Spectral density can be related to power or voltage. Usually, noise The measured voltage V is the rms value of v(t), and V is related to the noise power spectral density P(f) through the following equation:

$$V^2 = P(f)\delta f \tag{5.1}$$

When a small frequency bandwidth of $\Delta f = (f_2 - f_1)$ is considered (such as 1% of centre frequency f_0), equation (5.1) will become

$$V^{2} = P_{av}(f) \times (f_{2} - f_{1}) \approx P(f_{0}) \Delta f$$
(5.2)

where f_1 and f_2 are the lower and upper frequency limits of interest, $P_{av}(f)$ is the average spectral density in the frequency range from $(f_0 - \Delta f/2)$ to $(f_0 + \Delta f/2)$ and can be replaced approximately by spectral density at the centre frequency, $P(f_0)$. In the experiments, the noise voltage of a high-T_c superconductor was measured by a lock-in amplifier (set in ac voltmeter mode with a bandpass filter). Since the bandwidth, Δf , is related to the pole quality factor Q ($Q = f_0 / \Delta f$), the noise power spectral density can be expressed as follows:

$$P(f_0) = \frac{V^2}{\Delta f} = \frac{V^2 \times Q}{f_0}$$
(5.3)

where f_0 is the centre frequency, which along with Q can be adjusted. V is the voltage fluctuation across a sample at a fixed frequency when a current passes through the sample. Considering intrinsic background noise of the equipment, V_b , which can be regarded as the voltage fluctuation when a very small current passes through a sample (for example 3.8 μ A), the voltage fluctuation due to the transport current can be determined. Using f instead of f_0 , the final formula for calculating noise power spectral density due to transport current at a frequency, f, becomes

$$P(f) = \frac{V^2 \times Q}{f} \tag{5.4}$$

The Q value was usually set at 100 during the noise measurements. This means the bandwidth is 1% of the centre frequency. The larger the Q value is, the more selective the bandpass filter becomes. In the experiments, the voltage fluctuations measured by the lock-in amplifier were sampled by an IBM PC. Each data point was obtained by averaging 100 measurements.

5.3 Measurement Set Up

Figure 5-1 (a) shows a schematic diagram of the setup for the noise measurements. The setup has three main parts. The first part is a cryostat with a controller for operation in the temperature range from 80 to 350 K. The second part is a current source which consists of a 9 volt battery and a wirewound variable resistor. The variable resistor has a resistance much higher than that of the superconducting films so that a constant current can be maintained during the measurements. The last part includes a lock-in amplifier and a personal computer which are used to detect the noise voltages.

During the noise measurements, the BiSrCaCuO films were mounted on a metal stage inside the cryostat. Between the metal stage and film substrate, a very thin mica sheet and a layer of thermally conducting grease were applied to minimize leakage and enhance the thermal conduction between the substrate and the cryostat. The cryostat was evacuated to a pressure of 10⁻³ torr by a rotary pump. The temperature of samples was controlled by pumping liquid nitrogen from a Dewar into the cryostat or by applying current to a heater in the metal stage. Four gold probes located inside the cryostat were connected to four adaptors installed on the wall of the cryostat. Two of the gold probes were used to supply current to the samples, and the other two were used as voltage probes. The two voltage probes were connected to a Princeton Applied Research Model 124A Lock-In Amplifier with a PAR 116 preamplifier. The lock-in amplifier was set in ac voltmeter mode and the bandpass filter was adjusted to select noises to be measured. The IBM personal computer was used to sample output from the lock-in amplifier through an IEEE interface and was also used to average the noise values.

The setup described above was used for measurements at temperatures from 82 to 300 K. Below 82 K, a second setup was specially designed for those samples with low superconducting transition temperatures ($T_c < 82$ K). The second setup consisted of an aluminum box (62 mm × 48 mm × 2 mm) with four gold probes installed. Samples were mounted on a stage located in the centre of the box. A piece of mica with thermally conducting grease underneath was also used to minimize leakage and improve the thermal conduction between the substrate and the box. An iron-constantan (type J) thermocouple was glued with silver paste to the aluminum plate near the sample. The reference junction of the thermocouple was immersed in a mixture of ice and water during the measurements. The sample was cooled simply by immersing the whole aluminum box in liquid nitrogen, which was contained in a styrofoam box. Temperature of samples was controlled by applying current to a nickel ribbon heater inside the box. Figure 5-1 (b) shows a schematic diagram of this setup.

Noise measurements were carried out at different temperatures, applied currents and external magnetic fields. The external magnetic field was produced by a copper coil wire (diameter is 0.56 mm) wound around an aluminum cylinder frame. Total resistance of the coils was 82 Ω . The sample being measured was located in the centre of the aluminum frame. The magnetic field in the centre of the frame was calculated using $B = \mu_0 In$, where B is the magnetic induction in Tesla (1 T = 10⁻⁴ gauss), μ_0 is the permeability constant ($4\pi \times 10^{-7}$ T×m/A), n is the number of turns per meter length, and I is the current passing through the coil. Figure 5-1 (b) gives the setup for the noise measurements under the external magnetic field.

5.4 Sample Preparation

Before doing the noise measurements, the superconducting films, which were fabricated using either CO_2 laser ablation or rf-sputtering, were patterned by photolithography. First, a layer of $1 \sim 1.5 \mu m$ photoresist (Shipley AZ-1350 or 1400) was applied on a cleaned BiSrCaCuO superconducting film. The film with photoresist was pre-baked at 90 °C for 10 minutes. The photoresist was exposed to UV light (300 W) through a photo mask for about 30 seconds. After this, the film was developed at room temperature for $20 \sim 30$ seconds. After the developing, a post-baking of photoresist was carried out at 100 °C for 10 ~ 15 minutes. Figure 5-2 shows the mask patterns and the patterned BiSrCaCuO films for the noise measurements.

The BiSrCaCuO film was etched in diluted hydrochloric acid (HCl) (10 drops of concentrated HCl in 20 ml DI water). The etching time varied depending on the thickness of films. Following this, the photoresist was removed and the sample was introduced into a vacuum system for contact evaporation. Ohmic contacts to the samples were made by evaporating high purity silver (99.999%) through a metal mask directly onto four areas created during the patterning process. Resistance of the contacts was measured and found to be in the range from 10^{-2} to $10^{-1} \Omega/cm^2$.

5.5 Results of Noise Measurements

5.5.1 Contact Noise

Before any measurements, the contribution of noise from contacts to the BiSrCaCuO film must be examined at temperatures in the range from 82 K to 300 K. The contact noise can be neglected only if the noise power spectral density measured is proportional to the sample length. In the experiments, samples with large contact noise were discarded. Only those samples with negligible contact noise were selected and used. During the noise measurements, the current and voltage probes were often reversed to further ensure the absence of contact noise. Figure 5-3 is a plot of the measured noise results at 100 K for one of the samples with good contacts. This sample had six contacts with different spacings. Noise power spectral densities were measured across different contact pairs at two currents (0.2 and 0.5 mA). As seen in figure 5-3, the noise power spectral density is nearly proportional to the distance between the contacts. The above results show that the contact noise, which is much smaller than the noise arising from the film, can be neglected for this sample.

