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Vinod. Kataria
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Ba-Y-Cu-O Superconductive Ceramics and Thin Films

by

Vinod Kataria

A Thesis
submitted to the
Faculty of Graduate Studies and Research
through the Department of
Engineering Materials in Partial Fulfillment
of the requirements for the Degree of
Master of Applied Science at the
University of Windsor

Windsor, Ontario, Canada
1989

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ABSTRACT

Bulk superconducting ceramics of $Y_1\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ were fabricated by mixing stoichiometric amounts of $Y_2\text{O}_3$, $\text{BaCO}_3$, and $\text{CuO}$ and heat treating in a tube furnace. Superconductivity in the bulk samples was demonstrated by Meissner effect, and zero resistance by four probe method.

Thin films of $\text{YBaCuO}$ were fabricated by reactive sputter deposition using ceramic targets. The deposition unit was equipped with a triode sputtering source and an auxiliary RF power supply. The flow rates of the sputtering gas ($\text{Ar}$) and the reactive gas ($\text{O}_2$) were controlled by mass flowmeters. The sputter deposition parameters monitored in this experiment were substrate to target distance, RF power density, and target composition. The deposited films were analyzed by X-ray diffraction and X-ray photoelectron spectroscopy.

The films deposited from stoichiometric target were found to be deficient in barium content. The target composition was varied in the ratio of $\text{Y:Ba:Cu}$ from 1:2:3 to 1:4:6 and 1:6:3 and the target composition for obtaining stoichiometric films was projected from the data obtained in this way.

The as deposited films were amorphous and were crystallized by annealing under flowing oxygen. The crystallization temperature for the superconducting phase was determined. The crystallization kinetics of the films were performed and an approximate value of activation energy was found that gave an indication of mechanism of crystallization for the superconducting phase.
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Chapter I
INTRODUCTION

In 1913, the Dutch physicist, Kamerlingh Onnes(1), discovered that the electrical resistance of mercury drops absolutely to zero at a temperature of about 4K, and below this temperature, the resistance remains zero. Electric currents flowed in the mercury in the absence of voltage differences and without causing the heating associated with electric resistance in conductors. Onnes declared that "No doubt was left of a new state of mercury in which its resistance has practically vanished . . . Mercury has passed into a new state which on account of its extraordinary properties may be called the superconducting state."

For about half a century after its discovery, superconductivity was one of the outstanding mysteries of physics. Then in 1957, physicists John Bardeen, Leon Cooper, and Robert Schrieffer published a historic series of papers describing the phenomenon(2). The scientists, who won a Nobel prize for their work in 1972, proceeded from an already well-established observation; that an electric current moving through an ordinary metal is essentially a stream of electrons flowing through a fixed crystal lattice. Electric resistance arises when from time to time, electrons smash into the crystal lattice, losing energy. But in superconductors, the electrons become attracted to one another, and instead of travelling the lattice one by one, travel in pairs. These electron pairs engage in an elaborate kind of dance: when one zigs, the other zags: when one moves to the right the other moves to the left. In other words, they become mirror images of each other, so that when one bangs into an impurity, the second one ricochets, regaining the energy that the first one lost. The net result is that the pair neither gains nor loses its energy as it travels through the crystal lattice.
Spurred by high tech dreams, scientists have spent entire careers searching for materials that become superconductors at higher temperatures. Superconductivity is not a rare phenomenon. About half the metallic elements are superconductors and niobium is the metallic element with the highest transition temperature (9.3K). In addition to metals, a large number of alloys are superconductors and the highest transition temperature is 23K for Nb₃Ge. Even conducting polymer, (SN)x has been found to become superconducting at about 0.3K. In their search for better superconductors, scientists left no plausible stone unturned and even had a go at some pretty implausible stones. In the belief that some biological molecules might be superconducting, for instance, one investigator bred bacteria in a strong magnetic field, hoping to grow superconducting bacteria. It was a crazy idea but not too crazy to work with.

After 75 years of research, the practical high temperature extreme of superconductivity was about 23K for Nb₃Ge. All materials from that era entailed the use of liquid helium refrigeration systems. When cooling cost and other factors are taken into account, liquid helium is 1000 times more expensive than a liquid nitrogen cooling system. So all the wonderful applications of superconductors have been used so far where nothing else would do - as the magnets in giant atom smashers, and in the latest medical scanners.

Doctors Alex Mueller and George Bednorz at IBM's Zurich Research Labaratory had read a report in a French chemistry journal about a promising new compound oxide of lanthanum, barium, and copper and decided to test this compound for superconductivity. After three years of trial and error, they found a sharp drop in resistance at 30K. The paper was published in September 1986 (3), and opened the floodgates. Early in 1987, Chu and his associates found superconductivity near 95K in a mixed phase sample containing yttrium, barium, copper and oxygen (4). The discovery of the superconductors that can operate above liquid nitrogen temperature was called "the Woodstock of physics", "a new industrial revolution", and "an incredible advance" by some,
and it generated a wave of shock and excitement in the scientific community. The nature of the research which requires physicists, material scientists, electrical engineers, chemists, and ceramists is a textbook example of the vitality of interdisciplinary research—the hallmark of modern materials research.

**Landmark Advances of High Temperature Superconductors**

Since the discovery of Dr. Chu, much more has been accomplished in newly established field of high temperature superconductivity (HTSC) than anyone would have imagined in such a short time. Bell Labs was the first to achieve the single phase compound of Y_{1}Ba_{2}Cu_{3}O_{7-x}, with a critical temperature of 91K, and a critical current density Jc, of only about 1100A/cm² at 77K in a zero magnetic field. So a couple of years ago, very brittle superconductive oxide material was discovered with a startling high critical temperature, a current carrying capacity too low to be useful, and very challenging processing problems. Of particular concern was its instability to atmospheric moisture. But the worldwide research effort has raised the Jc of the bulk material to 17,000A/cm² at zero field and 4000A/cm² at 1 Tesla, via melt texturing (5).

Until quite recently, however, it seemed as if the 1,2,3 rare earth compounds were a serendipitous discovery that might be unique. Then on Jan. 21, 1988, researchers at Japan's National Institute of Research in Inorganic Materials (NIRIM) announced the preparation of an HTSC compound that did not contain any rare earths. This stable bismuth, calcium, strontium, copper oxide compound showed a drop in resistivity and susceptibility at 120K and still retained its properties after a month in air. At the World Congress of Superconductivity in Houston, University of Arkansas physicist Allen M. Herman described his discovery of a thallium, calcium, barium, copper oxide compound containing a high temperature phase (Tl_{2}Ca_{2}Ba_{2}Cu_{3}O_{10+x}) with a Tc onset of 120K and zero resistivity at 100K. The high Tc onset phase was isolated and found to have a Tc onset of 140K.
With two more High Tc compounds appearing within one year, there is every reason to believe that many others exist. As with melt texturing of 1,2,3 material, there is no fundamental limitation to current carrying capacity.

Applications

Before practical applications can be realized, the material properties must be improved. For example, critical current density must be improved substantially. Some possible applications for this embryonic technology are discussed below.

Power Transmission

Conventional overhead transmission systems typically sacrifice ten to fifteen percent of power through resistance loss. Recovery of this lost energy would represent enormous savings. Superconductors used in this way must be able to carry large currents. But so far, the new materials are far from their ideal critical current density. This will probably be improved through research.