Another point to be noted in figure 5-3 is that the noise power spectral density at 0.2 mA is larger than the noise power spectral density at 0.5 mA. This is because the noise power spectral density is not proportional to current applied to the films in superconducting state. An explanation on this will be given in the later sections. For those samples with small dimensions, the above method could not be used. The only way to examine the contact noise was to exchange the current probes and the voltage probes. Since a four-probe configuration was adopted for the noise measurements, the contact noise at the current carrying contacts was eliminated.

5.5.2 Variation of Noise Power Spectral Density with Temperature

Noise power spectral density of BiSrCaCuO films was first measured in a range from room temperature down to a value below zero T_c . The original purpose of this measurement was to study the noise behaviour near the superconducting transition, which would be an interesting region for the operation of infrared bolometers. In the measurements, the dc current applied across the samples was from 0.1 to 0.5 mA. The frequency was typically set at 100 Hz. It was found that for all the BiSrCaCuO superconducting films measured, the noise power density did not change much from room temperature to 120 K. Near the superconducting transition region, the noise power spectral density increased as the temperature was decreased and reached a maximum at a point near the tail range of the resistive transition. A further decrease of the temperature resulted in a decrease of the noise power spectral density. The noise power spectral density was undetectable at temperatures several K below the zero resistance temperature. The width of the noise peak depended on the width of the resistive transition. The wider the resistive transition was, the wider the width of the noise peak would be.

These noise-peak characteristics were observed in the BiSrCaCuO films deposited either by laser ablation or by rf sputtering. The phenomena were also observed in the films grown on either MgO single crystals or LaAlO₃ crystals, although the shape and height of the peaks observed were different. Figure 5-4 shows the noise peak results for one of the BiSrCaCuO films. The noise power spectral density rises near 106 K and reaches a peak at around 100 K. At a temperature of 90 K, the noise power spectral density becomes very small and undetectable. The variation of resistance versus temperature $(R \sim T)$ and the variation of derivative-resistance versus temperature $(dR/dT \sim T)$ of this sample are also shown in figure 5-4. The peak of the noise power spectral density is about 5 K below the peak of the dR/dT $\sim T$ curve and the peak is in the tail region of the $R \sim T$ curve.

To understand the origin of noise peaks in the BiSrCaCuO superconducting films, a thermal fluctuation model was used to analyse the noise behaviour of the films studied. If the noise peak near the superconducting transition is considered to be the result of thermal fluctuation, according to the thermal fluctuation model of Voss and Clarke^[5,24], the peak should obey the relation of

$$\frac{P_{v}(f)}{V^{2}} = \frac{\beta^{2} K_{B} T^{2}}{C_{v} [3+2\ln(l/w)] f}$$
(5.5)

where V is the average voltage across the voltage probes of the sample, K_B is Boltzmann's constant, T is the temperature, l and w are the length and width of the sample, f is the measuring frequency and C_V is the heat capacity of the sample. Based on the results published for BiSrCaCuO,^[5,26] the relation between C, and T is quite complicated near T_c . This is due

to a drastic change in C_v at the superconducting transition. In equation (5.5), β represents (1/R)dR/dT. Values of β^2 were calculated from data obtained in the resistance measurements. A comparison between the calculated β^2 and measured $P_v(f)/V^2$ (normalized noise power spectral density = noise power spectral density / square of the voltage drop across the sample) was then made. Figure 5-5 and figure 5-6 show the measured normalized noise power spectral density $P_n(f)$ (= $P_v(f) / V^2$) curves and the calculated β^2 curves for two of the samples. It can be seen that variation of the measured $P_v(f)/V^2$ with temperature is similar to one for the calculated β^2 , except for the shift of curves.

Using the Voss and Clark model and taking the value of heat capacity from a published paper,^[5,30] the absolute value of normalized noise power spectral density was also calculated and listed in Table 5-1. It is noted that the experimental values are much larger than those from the calculation.

 Table 5-1. Normalized Noise Power Spectral Density Values From

Measurements and Calculation for the BiSrCaCuO Fil	ms
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Sample	Temperature	Experimental Data (P/V ²)	Calculated Data (P/V ²)
Number	(K)	(Hz ¹)	(<u>Hz</u> ⁻¹)
B6S1	84.1	1.22×10 ⁻⁹	2.62×10 ⁻²³
B6S1	100.5	9.59×10 ⁻¹¹	1.49×10 ⁻²³
B6-10-2	79.2	1.31×10-9	1.63×10 ⁻²¹
B6-10-2	90.8	3.11×10 ⁻¹⁵	1.03×10 ⁻²⁴

A conclusion can be made by comparing the measured and calculated values of the normalized noise power spectral density. The noise value near the superconducting transition of the BiSrCaCuO films is about 9 to 14 orders of magnitude larger than that predicted using the thermal fluctuation mechanism. Therefore, it is apparent that thermal fluctuation mechanism can not be used adequately to explain noise peak properties in the superconducting BiSrCaCuO films, not only in terms of the absolute values of noise but also in terms of the change of noise in the superconducting transition temperature range.

5.5.3 Variation of Noise Power Spectral Density with Applied Current

In order to further understand the origin of the noise peaks in the BiSrCaCuO superconducting films, the relationship between the noise power spectral density and the dc current across the samples was specially studied at both room temperature and a low temperature (below the critical temperature). For the measurements at room temperature, the frequency of the lock-in amplifier was set at 100 Hz and a bias current of up to 7 mA was applied. Higher currents were not used since the thermal effect of the contacts would have been large enough to change the temperature of the samples, causing excess noise. Figure 5-7 presents the results for three of the BiSrCaCuO films deposited using laser ablation. Since the width of patterns on these BiSrCaCuO films was small, the maximum current that could be applied that would not result in a change of the sample temperature was around 1 mA.

From figure 5-7 it can be seen that the square root of noise power spectral density varies linearly with the variation of current across the samples. Since this relationship is the same as that predicted by the room temperature Voss and Clark model, $P_{\nu}(f) = I^2 (dR/dT)^2 T^2/3N$ (where N is the number of atoms in the sample), the normal state superconductor noise, from this point of view, seems to be caused by a thermal fluctuation mechanism. However, the actual measured values of the noise power spectral density at room temperature were about 6 orders of magnitude larger than the noise values calculated based on room temperature Voss and Clark's model. Therefore, other mechanisms may have contributed to the noise in BiSrCaCuO films at room temperature.

The Hooge's empirical formula, which is based on resistance fluctuation, was also applied to analyse the noise in normal state BiSrCaCuO films.

$$P_{\nu}(f) = \gamma V^2 / N f \tag{5.6}$$

where N_c , which is the total number of charge carriers in the sample, is equal to the product of the charge-carrier density and the volume of the sample, $P_v(f)$ is the noise power spectral density at a given frequency, V is the voltage drop across the sample, and f is the measuring frequency. The γ value was calculated from the experimental data of $P_v(f)$, V and f. The charge carrier density is taken as 10^{21} cm⁻³. Table 5-2 lists the calculated γ values for three samples. The resulting γ values are in the order of 10^4 to 10^7 for three samples at room temperature. These γ values are 5 to 12 orders of magnitude greater than that of a normal metal ($\gamma = 10^{-1} \sim 10^{-5}$).

Table 5-2 Value of γ for Three BiSrCaCuO FilmsCalculated Using Hooge's Empirical Formula

Sample Number	Temperature (K)	Applied Current (mA)	γ Value
B6-6- 1	290.3	0.51	1.15×10 ⁷
B6Q10	299.5	0.51	3.54×10 ⁴
B6S1	301.2	0.51	5.11×10 ⁵

From the results described above, neither thermal fluctuation nor resistance fluctuation can explain satisfactorily the noise behaviour in the normal state BiSrCaCuO films. The actual measured noise power spectral densities from the films at the room temperature are far larger than that predicted by these two models.

Noise measurements at different applied currents were also made at low temperatures (near the noise peaks). The frequencies used for the measurements were 100 Hz and 1 kHz. In contrast to the results obtained with the samples in normal state, the relationship between

the applied current and the square root of noise spectral density was not linear. These results are not surprising, since thermal fluctuation was excluded as the source of noise near or below the superconducting transition (as mentioned in the last section). Figure 5-8 shows the variation of the square root of noise spectral density with the applied current for two rfdeposited samples in the normal state and the superconducting state respectively. For the sample SC at a low temperature (T = 99.8 K), the average value of the square root of noise power spectral density increases slightly with the applied current and then reaches a maximum. A further increase of the applied current results in a decrease in the noise. Results on the sample SC are thus very different from that for sample M7W at 300 K.

Since the peak of the noise power spectral density near the superconducting transition is important for bolometric and non-bolometric applications, the effect of applied current through the films on the shape and height of noise peaks was also specifically studied. Noise measurements were made in the 77 K to 130 K temperature range and the centre frequency of the bandpass filter of the lock-in amplifier was set at 100 Hz. Figure 5-9 shows results obtained from two parts of a BiSrCaCuO superconducting film (B6S1 and B6S1A) deposited on MgO using laser ablation. The height of noise peak increased when the current of the sample was increased from 0.04 mA to 0.1 mA. The height of the noise peak decreased when the current further increased from 0.1 mA to 0.3 mA. This tendency is similar to the one observed in figure 5-8, except the current values corresponding to the maximum of the peak are different. This current is determined by different samples and different patterns. The location of the peaks in the temperature range is almost unchanged, but a second peak at lower temperature is observed at an applied current of 0.3 mA. Because the thermal fluctuation model, that is the Voss and Clark model, is not appropriate to explain the noise origin of BiSrCaCuO films in the superconducting state, and because the noise peaks were affected by the sample current, a vortex motion model was then considered.

The following equation, which is based on vortex motion, was used to analyse the noise.^[5.27]

$$P_{\nu}(f) = 4\Phi_{\rm p}V \tag{5.7}$$

Here Φ_0 is the flux quantum and is equal to 2.0678×10^{-15} Weber (=V/Hz), and V is average voltage drop across the samples. It should be mentioned that the equation was deduced with the assumption that density of free vortices was small and with the assumption that the phase slips of the vortices were 4π (2π for each member of the pair). In the derivation of the above equation, the noise from random voltage pulses generated by the vortex motion was considered. The Josephson relation was used to calculate the noise voltage and a shot noise model was adopted.

At a low applied current, density of free vortices is small and the vortices acts independently. Hence, noise spectral density can be explained by equation (5.7). The noise peak increases with the average voltage across the sample because the current passing the sample is increased at a fixed temperature. The increased current generates more free vortices and thus more noise. When the applied current is large enough, the density of free vortices increases to a level which causes a decrease in the mean free path. Under this condition, the free vortices are correlated to each other and phase slips are far smaller than 4π . Therefore, the Josephson relation gives a low value of voltage, resulting in reduction of the noise. This idea can be used to explain the phenomena displayed in figure 5-9. At a small current in the range from 0.04 to 0.1 mA, the magnitude of noise peak increases with the increase of current across the sample due to the effects described by equation (5.7). Further increase of the current, from 0.1 to 0.3 mA, causes a decrease of the noise peak due to the correlated vortices. The noise power spectral density was calculated based on equation (5.7) and compared with the measured $P_{i}(f)$ data in the small current range. Table 5-3 lists both experimental and calculated $P_{n}(f)$ data for one of the samples (B6S1 at an applied current of 0.1 mA).

Table 5-3 Measured and Calculated P.(f) for the Sample B6S1

Temperature (K)	Experimental data ($P_v(f)$) (10 ⁻¹⁶ V^2 Hz ⁻¹)	Calculated data ($P_{v}(f)$) (10 ⁻¹⁶ V ² Hz ⁻¹)
78.5	1.56×10 ⁻²	9.8×10 ⁻¹
80.2	1.09×10 ⁻¹	2.00×10 ⁻³
83.5	8.10×10 ⁻¹	8.27×10 ⁻³
85.9	1.65	1.30×10 ⁻²
87.7	2.18	1.63×10 ⁻²
89	3.72	2.04×10 ⁻²

at Different Temperatures.

Table 5-3 indicates that the calculated values are about 2 orders of magnitude less than the measured ones. It is obvious that the results obtained with equation (5.7) are much closer to the experimental results than the predictions made using Voss and Clarke's thermal fluctuation model. It is noted that the values predicted by the thermal fluctuation model are 9 to 14 orders of magnitude smaller than those from the experiments. Thus, it is believed that the noise near the superconducting transition in BiSrCaCuO films is associated with the vortex motion, rather than with thermal fluctuation. The two orders of magnitude of difference between the theoretical results predicted by equation (5.7) and the experimental results could be due to pinning of flux bundle. The reason for the second noise peak in the lower temperature range in figure 5-9, at an applied current is 0.3 mA, is still unknown. It is also noted that the location of noise peaks in figure 5-9 is almost unchanged at different applied currents. This is consistent with the resistance measurements of this sample. The resistance versus temperature curves do not show a shift even though the applied current reaches 0.3 mA. This fact suggests that the current across the sample is low enough to prevent apparent dissipation of vortex flow.

5.5.4 Variation of Noise Power Spectral Density with External Magnetic Field

Noise characteristics of BiSrCaCuO films were also investigated under an external magnetic field. As shown in figure 5-1 (b), the measurements were carried out inside a copper coil wound around an aluminium cylinder. The magnetic field was controlled by passing a current through the copper coil. During the measurements, the frequency of lock-in amplifier was again set at 100 Hz and a bias voltage was applied to the sample. Figure 5-10 shows the results for one of the samples.

The magnetic field was applied perpendicular to the *ab*-plane of the BiSrCaCuO film. The peak of the noise power spectral density decreased when the magnetic field was increased. The temperatures of noise peak was almost unchanged for the three curves, suggesting that the external magnetic field applied was far less than B_2 , which is the upper critical magnetic field. This change of the height of the noise peak with the external magnetic field can easily be understood if vortex motion as a source of noise is reconsidered. The increase of the magnetic field along the c-axis of BiSrCaCuO films resulted in an increase of number of vortices in the films, and subsequently a decrease in the mean free path. The phase slips of the correlated vortices decreased, causing a lower fluctuation voltage (Josephson relation $V=2\Phi_0 r$, where r is the rate of phase slips) and thus the generated noise.