Low temperature underground transmission lines are technically feasible; but economic viability depends on large power transfer capability. Large scale hydro generators are technically feasible, but there will be a need for them to handle enormous fields up to fifty years. It may be many years before this application is realized.

Any new magnet design will spin off better generators, motor and energy storage devices. In fact, the availability of superconducting magnets could change the entire concept of motor design.

There appear to be two barriers to the realization of good magnets for motor and other applications. The materials are still too brittle, and the critical current densities needed are much larger than those yet attained. The magnetic field produced by any electromagnet is a function of the number of ampere-turns of the magnet. If the current carrying capacity of the new superconducting wires is less than that of copper, new magnet devices will be bulkier and more expensive.
Magnetic Energy Storage

This concept has created enormous excitement. Until now, electricity has been governed by the dictum, "use it or lose it". Now a moving electrical charge could be stored in enormous superconducting rings, for use in peak periods. A superconducting magnetic field of 10 Tesla could store 40MJ per cubic metre. In more exotic schemes, magnetic storage could replace batteries, thus providing the power for practical electric cars.

Microelectronics and Computers

Will superconducting electronics technology herald what some have called the "third wave of electronics", following on the heels of vacuum tube and transistor? Predicted benefits in electronics include high speed circuits, reduced power consumption and Josephson junction technology. However, some of the early excitement about these applications has moderated with the realization that 80 percent of the resistance in microelectronics circuits is in the wiring, which is also responsible for time delays.

Medical Diagnosis

Nuclear Magnetic Resonance (NMR) body imaging scanners rely on conventional superconducting magnets. High temperature superconductors could provide magnets ten times more powerful than any now in use.

Magnetic Levitation

With the development of high temperature superconducting magnets, technological limitations to the development of Maglev transportation - particularly those linked to reliability and refrigeration are considerably lessened. This technology, like most others, will wait for a good, non-brittle, high-current-density, affordable, flexible, high-temperature superconducting wire.
Chapter II

LITERATURE REVIEW

2.1 Properties of the Superconducting State

To obtain some clues to the origin of superconductivity it is helpful to summarize the more important properties of superconductors.

Zero Resistance

Superconductors show zero resistance for direct currents and not-too-high frequency alternating currents. The frequency at which resistance begins to appear corresponds to the microwave or long-wave infrared portion of the spectrum. The difference between the reflection coefficient of a superconductor in its superconducting and normal state is shown as a function of frequency for a few typical metals in Fig. 1. The curves are all roughly similar in shape, and show a steep fall to zero commencing at a frequency vo which varies from metal to metal. The value of vo for a particular metal depends on the temperature, and tends to zero as the temperature rises towards the critical temperature.

Crystal Structure

Studies of the crystal structure of superconductors by X-ray crystallography as the metal is cooled below the critical temperature have revealed no change in the lattice structure, either as regard the symmetry of the lattice or the actual lattice spacing. It has also been found that properties that depend on vibration of the crystal lattice such as the Debye temperature θ and the lattice contribution to the specific heat, are the same in normal and superconducting phases. Therefore,
we can infer, that superconductivity is not associated with any change in the properties of the crystal lattice.

2.2 The Bardeen-Cooper-Schrieffer theory

The Electron-Lattice Interaction

An early step forward in the search for a microscopic theory of superconductivity came in 1950 when Froehlich (7) pointed out that the electron-phonon interaction was able to couple two electrons together in such a way that they behaved as if there were a direct interaction between them. In the interaction postulated by Froehlich, one electron emits a phonon which is then immediately absorbed by another electron. He was able to show that in certain circumstances this emission and subsequent absorption of a phonon could give rise to a weak interaction between the electron of the sort. This interaction can be represented schematically as in Fig. 2, where the straight lines represent electron paths, the wavy line represent a phonon and momentum is conserved during the process.

It turns out from the detailed quantum mechanics of the process that if \( e_1 - e_1' \) is less than \( h\nu_q \), where \( e_1 \) and \( e_1' \) are the energies of the first electron before and after the virtual emission of the phonon and \( \nu_q \) is the frequency of the phonon, then the overall result of the emission and absorption processes is that there is an attraction between the two electrons. There is also the Coulomb repulsion between the electrons; whether the net interaction is attractive or repulsive depends on whether the phonon-induced attraction exceeds the Coulomb repulsion.

Cooper pairs

The conduction electrons in a metal in the normal state can be described as having energy \( e \) and momentum \( p \), and for nearly all practical purposes, it is permissible to neglect interactions between them. The probability that a given eigenstate is occupied by an electron is given by the Fermi-Dirac distribution function
\[ f(e) = \frac{1}{\pi} \frac{1}{e^{\frac{e}{e_f}} + 1} \]

where \( e_f \) is the Fermi energy. At absolute zero temperature, the Fermi-Dirac distribution function takes the form of a step-function, as shown in Fig. 3. The points that represent the momenta of the electrons in three-dimensional momentum space occupy a sphere of radius \( p_f \), known as the "Fermi sphere," where

\[ p_f = \sqrt{2me_f} \]

Following Froehlich's hypothesis that the electron-electron interaction can be transmitted by phonons, the next step towards a microscopic theory of superconductivity was taken by Cooper(8). He discussed what happens when two electrons are added to a metal at absolute zero so that they are forced by the Pauli principle to occupy states with \( p \) greater than \( p_f \) as shown in Fig. 4. He was able to show that if there is an attraction between them, however weak, they are able to form a bound state so that their total energy is less than \( 2e_f \). As shown in Fig. 4, the two electrons scatter each other repeatedly in such a way that their individual momenta are constantly changing. In each scattering event, the total momentum of the two electrons is conserved. During this scattering process, the electrons are subject to their mutual interaction. If this is an attractive one, the potential energy which results from it is negative. If the interaction is of the sort as described by Froehlich, arising from virtual emission and absorption of a phonon, it turns out from the detailed theory of Cooper that the probability of scattering is appreciable only if the energy deficit between the initial and intermediate states is small, i.e., \( e_1 - e_1' \approx hv_q \). If the metal is considered to be at absolute zero, all the eigenstates with energies up to \( e_f \) are occupied, so both \( e_1 \) and \( e_1' \) must be above \( e_f \) in order not to violate Pauli principle. The lowest values of \( e_1 \) and \( e_1' \), which are above \( e_f \) and at the same time satisfy \( e_1 - e_1' \approx hv_q \) lie within an energy in the interval \( hv_1 \) in the neighborhood of \( e_f \), where \( v_1 \) is an "average" phonon frequency typical of the lattice, about half the Debye
frequency. Since $e = p^2/2m$, this limitation on the allowed values of $e_1$ and $e_1'$ means that $p_1$ and $p_1'$ must lie within a range of $p = mv/|v|$ of the Fermi momentum $p_f$. And all the pairs of $p_i$ and $p_j$ must satisfy the condition $p_i + p_j = P$, the allowed values of $p$'s can be found by the construction shown in Fig. 5. These momenta all begin or end in the ring whose cross section is shaded. The number of such pairs is proportional to the volume of this ring and has a very sharp maximum when $P = 0$, in which case the ring becomes a complete spherical shell. Thus the largest number of scattering processes, yielding the maximum lowering of energy, is obtained by pairing electrons with equal and opposite momenta. The most important result from Cooper's analysis is that in forming a pair with equal and opposite momenta, the lowering of potential energy due to interaction exceeds the amount by which the kinetic energy is in excess of $2e_f$.