5.5.5 Variation of Noise Power Spectral Density with Frequency

In most metals and semiconductors, noise varies with 1/f. It is not clear whether a similar variation is present in the high-T_c films. Accordingly, variation of noise power spectral density with the variation of frequency was also measured in the BiSrCaCuO films. The frequency of the lock-in amplifier was adjusted at values in a range from 2 Hz to 100 kHz. A fixed bias was applied to the samples during the measurements. Figure 5-11 shows the results for two samples deposited on MgO substrates by rf-sputtering. The bias current used in these cases was 0.2 mA and temperature was set at a value (100 K) near the noise peak.

The least square method was then used to fit the experimental data shown in figure 5-11 to the formula $P_v = Af^{\alpha}$ in order to determine the value of α . The resulting α is 0.78 \pm 0.06. Since the noise measurements at low frequencies were not as stable as the noise measurements at higher frequencies, an α value (f > 50 Hz) of about 1.12 was extracted by omitting low frequency data.

Noise measurements similar to the one described above were also carried out on the BiSrCaCuO films deposited on MgO substrates by laser ablation. Both low temperature and room temperature noise properties were investigated. The low temperature measurements were carried out at 77 K. Figure 5-12 shows the results for one of the samples. The applied current was 0.5 mA. It should be noticed that the measuring temperatures (77 K and 300 K) in figure 5-12 were not the temperature where the noise peak occurs. Therefore, it is not surprising that the noise at 300 K is larger than the noise at 77 K. The figure 5-12 also shows that the noise power spectral density has a near 1/f relation in the intermediate frequency range. At very high frequencies (f > 10 kHz), noise power spectral density has a relation between $1/f^2$ and $1/f^3$. At low frequencies, the noise power spectral density decreases and becomes unstable.

5.6 Discussion and Conclusions

Values of noise power spectral density have been measured with the variation of temperature, frequency, applied current and external magnetic field. The main conclusions from the present study are as follows. Noise power spectral density had a peak near the superconducting transition. The peak magnitude increased to a maximum with the increase of applied current. After this maximum, a further increase in the applied current caused a decrease in the noise peak. Also, for films in the superconducting state, the square root of the noise power spectral density was not proportional to the applied current. However, it did vary in a linear fashion with the current through the normal state BiSrCaCuO samples (at room temperature). Under the external magnetic field, which was applied perpendicular to the

ab-plane of the BiSrCaCuO structure, the noise peak near the resistive transition decreased when the magnetic field increased. In addition, the noise power spectral density of BiSrCaCuO films was found to have 1/f variation near intermediate frequency range (10 Hz to 10 kHz) in both superconducting and normal states.

For analyzing the noise behaviour of BiSrCaCuO films in normal state, effects of thermal fluctuation (room temperature Voss and Clark's model) and resistance fluctuation (Hooge's empirical formal) were considered. Although the noise power spectral density increased linearly with the applied current, the thermal fluctuation was not considered as a cause for the noise of the films in normal state because the actual measured noise values were 6 orders of magnitude larger than the ones calculated by the model of Voss and Clark. From the fitting of Hooge's empirical formula, very large γ values were resulted. Those γ values were 5 to 12 orders of magnitude greater than that of a normal metal. A. Maeda et al^[5,1] explained noise of superconductors in normal state by the universal conductance fluctuation and the local interference models, which are the models employed to explain noise in normal metals due to the defect motion. Unfortunately, they also found these models to be inappropriate. In summary, the noise of BiSrCaCuO films in normal state prepared in this work is much larger than that of normal metals. The noise appears to be due to mechanisms which are different from those in normal metals.

For noise behaviours of BiSrCaCuO films in superconducting state, the thermal fluctuation model and vortex motion model were used in order to understand the origin of the noise. The thermal fluctuation can not explain noise peaks near the superconducting transition mainly because the noise peaks did not have a linear relationship with applied current. Furthermore, the measured noise power spectral densities were 9 to 14 orders of magnitude greater than the noise values calculated based on thermal fluctuation. In addition, there was a temperature shift between the measured noise curve and the one calculated using the thermal fluctuation model. Thus, it was concluded that the noise peak near the superconducting transition was not caused by thermal fluctuation.

Vortex motion was used to explain the noise characteristics of samples in superconducting state. When the density of free vortices was small, the noise power spectral density was proportional to the voltage drop across the samples (or applied current). When the density of free vortices was large enough due to the applied current or external magnetic field, the mean free path of the vortex motion decreased and a strong correlated interaction was present among vortices, resulting in a decrease of the noise. These effects were corresponding to the noise properties measured with different applied currents and under different external magnetic fields. The actual measured noise values were only two orders of magnitude greater than the ones calculated by vortex motion model. Thus, the vortex motion model is more appropriate for explaining the origins of the noise in the BiSrCaCuO superconducting films. The two orders of magnitude difference in the noise magnitude could have been caused by another unknown noise mechanism.

In order to study the effects of grain boundary and / or sample quality on the noise of the superconducting samples, a comparison of the noise power spectral density of samples with different morphologies was also made. Figure 5-13 shows SEM photographs for three samples, and Figure 5-14 gives the results of the noise measurements on these samples. Sample 3 (B6-10-2) has the worst morphology uniformity and the smallest grain size among the three samples. The magnitude of the noise peak is the greatest (the geometry difference among samples was considered already). Sample 2 (H6S1) and sample 1 (LAL13) have almost the same grain size, but there are more micro-particles in sample 2. The magnitude of the noise peak for sample 2 is greater than that of sample 1. Therefore, it can be concluded that the noise of the superconducting films could be related to grain size, grain boundary and defects in the films. The increased noise could be due to pinning of flux bundle at defects and grain boundaries. From the above results, it is thus clear that more work is needed to improve further the morphology and grain uniformity for the BiSrCaCuO thin films. This is required before high quality films can be prepared for various optoelectronic applications.



Figure 5-1 (a) A set up for







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Figure 5-2 Masks and patterned BiSrCaCuO films.



Figure 5-3 A linear relationship between noise power spectral density and sample length at applied currents of 0.2 and 0.5 mA, suggesting negugible contact noise.



Figure 5-4 Noise power spectral density, resistance, and derivative resistance versus temperature for one of superconducting films deposited on a MgO substrate.



Figure 5-5 A comparison between measured $P_n(f)$ and calculated β^2 (sample B6S1).


Figure 5-6 A comparison between measured $P_a(f)$ and calculated β^2 (sample B6-10-2).



Figure 5-7 Variation of the square root of noise power spectral density with the applied current for three BiSrCaCuO samples.



Figure 5-8 Variation of the square root of noise power spectral density with applied current for films in the normal (bottom axis) and superconducting (top axis) states.



Figure 5-9 (a)

Variation of noise peaks with applied current in a small current range for a BiSrCaCuO film deposited by laser ablation.



Figure 5-9 (b)Variation of noise peaks with applied current in a large current rangefor a BiSrCaCuO film deposited by laser ablation.



Figure 5-10 Variation of noise peaks with external magnetic field for one of BiSrCaCuO samples deposited by laser ablation.



Figure 5-11 Variation of noise power spectral density with frequency at T =100 K for two samples deposited by rf sputtering.



Figure 5-12 Variation of the noise power spectral density with frequency for a sample (B6Q10) deposited on a MgO substrate by laser ablation.



Figure 5-13 (a)

A SEM photograph of a BiSrCaCuO film with medium grain size (sample 1, LAL13).



Figure 5-13 (b)

A SEM photograph of a BiSrCaCuO film with medium grain size and micro-particles (sample 2, B6S1).



Figure 5-13 (c)

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A SEM photograph of a BiSrCaCuO film with small grain size and micro-particles (sample 3, B6-10-2).



Figure 5-14 A comparison of noise peaks among the samples with different grain sizes and defects

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Chapter 6

Microwave Response in BiSrCaCuO Films

Several possible effects can be present when a superconductor is exposed to radiation. These effects give rise to bolometric and non-bolometric responses. The bolometric effect is a thermal process that is observable only near the resistance transition of the superconductor. Since it is a thermal process, the bolometric effect usually has a wide spectral response. However, it is slow compared to non-bolometric effect.^[6,1-6,6] When bolometers are fabricated using high-T_c superconducting material, the theoretical sensitivity can be two orders of magnitude greater than any other liquid-nitrogen-cooled detector currently available in the market^[6,7] at infrared wavelengths longer than 20 μ m. Thus, it is very useful to fabricate and study the bolometers made by high-T_c superconductors.

The non-bolometric effect often yields a response which is wavelength dependent. The possible mechanisms of non-bolometric response in superconductors include a nonequilibrium effect ^[67,68], phase slip effect ^[6,9], or an effect related to vortex motion^[6,10,6,11]. For high-T_c films with a granular structure, a random network of Josephson junctions at grain boundaries was thought to be responsible to non-bolometric effect ^[6,4,6,12]. In addition to the wavelength dependence of response, the response time of non-bolometric effect is extremely fast (< 1 nsec). Hence, detectors using both bolometric and non-bolometric effects can be constructed for detection of radiation.

In this chapter, the response of patterned high-T_c BiSrCaCuO films to microwave will be described. The films used were fabricated by rf sputtering. Analysis of the microwave response of the films at frequencies near 10 GHz will then be made based on bolometric and non-bolometric models. The responsivity of the BiSrCaCuO films will finally be presented and further improvement will be suggested.

6.1 Bolometric and Non-bolometric Effects

The bolometric effect is a pure thermal process and hence is wavelength independent. Assuming a bolometer is driven by a constant bias current, the change of voltage across the bolometer depends on the power absorbed by the bolometer:

$$\Delta V = S \cdot P \tag{6.1}$$

Here S is the responsivity of the bolometer given in V/W. P is the power of the incident radiation in W. In a superconductor bolometer which is operated near the resistance transition, S is strongly temperature dependent. The responsivity, S, can be expressed as:

$$S = \eta \frac{I_{B} \Delta R}{G \Delta T}$$
(6.2)

Where I_B is the bias current, $\Delta R / \Delta T$ is the slope of the resistance versus temperature curves at a temperature near transition, η is the optical absorptance of the material, and G is

the thermal conductance of the film to its surroundings. If the incoming irradiation is chopped at a chopping frequency ω , the responsivity becomes

$$S(\omega) = I_B \eta \frac{\Delta R}{\Delta T} \frac{1}{\sqrt{G^2 + \omega^2 C^2}}$$
(6.3)

where C is the heat capacity of the bolometer.

Under normal conditions, a superconductor bolometer is operated at a temperature near the midpoint of the resistance transition. Therefore, the width of the resistance transition of a superconductor bolometer determines the responsivity. The narrower the resistance transition region is, the larger the responsivity $(\Delta R/\Delta T)$ will be. The thermal conductance of the superconducting material also affects the responsivity. If a bolometer is made from a superconducting film deposited on an insulating substrate, the thermal conductance of the substrate is crucial to the responsivity of this bolometer. The lower the thermal conductance of the substrate is, the higher the responsivity of the bolometer will be. However, if the thermal conductance of the substrate is too low, the speed of the bolometers would decrease.

Normally, the response speed of a superconducting film bolometer is determined either by the heat capacity of the film and the thermal resistance of the film-substrate interface or heat conductivities of the film and the substrate. The responsivity of the bolometer increases in a linear fashion when the bias current increases. However, a too large bias current would cause self-heating of the device, which will move the operating temperature of the device to a point beyond the resistance transition edge and finally reduce the responsivity. For this reason, there is an optimal bias current for the responsivity of superconductor bolometers. In addition, optical absorptance of the superconducting material affects responsivity. To insure that most of the radiation is absorbed by the superconducting material, the thickness of the superconducting film should be comparable to the reciprocal of the absorption coefficient. Several models have been proposed by various researchers to explain mechanisms of non-bolometric effect in the superconductors. One of the models is based on the photoenhanced flux creep mechanism. In the photo-enhanced flux creep model, the pinned vortices are considered to be liberated by direct photon absorption or by thermal activation due to photon absorption. The dissipation of these liberated vortices produces a voltage, which is proportional to the number of free vortices and thus the intensity of the radiation.

The model used to explain the non-bolometric effect of a granular high-T_c superconducting film is based on the mechanism related to Josephson junctions at grain boundaries. The granular superconducting film can be viewed as an ensemble of many weak-linked junctions. Irradiation with photons having energies larger than the gap energy of the superconducting film breaks cooper pairs. A nonequilibrium population of quasiparticles is produced which reduce the critical current of the grain boundary Josephson junctions. If a constant bias current is applied to the superconducting film, the decrease in the critical current of the junctions by the irradiation will change the voltage across every junction. Hence, a voltage response of the films will be produced.

6.2 Sample Preparation and Measurement Set Up

Thin films of BiSrCaCuO deposited on unheated MgO or LaAlO₃ substrates by rf sputtering were used for the microwave response measurements. The BiSrCaCuO films deposited by laser ablation were not used at this stage because of the limitation of patterned sizes. The thickness of the superconducting films used is about 1 μ m.

The superconducting films were patterned into a bridge structure using photolithography. The patterning process was carried out by first coating the films with a layer of positive photoresist (about 1 µm thick). The coated photoresist was then exposed to ultra violet light with a photomask placed directly on it for about 30 to 40 seconds. The photomask containing the bridge structure was designed and fabricated in the laboratory. After the exposure, the photoresist was developed and subsequently washed in de-ionized water. Diluted HCl solution (20 drops of HCl in 40 cc of water) was used to remove the unwanted BiSrCaCuO areas, and the sample was finally immersed in acetone to wash away photoresist from the superconductor pattern. In most cases, the patterned samples had dimensions of $0.3 \times 3 \text{ mm}^2$.

Electrical contacts to the BiSrCaCuO films were made by evaporating high purity silver through a metal mask. Thickness of typical silver films for contacts is 1 µm.

The microwave response measurements were carried out with a microwave generator (HP model 8684A), a low frequency square wave signal generator, a lock-in amplifier (PAR model 124A) and a cryostat. During the measurements, the microwave generator was operated in the 5 to 12 GHz range and modulated at a frequency up to about 10 kHz. The microwave output was coupled to a rectangular waveguide and guided with a horn into the cryostat through a glass window on the top of the cryostat. To monitor the output power, part of the microwave was guided by a magic-T to a Schottky diode detector. Figure 6.1 shows a schematic diagram of the set up. A superconducting sample was located on the cold finger of the cryostat and a bias current was applied through two outer probes. The microwave response to the radiation was detected by measuring the voltage change across two inner probes, with the lock-in amplifier frequency tuned to that of the microwave modulation frequency.