The Superconducting Ground State

The great step forward towards a microscopic theory of superconductivity came in 1957 when Bardeen, Cooper and Schrieffer (2) were able to show how Cooper's result could be extended to apply to many interacting electrons. The fundamental assumption of the BCS theory is that the only interactions which matter in the superconducting state are those between any two electrons which happen to make up a Cooper pair. The effect of any one pair on the presence of all other electrons is simply to limit, through the Pauli principle, those states into which the non-interacting pair may be scattered, since some of these states are already occupied. Cooper's result can be applied equally to the situation in which two non-interacting electrons originally occupying the states in the Fermi-sea, with initial momenta infinitesimally below $p_f$, are transformed into a Cooper pair above the $p_f$ with equal and opposite momenta when the pairing interaction is switched on. The lowering of their potential energy due to their mutual interaction exceeds the amount by which their kinetic energy exceeds $e_f$. If we can do this for one pair, we can do this for many pairs and lower the energy even further. There is a limit to the number of electrons which
may be raised from \( e \) less than \( e_r \) to form Cooper pairs with a resultant lowering of the total energy. In the beginning, when Cooper pairs are formed, they occupy states very close to \( e_r \) and the interaction reduces the net energy of the system. But when more and more pairs are formed, they must occupy higher energy states (Pauli principle), whose kinetic energy cannot be offset by pairing energy. Thus a condition is reached in which the lowering of the potential energy is insufficient to outweigh the increase in kinetic energy, and it is no longer possible to lower the total energy of the electrons by forming Cooper pairs.

The state of lowest energy (the ground state) occurs when all the electrons with momenta within a range \( p = m \hbar v / p_f \) about \( p_f \) are coupled together in Cooper pairs having opposite momentum and spin. The total energy of the interacting electron pairs is constant despite the fact that their momenta are constantly changing.

### 2.3 The Concept of an Energy Gap

The absorption of infrared radiation by superconductors is shown in Fig. 1, and the radiation is heavily absorbed when the photon energy reaches a threshold value to excite an electron to next available energy level. The energy of the Cooper pair simply cannot be increased by increasing the momenta of the electrons and at the same time maintaining the condition that their momenta are equal and opposite. The pairs break up so that the electrons no longer have equal and opposite momenta. In this case they are unable to take part in as large a number of scattering events as when they formed a Cooper pair, and the net negative potential energy contribution resulting from their interaction is zero. The splitting of the pair results in the disappearance of their binding energy; rather in the same way that external energy is necessary to split up a molecule into its constituent atoms. Also if the state \( p_i \) is occupied by an electron but the state \(-p_i\) is empty, then the pair state \((p_i, -p_i)\) is not available to the remaining Cooper pairs. Therefore the number of scatter-
ing events in which they can participate is reduced, and a corresponding decrease in their binding energy results in an increase in total energy of the entire system of the electrons.

According to BCS theory, the amount of energy required to break a Cooper pair to produce two electrons with momentum $p_i$ and $p_j$ (also called quasi particles of momentum $p_i$ and $p_j$ with complementary states $-p_i$ and $-p_j$ being empty) is

$$E = E_i + E_j = \left[ (e_i - e_j)^2 + \Delta^2 \right]^{\frac{1}{2}} + \left[ (e_j - e_i)^2 + \Delta^2 \right]^{\frac{1}{2}}$$

where $e_i = p^2/2m$ and the positive square roots are taken. Hence the minimum amount of energy required is $2\Delta$ which occurs when $p_i = p_j = p_f$ is mathematically satisfied. There is thus an energy gap of magnitude $2\Delta$ in the excitation spectrum of the superconductors and radiation of frequency $\nu$ is absorbed only if $\hbar \nu > 2\Delta$.

**The Critical Temperature**

If the temperature of the superconductor is raised from below critical temperature towards critical temperature, a number of Cooper pairs are broken into quasi particles by thermal agitation. The energy gap as explained above is not constant but decreases as the temperature is increased. An electron in the state ($p_i$) without a partner in ($-p_i$) prevents the pair state ($p_i$, $-p_i$) from being available to Cooper pairs, and the pair interaction energy is diminished because the number of scattering events in which they may participate is lessened. This decrease in the pair interaction energy means a decrease in energy gap. As the temperature rises, the number of quasi particles increases and the energy gap continues to fall until a critical temperature is reached where the energy gap is zero. This value of critical temperature is predicted by BCS theory as

$$2\Delta = 3.5kT_c$$
2.4 New Superconductors and Theory

After the new superconductors were discovered, one of the first questions was, "What type of superconductivity do they have?" Does one again have Cooper pairs or not? Esteve et al.(9) measured the I-V characteristics of sintered ceramic and observed weak link characteristics inherent to the superconductors. They also conducted microwave irradiation experiments to conclude that Cooper pairs were present.

The presence of Cooper pairs was confirmed by Gough et al.(10) by investigating the output of an r.f.squid magnetometer, identifying small number of flux quantum $Q_0$ jumping into and out of a ring of YBC superconductors.

2.5 Validity of BCS Theory

In the BCS theory, the electron-phonon interaction is responsible for Cooper pair formation and the maximum value of critical temperature as predicted by BCS theory is in the range of 30 K for any type of superconductors. The actual transition temperature of over 90 K in Y$_2$Ba$_2$Cu$_3$O$_{7-x}$ cannot be explained by BCS theory. New theories with different mechanisms for electron interaction have been cropping up everyday since the oxide superconductors were discovered. The amount of literature published on this subject is enormous, and the right information (mechanism) may be buried in the volumes of papers available on this subject.

2.6 Bulk Superconductors

Bednorz and Mueller found a high Tc superconductor in La-Ba-Cu-O system (3), and since their discovery oxide superconductors have attracted the attention of many researchers. The superconductor phase in this system was identified to be tetragonal K$_2$NiF$_4$ type structure (12, 13). The critical temperature of this oxide is 40K. It was later shown that the whole family
(La\textsubscript{1-x}M\textsubscript{x})\textsubscript{2}CuO\textsubscript{4} (where M = Ca, Sr, Ba) are superconductors by Kishio et al. (14) and by Cava et al. (15).

The Y-Ba-Cu-O superconductor with Tc above 90K was reported by Wu et al. (16). They reported that the samples examined by them had nominal composition of (Y\textsubscript{0.6}Ba\textsubscript{0.4})\textsubscript{2}CuO\textsubscript{4-\gamma} and contained more than three different phases, whose X-ray diffraction pattern did not seem to fit with K\textsubscript{2}NiF\textsubscript{4} or ABO\textsubscript{3} structure.

Muromachi et al. (17), in order to identify the superconducting phase in the YBaCuO system, performed a phase search and electron microscopic studies. Based on powder X-ray diffraction, they concluded that the composition of the superconducting phase was Y\textsubscript{1-x}Ba\textsubscript{x}CuO\textsubscript{4} (where 0.6 < x < 7) and that the structure of the phase was a perovskite related structure (orthorhombic a = 3.89Å, b = 3.82Å, c = 11.72Å or possibly tetragonal a = 3.83Å, c = 11.7Å).