6.3 Microwave Measurements

Microwave measurements on the patterned BiSrCaCuO superconducting films have been carried out at different temperatures, bias currents, incident microwave powers, and modulating frequencies. This section describes the results obtained from these measurements.

6.3.1 Effect of Temperature on Microwave Response

Microwave response was measured in the 80 K to 130 K temperature range where the superconducting transition occurred. During the experiments, a dc current of 200 μ A was applied. The output power of the microwave source was set at 10 dB (8 mW) and the frequency was set at 10.28 GHz with a modulation frequency of 1.65 kHz. The microwaveinduced voltage was measured using the lock-in amplifier set at 1.65 kHz.

Figure 6-2 (a) and figure 6-2 (b) show the results obtained for two of the samples. The microwave-induced electrical signals were very small at temperatures above the onset temperature of the resistance transition for both samples. At temperatures below the onset of resistance transition, a clear response can be detected. Figure 6-2 (a) shows results for the sample N10 where a clear voltage peak near the midpoint of the resistance transition (106 K) can be seen. In addition to the response within the resistance transition region, a wide voltage response with two other peaks is present at temperatures below the zero resistance range of the sample. The peak in the resistance transition region is roughly consistent with the variation of dR/dT for this sample. The response in the transition region (peak 1) could be due to the bolometric effect, which is proportional to the slope of the transition as described in equation (6.2). The response peaks (peak 2 and peak 3) at the temperatures below the transition region were not related to the slope of the resistance transition, and therefore were not due to the bolometric effect. The responsivity for the peak 1 was 0.02 V/W, and the resposivities for the peak 2 and peak 3 were about 0.06 V/W.

In figure 6-2 (b), the signal voltage of sample SC increases with the decrease of temperature from the onset value of 112 K and reaches the first maximum at 100 K. The signal voltage decreases to a minimum at 95 K and then increases to a second maximum at about 90 K. Finally, the signal voltage decreases as the temperature is decreased further. The peak, near the resistance transition of the sample, is seem to be shifted from the maximum of dR/dT. It is believed that this shift of the peak to a lower temperature is caused by the merging of bolometric and non-bolometric effects. To understand the origin of these different

signal responses, microwave measurements under different biases and incident powers were studied.

6.3.2 Effect of Bias Current on Microwave Response

To investigate the effect of the dc bias current, the microwave-induced voltage was measured as a function of bias current with the BiSrCaCuO sample under the illumination of a 10.28 GHz wave. The modulation frequency was again set at 1.65 KHz. The measurements were made specifically at the temperatures where the peaks of the microwave response occurred. Figure 6-3 displays the results for sample N10. At the temperature near the resistance transition of the sample (106 K), it is seen that the microwave-induced voltage increases linearly with the bias currents from 0 to 600 μ A. It is noted in the equation (6.2) for the bolometric response, the responsivity of the bolometric effect is proportional to bias current. This variation suggests that the microwave response near the resistance transition [peak 1 in Fig. 6.2 (a)] was the result of the bolometric effect. At 94 K, a temperature below the resistance transition, the microwave-induced voltage of the sample N10 remains essentially constant in the bias current range studied. This difference hence suggests that the microwave response below the superconducting transition in figure 6-3 was due to nonbolometric effect.

6.3.3 Effect of Incident Power on Microwave Response

The voltage response of the patterned superconducting films exposed to different microwave radiation powers was also investigated. The microwave power was varied from -15 dB to 10 dB with a fixed modulation frequency of 1.65 kHz. A constant bias current of 200 μ A was applied to the sample during the measurements. The measurements were carried out at two selected temperatures. One was at a value near the midpoint of the resistance transition where the first peak of the microwave response was located. The other was at a value below the zero resistance temperature of the sample where the second peak of microwave response appeared.

Figure 6-4 displays four voltage response curves versus microwave power for one sample. Two of the curves were taken at a temperature of 106 K with and without bias current. The other two curves were measured at a temperature of 94 K. It is seen that the signal voltage measured at the peak near the resistance transition (at 106 K) increases smoothly with the increase of incident power. This is again consistent with bolometric effect behaviour which may be described by $S = \Delta V/P$ (S is responsivity, P is incident microwave power and ΔV is the response voltage). The response voltage is proportional to the incident microwave power for a given responsivity. The responsivity is determined by the slope of the resistance transition, bias current and material itself.

Microwave response of the sample at a lower temperature (94 K) shown in figure 6-4 also increases with the incident microwave power but there appear to be steps in the curve at -5 dB and 5 dB. The increase of microwave response with incident power was expected with a non-bolometric effect because the density of quasiparticles is proportional to the absorbed microwave power. However, the steps in the curve were not expected.

In order to better study the phenomena, measurements similar to the above were carried out on another sample (N12B) with a small active area ($40 \times 40 \mu m^2$). The results for this sample are displayed in figure 6-5. The curve taken at 110 K is smooth. The one taken at 94 K which is below the zero resistance temperature increases with the incident power with three steps. This phenomenon suggests that the change of photoexcitation quasiparticles in the sample was not continuous with the increase of microwave power. In addition, it is noticed in figure 6-4 that the microwave-induced signals are present even without the dc bias current. This phenomenon was observed for both temperature ranges. However, the cause for the signals is still not known.

6.3.4 Effect of Modulation Frequency on Microwave Response

In addition to the above study, it is necessary to investigate the response speed of the BiSrCaCuO to the incident microwave radiation. This is because response speed is critical for a microwave detector. Generally, the response speed can be determined by applying a short microwave pulse and observing the corresponding voltage decay with time. Since a pulse microwave generator is not available in the present work, the transient measurements could not be made directly. Instead, an indirect method is applied to estimate the response speed of the BiSrCaCuO to microwave radiation. The method involves the measurement of the variation of the signal voltage with the variation of the modulation frequency. If the modulation frequencies are less than the inverse of response time of the film, the measured voltage is constant. However, if the modulation frequency is comparable to the inverse of response time of the film, the value of the microwave-induced signal starts to decrease.

During the measurements, the sample was maintained at a fixed temperature with a constant bias current passing through it. Power of the incident microwaves was kept constant and the modulation frequency was varied from 200 Hz to 50 kHz. Modulation frequencies higher than 50 kHz were not applied since the output power of the microwaves began to decrease at a modulation frequency of 20 kHz.

Figure 6-6 shows results of the microwave-induced voltage versus modulation frequency on the sample N10. At a temperature of 106 K where the peak of the bolometric response appeared, the microwave-induced voltage is essentially constant up to frequencies of 10 kHz. A further increase of the modulation frequency resulted in a sharp decrease of the voltage. This decrease of the voltage was not related to the decay time constant., but due to a reduction in microwave output. Hence, the real response time of the BiSrCaCuO to the incident radiation could not be determined due to the limitations of the equipment. However, the response time of the film still could be estimated. The bolometric response speed was less than 0.1 msec (the inverse of 10 kHz). Similar measurement was also carried out at a temperature of 94 K, where the non-bolometric effect appeared. As shown in figure 6-6, the characteristics were much the same as those at 106 K, except there is an increase of the response voltage from 3 kHz to 10 kHz.

6.4 Conclusions and Discussion

In order to study the potential application of BiSrCaCuO superconducting films for microwave detection, the microwave response of the patterned films was investigated. It was found that there were three peaks of microwave-induced voltage response in the 80 to 130 K temperature range. One was near the midpoint of the resistance transition, and the other two were below the zero resistance temperature. The response peak near the midpoint of the resistance transition has the following characteristics:

- The magnitude of response was proportional to the slope of the R-T curve (dR/dT).
- (2) The magnitude of response increased with the increase of bias current (I_R) .
- (3) The magnitude of response increased linearly with the increase of incident microwave power.

The above characteristics thus suggested that the microwave response in the resistance transition region was caused by a bolometric effect, since bolometric responsivity is proportional to these parameters.

The microwave-induced voltage response below the zero resistance temperature has the following characteristics:

- (1) The magnitude of microwave response was independent of the slope of the resistance versus temperature curve (dR/dT).
- (2) The response peak was not related to the bias current through the BiSrCaCuO samples.

(3) The microwave-induced voltage increased with the incident microwave power.

The above characteristics suggested that microwave response below zero resistance temperature was caused by a non-bolometric effect.

The origin of the weak microwave response of superconducting films at zero bias current is still not known (Fig. 6-4). One possible explanation is due to the enhancement of the noise response of the films. The incident microwaves generate excess quasiparticles or produce more free vortices. Thus the microwaves increase the dissipation of the films.

The response speed of the bolometric effect was also studied by measuring the change of response voltage with the modulation frequency of the incident microwaves. The resulting response time was estimated to be less than 0.1 msec. The bolometric responsivity of the films was measured to be 0.03 V/W (sample N10). The detailed calculation of the responsivity of the BiSrCaCuO films, based on the equation (6.3), could not be completed because the real thermal response time τ , which equals C/G (C and G are the heat capacity and thermal conductance of the sensitive region of the films), was not obtained due to the limitations of the equipment.

To improve further the responsivity of the bolometric effect of the BiSrCaCuO films, some considerations need to be taken. The films should be fabricated to a specific thickness so that there is uniform absorption of radiation. In addition to the thickness, it is necessary to apply a layer of antireflecting coating to the top of the BiSrCaCuO films in order to reduce the loss of microwave radiation due to reflection. The reflection from the high-T_e films is expected to be high due to the high density of carriers. Furthermore, the thickness of substrate used is important for the responsivity and response time. A thin substrate can reduce additional thermal effects and increase the response speed.

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Figure 6-1 A schematic diagram showing the set up for the measurements of the microwave-induced signals.

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Figure 6-3

Variation of microwave response with bias current at a temperature near the midpoint of the resistive transition (106 K) and at a temperature below the zero resistance temperature (94 K).



Figure 6-4 Variation of microwave-induced voltage of the superconducting films with incident microwave power.



Figure 6-5 Variation of microwave-induced voltage with incident microwave power for a sample with a fine size structure.



Figure 6-6 Microwave response of a BiSrCaCuO film with different modulation frequencies.

Chapter 7

Conclusions

The development of deposition processes and the study of the resulted thin films are important for the application of high-T_c superconductor materials. In the present work, the growth, characterization, noise analysis and microwave response measurements have been carried out on BiSrCaCuO thin films. One of the main contributions of this work is the development of CO₂ pulsed laser ablation technique for the deposition of high-T_c BiSrCaCuO superconducting films, which has not been studied in detail previously. The investigation results indicate that BiSrCaCuO superconducting films with high critical temperatures (up to 106 K) can be formed using CO₂ laser ablation, which has a lower cost than excimer laser ablation. Another contribution is the investigation of noise characteristics of BiSrCaCuO films both at room temperature and at temperatures below superconducting transition. The results from noise measurements in superconducting state BiSrCaCuO films are very useful to the determination of operation points of detectors or bolometers made from the films. Yet another contribution is the study of microwave response at temperatures below the superconducting transition. The conclusions of the thesis are summarized below.

7.1 Fabrication System

A laser ablation system has been designed and assembled to deposit BiSrCaCuO films. The system consisted of a 10.6 μ m TEM CO₂ pulsed laser, a vacuum chamber and auxiliary equipment. The pulse rate of the CO₂ laser used was 2 ~ 4 Hz, the pulse width was 200 nsec and the output power was 179 kW / pulse. The specially designed vacuum chamber was evacuated by a rotary pump and a diffusion pump. The angle between the incident laser beam and the normal of target surface was adjusted to 45 °C in order to obtain maximum deposition efficiency. A germanium window installed on the vacuum chamber was used to focus the laser pulse to a energy density of 3.6 J/cm² on the target. During the deposition of BiSrCaCuO films, the target was rotated to give uniform deposition. The oxygen pressure in the chamber was controlled so that films with appropriate compositional ratio would be obtained.

During the deposition, MgO substrates were placed parallel to the target surface with a typical distance of $2 \sim 5$ cm. A substrate heater was constructed for heating the samples. A substrate holder was specially designed using graphite so that the distribution of heat was uniform. The temperature of the substrate holder was monitored by a thermocouple and adjusted by a dc power supply, which was connected to the substrate heater. The range of substrate temperature was from 100 °C to 650 °C, and typical operating temperature was chosen at a value between 400 °C and 500 °C.

An annealing system containing a furnace and a stepping motor controller was used to heat treat the as-deposited BiSrCaCuO films. The stepping motor controller was specially designed so that the temperature of the furnace can be increased at a rate from 3 to 5 °C/min..

7.2 Growth and Characterization of BiSrCaCuO Films

The targets used for the deposition were prepared by mixing and sintering the pellets containing compounds of Bi_2O_3 , $SrCO_3$, $CaCO_3$, PbO and CuO. Several targets were tried and the ratio of Bi : Pb : Sr : Ca : Cu for the best target, B6, was 2 : 2.5 : 2 : 2.15 : 3.3. The films deposited using this target can be easily converted into superconducting phases after a heat treatment. It was confirmed that the presence of Pb in the films can enhance the formation of the 2223 high-T_c phase during the heat treatment. The effects of both oxygen pressure and substrate temperature during the deposition were specifically studied. It was found that the stoichiometry of the as-deposited BiSrCaCuO films was determined by the oxygen pressure in the deposition chamber. Although the substrate temperature was found to improve the morphology of the as-deposited films, it did not have strong influence on their stoichiometry.