Katano et al. (18) confirmed that the superconducting phase in the YBaCuO system has the composition Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x}. By preparing a single phase material that showed a metallic character with a sharp transition at 94 K. The crystal structure of Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x} was determined by Rietveld profile analysis of neutron powder diffraction data measured at 10K and 120K. The structure of this compound was confirmed to be orthorhombic with lattice constants a = 3.8869Å, b = 3.8238Å, and c = 11.653Å at 10K and a = 3.8875Å, b = 3.8265Å, and c = 11.662Å at 120K. The refined crystal structure parameters are listed in Table 1 for the measurements at 10K and 120K. As shown in Table 1, no anomalous change in the crystal parameters between the superconducting and normal conducting phases were observed, i.e., there is no phase transition or other structural anomalies.

The crystal structure of the Y\textsubscript{1}Ba\textsubscript{2}Cu\textsubscript{3}O\textsubscript{7-x} is shown in Fig. 6 and as can be seen.

1. The Ba layers, the Cu Layers and the Y layers have a stacking order of Cu, Ba, Cu, Y, Cu, Ba.
2. The Y layer does not contain oxygen atoms.

3. The Cu layer which intervenes between two Y layers (this Cu layer is conventionally called basal plane) has an oxygen deficiency.

4. That O atoms align themselves preferentially along the a-axis and causing the orthorhombic distortion ao>bo of the lattice.

Effect of Oxygen

The effect of oxygen on the crystal structure and the superconducting properties of Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ was studied separately by Kubo et al.(19) and Muromachi et al.(20). Kubo et al.(19) reported that with increasing oxygen deficiency, superconductivity was suppressed reversibly and that the axial ratio ao/bo in the orthorhombic phase approached unity and co value increased. The reported temperature of the structural transformation from orthorhombic to tetragonal is between 950°-980°C as per Kubo et al.(19), while Muromachi et al.(20) report the same transformation around 900°C. Kubo et al. give the number of oxygen atoms in tetragonal phase from 6.3 and below, while Muromachi et al. report the number to be less than 6.0 in a unit cell of Y$_1$Ba$_2$Cu$_3$O$_x$ of tetragonal symmetry. In both cases, it is reported that the oxygen content is strongly affected by the cooling/quenching process of the sample from higher temperatures.

2.7 Thin Films

Perrin et al.(21) deposited films of 123 material by a simple dc sputtering technique on Y$_2$BaCuO$_3$ substrate and then found the effect of annealing conditions on the properties of film. The as deposited films were amorphous and insulating. The films were found to be very sensitive to atmospheric contamination. On the other hand, the high temperature annealing needed in order to crystallize the film has to be accurately controlled, as crystal growth competes with "internal" contamination coming from film-substrate interaction. A drastic degradation of the resistive
behaviour was observed when the films were annealed in air instead of an oxygen environment. This was apparently due to formation of BaCO₃ as detected in the X-ray diffraction patterns of the films. The critical temperature of the films also depended on the annealing temperature through crack formation due to thermal strains. T_{cm}(mid point transition temperature) was 75 K for films annealed at 875°C, and 72 K for films annealed at 950°C. The rate of cooling also affected the properties of the films because of oxygen concentration in the films. For a cooling rate of 3°C/min., the T_{cm} was higher than compared to films cooled at 20°C/min.

Yoshida et al. (22), have studied the effect of annealing temperature on the as-deposited amorphous films on MgO(100) substrates. For an annealing temperature of 800°C, diffraction lines from Y₁Ba₂Cu₃Oₓ, CuO, BaCO₃, and Y₂BaCuO₅ were observed. As the annealing temperature was increased, the intensity of Y₁Ba₂Cu₃Oₓ lines increased as compared to lines from other phases. For an annealing temperature of 920°C, the intensity of the diffraction lines was the same as that of bulk material, which was inferred to indicate the random growth of polycrystalline films.

Tanaka et al. (23) have reported the formation of high Jc(critical current) films of HoBaCuO on MgO(001) by RF-magnetron sputtering. The substrate temperature during deposition was kept between 600°C and 650°C, and the samples were annealed at 850-900°C. From X-ray diffraction, it was found that the (001) plane of the film was parallel to the (001) surface of the MgO. The critical current density was 2.54X10⁶ A/cm² at 77.3K and dropped to 1.5X10⁴ A/cm² in the presence of 1.0 Tesla magnetic field. The high critical current density, even in the presence of a magnetic field, was attributed to the absence of weak links due to presence of grain boundaries, that are easily broken by a magnetic field, and decrease the Jc substantially in the presence of a magnetic field.
Terada et al.(24) investigated the mechanism for composition deviation of thin films from that of the target by employing a high transverse magnetic field to suppress the bombardment of secondary ions on the substrate during deposition. They found that the deposition rate doubled when the magnetic field was applied. Also, the composition of the film was made closer to that of the target if the bombardment by secondary electrons was suppressed. The effect of high energy ions was also studied by the application of a bias voltage on the substrate (along with transverse magnetic field). No apparent change in the film composition was observed when compared with magnetic field alone.

The above results are indicative of the factors affecting compositional variation. The high energy secondary electrons which are emitted from the oxide target and which are accelerated by an electric field applied to the target, bombard the growing film and preferentially weaken the strength of the Ba-O and Cu-O bonds. This lowers the sticking coefficient of Ba and Cu atoms. On the other hand, the bombardment of high energy ions have a much weaker effect on the film composition than that of electron bombardment.

Shaw et al.(26) also reported the effect of resputtering on the thin films of Y$_1$Ba$_2$Cu$_3$O$_x$ and suggested that the Ar$^+$ ions cannot be responsible for this effect since the induced voltage on the substrate is positive. Resputtering due to negative ions of Y and Ba was also ruled out since both are highly electropositive. Two possible mechanisms of resputtering suggested were O anions and high energy neutral particles. The results of Shaw et al. sound unconvincing when compared with that of Terada et al.(24).

Wheatmore et al.(25) have studied the effect of using different substrates on the composition of the film, and found out that the sticking coefficients of Y, Ba, and Cu are different for different substrates. The results reported are not complete in any sense, but give an indication of the different parameters that can be involved while depositing the films. The sticking coefficients for Ba
was found to be lower and that of Cu was higher on Si substrate as compared with SrTiO$_3$ substrate. From these results, it is seen that deposition temperature might have a role to play in the compositional variation of the film: under otherwise the same deposition conditions the ratio of Y:Ba:Cu was 1:2.9:6 and 1:2.0:2.8 for deposition temperatures of 120°C and 80°C respectively.

The same authors also report the suppression of Tc to 40K by the diffusion of Sr and Ti into the film during annealing of the film at higher temperature.

Ohkuma et al. (27) studied the affect of annealing temperature on amorphous films deposited on an MgO substrate by RF-magnetron sputtering. They annealed the amorphous films between 850°C-940°C and reported that films annealed between 900°C-930°C showed superconductivity. The best films were obtained for an annealing temperature of 920°C. The diffraction pattern of films annealed at 920°C resembles the calculated diffraction pattern for c-axis oriented films (Fig. 7).

The same authors also report the deficiency of Y and Cu in the surface layers of the films to a depth of about a few hundred Å. It was also determined that the concentration of Y and Cu were considerably reduced by the annealing procedure.

Tsuda et al. (28) report that films deposited at room temperature and post annealed at 930°C had a higher Tc compared with films deposited at 650°C and post annealed. But the critical current density of the films deposited at 650°C was considerably higher.

The reaction of 123 films with MgO and SrTiO$_3$ substrate was compared, and it was reported that MgO does not react with films on post annealing. However Sr was observed throughout the thickness of films by Auger spectroscopy, even though the film thicknesses were about 2μm.

Films of thickness less than 0.5μm on MgO were not superconducting because of an island structure in such films.

Gurvitch and Fiory (28) deposited thin films of 123 compound on a variety of substrates, including Al$_2$O$_3$ (Sapphire), ZrO$_2$ + 5%Y$_2$O$_3$ (cubic zirconia), MgO, BaTiO$_3$, SrTiO$_3$, and Si, and Si
with the buffer layers of Y₂O₃, Ag, Nb, Cu, NbN, VN, and SiO₂. Ranking the substrates without buffer layers, the best results were obtained on ZrO₂ followed in order of increasing difficulty (lower Tc etc.) by SrTiO₃, MgO, Al₂O₃, BaTiO₃ and Si. The last two did not produce conducting films for annealing temperature above 900°C.

The explanation given by the above authors is that Zr appears to be less detrimental to superconductivity than Ti and Al. The Ti⁴⁺, Al³⁺, and Zr⁺⁺ ions are all small enough to fit Cu²⁺ sites, which according to a current hypothesis would be most deleterious to superconductivity owing to the breaking of Cu-O planes. It is possible that some small ions may prefer to avoid Cu sites because of chemical incompatibility - e.g. Zr which is far removed from Cu in the transition metal series.

2.8 Sputtering

The sputtering phenomenon which is the ejection of atoms or clusters of atoms from the surface of a target material by collision with energetic particules such as ions and high speed electrons, has been known for more than a century (since 1852) and has been applied to thin film deposition. Because of the high pressure of gas used and the high sensitivity to contamination in commonly used glow discharge sputtering, the technique was termed "dirty". However, improved technology and new variants of sputtering arrangements have now revived low-pressure sputtering as a versatile and powerful deposition technique for research and production purposes.

In 1965 an R.F. sputtering technique which could sputter deposited even insulating target material was developed (30). Afterwards, sputtering sources other than the diode gun - namely the magnetron and the triode gun sources were developed. The development and improvement of sputtering deposition techniques are remarkable, making it one of the best deposition technique for thin film fabrication.
The advantages of sputter deposition technique over vapor deposition are:

1. strong adhesion between deposited film and substrate
2. ability to sputter very high melting point materials
3. fabrication of wide homogeneous films
4. excellent reproducibility

**Diode sputtering**

A simple source of ions for sputtering is provided by the well known phenomenon of glow discharge caused by the application of an applied electric field between two electrodes in a low pressure gas. Fig. 8 shows the structure of a diode system. The gas is ionized to conduct electricity when a certain minimum voltage is reached between the target and chamber. The substrate onto which the film material is sputter is usually placed at the same electric potential as the chamber, as shown in Fig. 8. The sputtering gas (usually Ar) introduced into the chamber is now ionized. The ionized gas atoms (Ar⁺) are accelerated by the applied field towards the target and sputter the atoms from the target surface.

**Magnetron Sputtering**

The set up of magnetron sputtering is the same as that of diode sputtering except for the existence of magnets installed behind the target as shown in Fig. 9. The magnetic field induced by these magnets causes the electrons to move helically around the lines of magnetic force. These electrons collide with neutral sputtering gas atoms and ionizes them. In this way, the plasma can be maintained at low pressure, which results in a high deposition rate (31) and fewer contaminations in the thin films (32).
**Triode Sputtering**

Auxiliary electrons are provided thermionically from a filament and are drawn to the anode as shown in Fig. 10. With the discharge gas adjusted to the desired operating pressure, the cathode (filament) is electrically heated to a temperature at which it emits enough electrons to support a discharge. When the power is applied to the anode, electrons are accelerated towards it. Argon atoms are excited or ionized by electron collisions, and a plasma is initiated. The target may have a negative voltage applied to it without affecting the plasma, other than within the ion sheath (the dark field region) that forms around the target. Every ion reaching the edge of the sheath is accelerated to target and has a probability of causing ejection of atoms from the target surface.

Advantages of triode sputtering are that a plasma can be obtained at lower pressures and independently from the power applied to the target.

**Reactive Sputtering**

When a reactive gas is deliberately added to the sputtering system, the desired film compound may be produced using a metallic target. Reactive sputtering can be done using diode or magnetron sources. The reactive gas is introduced into the sputtering chamber directly or as a mixture of the reactive gas and a non-reactive gas. The reaction to form the compound takes place mainly on the substrate surface (32). Reactions may also occur on the target surface. Reactions in the gas phase have been considered unlikely because of the problem of conserving momentum and dissipating the heat of reaction (32, 33).

Advantages of reactive sputtering are as follows:

1. In general, metals are ductile and have lower melting temperatures than compounds such as metal oxides and metal nitrides. The manufacture of target shapes from metals is thus easier and less expensive than forming non-metallic materials into the target shapes.
2. by changing the ratio of reactive gas to non-reactive gas in the sputtering chamber, a precise compositional control can be achieved.

3. in most cases, the deposition rates of metals are higher than those of their compounds. Thus reactive sputtering gives higher deposition rates.

2.9 Method of Thin Film Analysis

Energy Dispersive Spectroscopy

When a solid is bombarded with an electron beam, electrons of various energies are emitted. When an electron in an atom in the specimen is ejected by a high energy electron (from the primary beam), the atom can return to its ground state by the release of energy when an electron from an outer shell drops down into the inner shell vacancy. Energy release is accomplished by photon emission resulting in characteristic X-ray spectrum. The characteristic lines K1, K2, L1, and so on are produced when electrons are ejected from the K, L, and other atomic shells in the target elements are replaced by higher energy shells. The decrease in energy of the electron falling into lower energy level is compensated by the emission of a photon of appropriate frequency, \( \nu \). The energy decrease and hence the photon frequency is characteristic of the element concerned.

Energy dispersive spectrometers work on the principle that the energy of a photon \( E \), is related to the frequency of the electromagnetic wave, \( \nu \), by the relationship

\[
E = h\nu
\]

Where \( h \) is the Planck's constant. Thus the measurement of the photon energies identifies the elements concerned. In this method, the specimen is bombarded with high energy electrons, and the whole range of energies thus produced are measured and displayed simultaneously as a spectrum of intensity against energy. This is achieved by using a solid state detector that pro-
duces a voltage pulse proportional in energy to the energy of incident photon. These pulses are sorted, measured, and counted, and output is displayed as the final spectrum on CRT. The signal from the spectrum peaks gives the picture of distribution of the elements.

**X-ray Diffraction Analysis**

In order to determine the presence of coexisting phases and the crystal structures of the specimen, X-ray diffraction method was used. Monochromatic CuKα (λ=0.1548nm) radiation from a Cu X-ray tube operated at 40kV and 20mA was used. Diffracted x-rays were detected by a counter connected to a chart recorder which had a scanning rate of 2°/min.