For the post-deposition annealing process, a two-step heat treetment process, instead of the conventional one-step treatment process, was used. The purpose of the two-step treatment is to avoid excessive evaporation of film materials, and to obtain a high-T_c BiSrCaCuO film efficiently. The temperature of first step annealing was 800 °C and that for the second step annealing was between 840 and 865 °C. It was confirmed that the film quality was affected by the increase rate of annealing temperature. The optimum rate of temperature increase was determined by the oxygen pressure during the deposition. Furthermore, it was confirmed that the temperature of second step annealing is critical for the crystallization of the 2223 high-T_c phase. By employing a lower temperature for the second step annealing, films with low-T_c phases (10 K and 85 K) were resulted. Too high a temperature for the second step annealing led to decomposition of high-T_c phase (110 K). The optimum temperature for second step annealing was about 850 °C for BiSrCaCuO films deposited at (7~8) × 10⁻² torr of oxygen. In addition, it was also observed that quality of the films was affected by the humidity in the annealing furnace. The crystalline and compositional properties of BiSrCaCuO films were characterized by XRD, SEM and EPMA. X-ray diffraction patterns showed a mixture of 2212 and 2223 phases in most of the BiSrCaCuO superconducting films, with the c-axis perpendicular to the surface. A dominant 2223 superconducting phase ($T_c = 110$ K) was observed in the films that had higher critical temperatures. However, even in the best films, X-ray diffraction patterns still revealed polycrystalline structures instead of single crystal structures.

SEM photographs of good quality superconducting films showed large grains with continuous structures. The photographs indicate that superconducting films can be produced both with and without melting. Some micro-particles were also observed on the film surface, like the ones on the films deposited by short wavelength laser ablation. It was found that the density and size of the particles can be reduced by applying substrate heating. The thickness of the films was determined by the cross section SEM photographs of the films. The thickness of as-deposited BiSrCaCuO films was between 0.8 and 1.5 μ m, and the final thickness after heat treatment was around 0.4 ~ 1 μ m.

The composition and compositional uniformity of both as-deposited and annealed BiSrCaCuO films were studied by EPMA. The results showed that these films have a uniform composition with an area up to of 10×10 mm². The as-deposited BiSrCaCuO films were Biand Pb-rich compared to the starting target materials, due to high evaporation rates of Bi and Pb. For the annealed BiSrCaCuO films with good qualities, a ratio of Bi : Sr : Ca : Cu close to the standard high-T_c phase (110 K) ratio of 2 : 2 : 2 : 3 was found.

Electrical characteristics of the BiSrCaCuO superconducting films were investigated to determine the critical temperature and critical current density. Before the measurements, the superconducting films were patterned into bridge structures using photolithography and wet etching. Contacts to the films were formed by evaporating high purity silver. It was found that the resistance of contacts increased after a post-baking. Typical contact resistance between Ag and BiSrCaCuO was in a range from 10^{-2} to 10^{-1} Q-cm².

The critical temperatures of the BiSrCaCuO superconducting films were determined by the standard dc four probe method. A cryostat with a liquid nitrogen pump and a resistive heater was adopted to control sample temperature. The resulting onset critical temperature for the films was between 86 and 118 K, and the zero resistance temperature was in the 77 to 106 K range. These critical temperatures are the highest ones reported so far for BiSrCaCuO superconducting films deposited by CO_2 laser ablation.

The critical current density was also determined by the four probe method with a criterion of 1 μ V/mm. Most of the measurements were made on BiSrCaCuO films without patterning. The critical current density of the superconducting films was about $10^2 \sim 10^3$ A/cm². It was found that the critical current density decreased with an increase of magnetic field perpendicular to the current direction, due to the reduction in critical current density decreased with an increase of magnetic field perpendicular to the current direction, due to the reduction in critical current density decreased with an increase of magnetic field with an increase of temperature, and vanished to zero at zero critical temperature.

7.3 Noise Properties of BiSrCaCuO Films

From the noise measurements carried out in the present work, it was observed that the noise power spectral density of BiSrCaCuO films in normal state increased linearly with the increase of applied current. At a given applied current, the noise power spectral density was inversely proportional to the frequency. The noise power spectral density of BiSrCaCuO films in normal state was 6 orders of magnitude larger than that from calculation based on room temperature Voss and Clark's model. From the estimation of the Hooge's empirical formula, the resulting γ values were 5 to 12 orders of magnitude larger than the ones in normal metals, indicating that the noise of BiSrCaCuO films in normal state is much larger than the noise of a normal metal. The noise mechanism of BiSrCaCuO films in normal state thus can not be explained by both thermal fluctuation and resistance fluctuation models, which are the basic noise mechanisms for metals. Noise power spectral density of BiSrCaCuO films in superconducting state had a peak near the tail region of the resistive transition. This noise peak would not affect operation of bolometric detectors since the operating temperature is usually at the midpoint of the transition. However, the noise peak may affect non-bolometric detectors because they are operated at temperatures near the tail region. The noise peak also showed a 1/f relation at intermediate frequencies (20 Hz < f < 10 kHz). The peak value of the noise increased with the applied current and reached a maximum at a given bias current. A further increase of the applied current caused a decrease in the peak value of the noise. Under an applied magnetic field, the peak value of the noise declined with the increase of magnetic field.

An attempt was made to interpret the observed noise characteristics by the thermal fluctuation model. Although the variation of noise with temperature was similar to the noise variation predicted by the thermal fluctuation model, the magnitude of the measured noise was 9 to 14 orders of magnitude greater than the noise calculated by this model.

It is believed that the noise peak in the superconducting state BiSrCaCuO films is related to vortex motion in the films. This was substantiated by the results of the noise measurements at different bias currents and under different magnetic fields. The decrease in the noise peaks with the increase of magnetic field, which was parallel to the c axis of the films, was due to a strong correlated interaction among vortices. Also, the decrease in the noise peaks under higher bias current was caused by vortex interaction. Both magnetic field and bias current generated more free vortices in the superconducting films due to excess energy. The movement of the generated vortices interacted with each other, leading to a reduction of noise. The confirmation of a relation between the noise and external magnetic field is very useful for real device design. Results of calculation using the vortex model, assuming the pinning of single flux line, showed values which were two orders of magnitude lower than that of the measured noise. Hence, the vortex motion model is more appropriate one to describe the mechanism of noise peak in the BiSrCaCuO films. The difference of two orders of magnitude could be due to the pinning of flux bundles. It could also be caused by the background noise in the superconducting films, due to the presence of grain boundaries

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and defects. Finally, it was observed that superconducting films with large and uniform grains have lower noise values than those with small and non-uniform grains.

7.4 Microwave-induced Response of BiSrCaCuO Films

Microwave-induced voltage measurements were carried out in the temperature range from 80 to 130 K using a 10.28 GHz microwave source modulated at 1.65 kHz. Three peaks were observed in the curves of microwave-induced voltage versus temperature. The peak near the midpoint of the resistive transition of the superconducting films is due to bolometric effect. The magnitude of this peak was proportional to the slope of the resistance transition, bias current, and incident microwave power. The response time of the bolometric effect was estimated from the variation of microwave-induced voltage with the modulation frequency of the microwave. The estimated value of response time was less than 0.1 msec. A precise response time value was not obtained due to limitation of the microwave source used. The other peaks, which appeared at temperatures below zero resistance transition and were independent of the applied current, are believed to be caused by non-bolometric effect. The non-bolometric response was observed to increase in steps when the incident microwave power increased continually, suggesting that the increase of quasiparticles of superconducting films is not continuous. Finally, a weak voltage response under microwave illumination was observed in BiSrCaCuO films even without the applied bias current. Although the origin of this weak response is not clear, it was speculated that this response was caused by the enhancement of noise of the films.

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