### 2.10 Basis For Plotting In t_{50\%crystallization} vs 1/T

With a few notable exceptions, reaction rates increase rapidly with increasing temperature. Furthermore, provided that the temperature range is not too great, the temperature dependence of the rates of most reactions obey Arhenius type equations. In these circumstances it is always possible to define an empirical activation energy Q and frequency factor A by the equation

\[ K = A e^{\frac{-Q}{RT}} \]

Where K is the rate constant and T is absolute temperature.

The general rate equation is

\[ \frac{dc}{dt} = K f(c) \]

Where c is the crystallization and t is time

The above equation may be written as

\[ dt = K^{-1} f^{-1}(c) dc \]

The time t_{50\%c}, required for a specified fraction C is equal to 50 percent to transform is given by
\[ t_{0.5c} = K^{-1} \int_{c=0}^{c=0.5} f'(c) \, dc \]

The reaction is studied at a series of temperatures, all other experimental variables being maintained constant and the time, \( t_{50\%c} \), to the chosen value of crystallization measured at each temperature. Provided that the function \( f(c) \) does not vary over the temperature range studied, the integral has a constant numerical value. Hence,

\[ t_{0.5c} = K^{-1} \]

\[ t_{0.5c} = A \, e^{-\frac{Q}{RT}} \]

and

\[ \ln t_{0.5c} = \text{const} - \ln A + \frac{Q}{R} \left( \frac{1}{T} \right) \]

A graph of \( \log t_{50\%c} \) against \( 1/T \) is linear if \( Q \) and \( A \) are independent of \( T \), the slope being \( Q/R \).
Chapter III
EXPERIMENTAL

3.1 Fabrication of $Y_1Ba_2Cu_3O_{7-x}$ Target

$Y_1Ba_2Cu_3O_{7-x}$ contains three oxides: yttrium oxide, barium oxide, and cupric oxide. The following relation shows the reaction of the formation of the compound:

$$Y_2O_3 + 4BaO + 6CuO \rightarrow 2Y_1Ba_2Cu_3O_{x}$$

In the present research, barium carbonate (BaCO$_3$) was used in place of barium oxide in order to avoid the formation of Ba(OH)$_2$ agglomerates. The BaO reacts with water (moisture) and forms the Ba(OH)$_2$ which results in poor mixing of the powders. The present experimental reaction can be written as:

$$Y_2O_3 + 4BaCO_3 + 6CuO \rightarrow 2Y_1Ba_2Cu_3O_{x} + CO_2$$

The fabrication procedure is shown in Table 2.

Step 1. $Y_2O_3$, BaCO$_3$, and CuO powders were weighed in proportions as required by the chemical formula to get the desired composition of the target (Table 3).

Step 2. Weighed powders were hand mixed thoroughly in a mortar for two hours. The hand mixed powders were put in a ballmill (JAR MILL, NORTON) and mixed with water for two hours to obtain homogeneous powder. The container jar and balls were made of "burrunder", a sintered alumina commercially available from NORTON U.S. Stoneware Inc.

Step 3. The mixed powders were placed in an alumina crucible and heated in a tube furnace, the arrangement of which is described in next section. The temperature of the furnace was raised to 500°C over 30 minutes and 30 minutes in order to evaporate the moisture present in the sam-
amples. At this stage, the oxygen flow was started through the tube at 944 scc/min. The oxygen flow was kept on for the rest of the heating cycle. The temperature of the furnace was raised from 500°C to 920°C over 45 minutes.

The powders were held at 920°C for 12 hours. This is the calcination or presintering process to get rid of the CO₂ gas. The samples were then cooled slowly at 2°C/min. to a temperature of 475°C and held here for 30 minutes to let it soak up oxygen. The samples were furnace cooled from this point onwards till it reached room temperature.

Step 4. The calcined samples were ground by hand in a mortar for two hours. When the hand ground powders were pressed into discs, the discs laminated and broke. It was found necessary to further grind the powders in a mechanical grinder for 30 minutes. The mechanical grinder reduced the particle size and permitted the powders to be pressed into acceptable disc form.

Step 5. The ground powders were once again put through the calcination cycle to get rid of any remaining carbon content in the samples.

Step 6. The samples were then ground into finest possible size, first by hand, and then by mechanical grinder.

Step 7. The ground powder was pressed into discs of 25.4 mm diameter and 2mm thickness in a die on a screw driven Instron Universal Testing Machine using a pressure of 3500psi. The pressure was applied in steps of 500psi.

Step 8. The discs were sintered at 930°C for 12 hours with the same heating and cooling schedule employed in Step 3.

**Tube Furnace**

A nullite tube was inserted in the tube furnace (Model LINDBERG HEVI-DUTY SB). The ends of the tube were sealed with aluminum end caps that were air tight. The end caps had the provision for inlet and outlet of oxygen, and also for a thermocouple. The oxygen flow was regu-
lated by a tube flowmeter (Model- Tube 2-65B, Brooks Instruments Inc.). The temperature of the specimen was recorded on a X-Y recorder by putting a Type-K (Alumel-Chromel) thermocouple close to the specimen. A cold junction compensator was incorporated with the thermocouple. The voltage from the thermocouple was converted to the temperature by using a standard conversion chart.

3.2 Critical Temperature Measurement by the 4-Probe Method

The 4-probe technique was employed to determine the critical temperature of the bulk samples (Fig. 11). The objective of the experiment was to pass a constant current between the outer probes and measure the potential difference across the centre probes. The constant current was established by applying a high voltage of 30V [V] across the outer probes with a very high resistance 30K-ohm [R] in series with the sample whose resistance was very small, about 0.12ohms [r] in the normal state, i.e. non-superconducting state. The current through the sample in the normal state is:

\[ I = \frac{V}{R + r} \]

When the sample is cooled below its transition temperature, the resistance of the sample goes towards zero, such that the current in the circuit now becomes:

\[ I = \frac{V}{R} \]

If the value of sample resistance (r) in its normal state is small as compared to series resistance (R), the change in the value of current through the sample is negligible and can be ignored for all practical purposes.
The biggest problem encountered during the course of these measurements was the contact between the probes and the specimen. When the specimen was cooled from room temperature to liquid nitrogen temperature, one (or more) of the contacts between the electrode and the sample was broken. A variety of arrangements of the sample holder were tested to establish and maintain a good contact between the sample and the electrodes. Finally, a successful arrangement was developed as explained below.

**Sample Holder for Four-Probe Resistance Measurement**

A schematic diagram of the sample holder for critical temperature measurement is shown in Fig. 12. The sample holder consisted of two ceramic plates - one base plate and one probe plate. The ceramic plates were cut from a machinable ceramic, and measured 4cm×4cm×0.75cm. The probes were made from thin copper wires of 0.05mm diameter that were passed around the four sets of holes in the electrode plate. In this manner line contacts were made between the copper wires and the sample. The distance between the probes was kept at 1.5mm. The sample was put on the base plate as shown in Fig. 12 and the electrode plate was clamped on top of the sample such that the four probes touched the sample. The ceramic plates were secured together with the sample sandwiched between them by four screws at each corner of the plate. The assembly was mounted on a copper block. A small amount of pressure was applied between probes and the sample to ensure good contact by tightening the screws. The outer probes (1 & 4) were current carrying probes, and the inner probes (2 & 3) were potential probes.

**Four-Probe Circuit**

A schematic diagram of the measurement circuit is shown in Fig. 11. The circuit consists of a constant current source between the outer probes and a voltage measuring device between the inner probes. The constant current was maintained by putting a variable resistance (Model- Resis-
tance Decade Box - RES-2, Emco Electric Meter Co.) in series with a power supply (Model- John Fluke Mfg. Co., Model 407). The current in the circuit was measured by a milliammeter (Model- Weston Electric Instrument Co., Model EEA34). The potential difference between the centre probes was measured by a high impedance multimeter. The temperature of the sample was measured by a K-type thermocouple in contact with the sample through a small hole in the electrode plate.

Critical Temperature Measurement

In order to find out the critical temperature of the bulk specimen, a small hole was drilled beside electrode holes in the electrode plate. A K-type thermocouple was inserted through this hole and made contact with the bulk superconducting specimen.

The first step in making critical temperature measurement was to mount the superconducting sample in the sample holder and ensure that the electrodes and the thermocouple made a contact with the specimen.

The second step was to start the constant current flowing through the outer probes and measure voltage across the center probes at room temperature.

The third step was to gradually reduce the temperature of the sample by bringing a dewar filled with liquid nitrogen close to the sample holder assembly. The sample holder was kept in this position, i.e., without touching the liquid nitrogen until thermal equilibrium was attained between the sample, sample holder and the surrounding nitrogen environment. During this process, it was assumed that the thermocouple maintained its contact with the specimen. The temperature was read from a digital readout attached to the thermocouple and the voltage across the center probes was recorded for these temperatures.

Once the thermal equilibrium between the sample and its surrounding was attained, that is the temperature of the specimen stopped going down, the temperature of the specimen was
reduced further by touching the bottom of the copper block to the liquid nitrogen surface. At the same time, the sample holder and the sample were still out of the liquid nitrogen. Once the thermal equilibrium in this position was attained, the entire sample holder was gradually dipped into the liquid nitrogen.

It took about thirty minutes to bring the specimen from room temperature to liquid nitrogen temperature. The temperature of the specimen was recorded and the corresponding voltage at these temperatures were recorded simultaneously.

3.3 R.F. Triode Sputtering Deposition System

The system consists of a vacuum chamber, a roughing pump, a high vacuum pump, sputtering sources, and an R.F. power supply for the sputtering sources as shown in Fig. 13.

Vacuum Chamber

The vacuum chamber is a vertical cylinder type, fabricated from non-magnetic steel (type 304). There are two windows to observe the inside of the chamber and cooling coils are mounted on the chamber to keep it at or near ambient temperature.

Pumping System

a) Roughing Pump - The roughing pump is a rotary vane pump for roughing the chamber and backing the high vacuum pump. A vacuum of about $10^{-2}$ torr from atmospheric pressure can be obtained in 20 minutes with this pump.

b) High Vacuum Pump - The high vacuum pump is an oil diffusion pump which has an integral water baffle, a liquid nitrogen trap and a high vacuum valve. A vacuum of $10^{-6}$ torr from $10^{-2}$ torr can be obtained in about 30 minutes. A variable orifice valve is set above the diffusion pump assembly for precise control of gas throughput of the sputtering chamber.
Sputtering System

a) General - The sputtering system consists of two sputtering sources, an emitter power supply, an R.F. power supply and three variable gas control valves.

b) Sputtering Sources - L.M. Simard Inc. Tri-Mag. Model 121 sputtering sources are utilized for this system. The source accepts targets of variable diameter up to 25.4 mm. The sources are mounted on bottom of the chamber and the substrate holder is above the sources. The source configuration is shown in Fig. 14. The sputter up mode configuration is performed in order to eliminate sputter dust problem.

c) Substrate Holder - The substrate holder is a steel plate having four substrate holder locations. The size of each location is 75 X 75 mm. The holder plate can be rotated from outside the chamber so that the substrate position may be adjusted under vacuum. The distance between the substrate and the target is also adjustable. Substitute holder pieces were fabricated in order to mount various sizes of substrates. The holder design is shown in Fig. 15.

d) Argon Gas Supply

A gas flow control valve is provided in the system for varying the Argon gas flow to the source. The oxygen gas flow to the substrate local area is controlled by a needle valve.

Tri-Mag Model 121 Sputtering Source

Two Tri-Mag 121 Sputtering Sources are installed in the sputtering deposition system. They are magnetron supported triode R.F. sputtering guns. A schematic figure of this type of source is shown in Fig. 16. Two magnets are placed on each side of the source so that the charged particles or the plasma may be confined in a region of higher density. Other basic elements are the thermal electron emitting filament, the anode, the plasma-confining enclosure, and the sputtering target. The filament is heated by an A.C. current (supplied from Filament Module) to a temperature sufficiently high for thermionic electrons to be emitted from its surface. These electrons are then
attracted to the anode biased positively with a D.C. power supply (Igniter Module). Argon gas atoms are then let into the enclosure where they collide with the accelerated electrons. If there is sufficient filament-anode voltage, numbers of gas atoms, and electrons present, the gas atoms will be ionized in their collisions with the electrons and a self-sustaining arc-type plasma will be initiated. Control of the plasma current is maintained with a constant current D.C. supply (Plasma Discharge Module). Control of the plasma voltage is achieved by the adjustment of both argon gas flow and filament electron emission.

3.4 Target Installation

The target (YBC ceramic target or Zirconium metal target in the present research) was made into a disc shape of 25.4 mm diameter and 1.5 to 2.5 mm in thickness and placed on a target holder for adjustment of the level of the target surface. The holder was made of 25.9 mm diameter copper rod in order to have sufficient conduction of both heat and electricity. The target was glued to the Cu holder by silver epoxy resin to ensure thermal and electric conduction. The ring shaped target insert to the confinement cover was modified according to the target diameter. The hole in the center of the insert was sized to be 1.0 mm larger in diameter than the target. This gives a clearance gap between target and insert of 0.5 mm. If the clearance gap is much larger than this value, plasma will leak down the target edge and sputter the target holder, contaminating the deposited films.

3.5 Zirconia Films

Target Preparation

Disc shaped targets of 25.4mm were cut from zirconium metal sheet of 3.5mm thick (99.9 % pure, Johnson Mathey). Silver epoxy was used to mount the target on a copper target holder. The epoxy was cured at room temperature for 24 hours.
Thin Film Preparation

The zirconia films were fabricated by means of a reactive sputtering technique using metal targets in an R.F. triode sputtering deposition unit. The reactive gas, oxygen, was not introduced in the sputtering source together with the sputtering gas, argon, because the filament which was made out of tantalum wire would oxidize and burned out. Thus the reactive gas was introduced through a copper pipe ring with gas outlet holes installed in the vicinity of the substrates so that the flow of oxygen was concentrated on the substrate surfaces.

Table 4 lists the sputtering parameters for zirconia film deposition. The substrate was kept at a distance of 6cm from the target.
Chapter IV
RESULTS AND DISCUSSIONS

4.1 Critical Temperature

The critical temperature of the bulk samples was determined by using the four-probe technique. A constant current of 1mA was passed between the outer probes and the potential difference was measured across the center probes. This voltage drop is proportional to the resistance of the specimen. The temperature of the specimen was determined by attaching an alumel-chromel thermocouple to the surface of the specimen.

The value of critical temperature recorded in this way may have errors because of the following reasons:

1. During the temperature measurement process it was assumed that the thermocouple was in contact with the superconducting specimen and recording the temperature of its surface. There was a possibility that the thermocouple could lose its contact with the specimen and was recording the temperature of the ceramic plate.

2. The K-type thermocouple used during our critical temperature measurements is not the most accurate means of recording the temperature in the lower temperature range.

3. There could be a temperature gradient present across the width of the specimen. The temperature recorded at the point of contact between the thermocouple and the specimen may be different at other points on the specimen.

The temperature versus resistance plot is shown in Fig. 17. As can be seen from the graph, the resistance of the specimen decreases gradually between 180K and about 98K. It then drops
sharply towards zero at 94K. The specimen was further cooled to 77K in liquid nitrogen. The voltage across the centre probes remained at zero.

In order to ensure that the measurements were correct, the specimen was taken out of liquid nitrogen and warmed up slowly by keeping it just above the liquid nitrogen. It was observed that the voltage across the centre probes increased sharply when the temperature of the specimen reached 94K, i.e. the specimen became normal at 94K.

The lowest value of the voltage that could be read was 0.0001mV so the specimen still might have some resistance left. In order to get a better idea of the resistance drop of the specimen, a more sensitive voltmeter (nanovoltmeter) could have been used and liquid helium could be substituted for the liquid nitrogen to obtain lower temperatures.

4.2 Thin Films of Zirconia

Zirconia was used as a buffer layer to avoid the reaction between the thin films of superconductor and the silicon substrate. Typical sputtering conditions for zirconia film deposition are given in Table 4. Zirconia films were deposited on Si(100) substrate from a metal target of zirconium for four hours using a power density of 9.87W/cm². The argon gas flow rate was \( F_{Ar} = 44.0 \) scc/min. The oxygen gas was introduced in the sputtering chamber at \( F_{O2} = 1 \) scc/min. through a copper tube.

The X-ray diffraction pattern of as deposited films of zirconia indicated that the films were amorphous. The as deposited films were crystallized by annealing in a tube furnace at a temperature of 900°C in flowing oxygen (flow rate of oxygen = 944scc/min) for 30 minutes. The films were then quenched to room temperature and were analyzed by X-ray diffraction.

A typical X-ray diffraction pattern of annealed zirconia film is shown in Fig. 18. The zirconia diffraction pattern was taken from JCPDS card and a plot of diffraction peaks versus 2\( \theta \) is
shown in Fig. 19. A comparison between the actual diffraction pattern of an annealed film and the calculated X-ray diffraction pattern of zirconia shows a sharp peak at $2\theta = 28.6^\circ$ corresponding to the (111) peak and smaller peaks at $2\theta = 31.5^\circ$, $40.9^\circ$, and $45.6^\circ$ corresponding to (111), (211), and (202) peaks.

4.3 Y-Ba-Cu-O Films

Composition of thin films

Energy dispersive X-ray spectroscopy (EDS) was used to find out the composition of thin films of YBaCuO deposited on various substrates. Electrons of 15KeV were used and the reference energies of different elements involved are as follows: Y-L$_{\alpha}$ = 1.952eV, Ba-L$_{\alpha}$ = 4.469eV, Ba-L$_{\beta}$ = 4.859eV, Ba-L$_{\gamma}$ = 5.194eV, Cu-K$_{\alpha}$ = 8.056eV, Cu-K$_{\beta}$ = 8.919eV, and Y-L$_{\gamma}$ = 14.956eV.

Effect of Substrate on Composition Analysis of Films

When EDS was performed on YBaCuO films deposited on silicon substrate, it was found that the signals from yttrium in the film and silicon from the substrate overlapped. An effort was made to deconvolute the overlapping signal to obtain the composition of the film, but the results obtained after deconvolution of the signal indicate that the deconvolution of the signals was not complete. This is evident by looking at the composition of sample 12 (Table 5, Table 6). The ratio of Y:Ba:Cu was found to be 6.8:0.08:3. The yttrium content of the film appears to be too high.

In order to avoid the overlapping signals, it was decided to use another substrate material whose signal would not interfere with that of Y, Ba and Cu. Low alloy steel was chosen as a suitable substrate material to give an indication of composition of the deposited film. The iron FeK$_{\alpha}$ signal for EDS analysis is 6.398eV and falls between Ba-L$_{\beta}$ = 5.194eV and Cu-K$_{\alpha}$ = 8.056eV and it did not interfere with any of the elements of concern - Y, Ba, Cu.
Stoichiometric Films

An attempt was made to obtain films with the stoichiometric superconducting phase, (the ratio of Y:Ba:Cu as close to 1:2:3 as possible) by changing the following parameters:

Power

The films were sputter deposited at higher R.F. power levels of 75W and 50W (Sample 2, 15, 16, 20, Table 5, Table 6). It was found that the targets were broken after the sputtering. This was probably due to overheating of the targets. So sputtering at higher powers was not a feasible choice.

The next step was to decrease the R.F. power during sputtering. Sputtering was done at 25W, 20W, and 15W for samples 7, 8, 11 12, and 13 (Table 5, 6). The thicknesses of the films for low power deposition were too small. Also the films were still deficient in their barium content. The films deposited at 35W seemed to have sufficient thickness and the subsequent depositions were carried at 35W.

Target to Substrate distance

For samples 2, 6, 7, 8 and 11, the substrate was kept at a distance of 6cm from the target. The thickness of all the samples except number 2 was very low. Also, the barium to copper ratio in the films indicated that the films were still deficient in barium. In order to increase the rate of deposition to get thicker films, the substrate to target distance was reduced to 4cm. At this distance, the barium content of the films also improved a little. Four cm was the smallest target to substrate distance possible on the sputtering system.

Target Composition

The films deposited from stoichiometric targets were deficient in barium content. To overcome this deficiency, barium enriched targets were made with the Y:Ba:Cu ratio of 1:2.5:3.
Deposition from these targets improved the composition of the films. The Y:Ba:Cu ratio was found to be 0.93:0.48:3, 0.81:0.43:3, 0.61:0.43:3, and 0.64:1.13:3 for samples 20, 21, 22, and 23, respectively.

Most of the films obtained were still deficient in barium. Therefore, the barium content of the target was increased again. Two more targets with Y:Ba:Cu ratio of 1:4:3 and 1:6:3 were fabricated. For the 1:4:3 target the thin film composition of sample 26 on the iron substrate was 0.62:1.45:3. The ratio of yttrium to barium improved in the films, but the copper content of the film was too high.

From the 1:6:3 target the film composition of samples 25 and 30 were found to be 0.51:1.14:3 and 0.60:0.676:3. This indicates that copper content of the films was too high.

4.4 Crystallization

Our first step towards the crystallization of the YBaCuO films deposited on silicon substrate with zirconia buffer layer was to find the the crystallization temperature for the superconducting phase from an amorphous film.

Crystallization Temperature

In order to find the crystallization temperature for the superconducting phase in the amorphous YBaCuO films, sample 20 was taken (the sputtering parameters of the film are in table 6. The film was deficient in yttrium and barium content, also the thickness of the film was very small) and X-ray diffraction pattern of the film in as deposited state is shown in Fig. 20. The sharp peak at 20 = 28.6° in the diffraction pattern is due to the zirconia buffer layer. There is a broad halo in the region of 20 = 23° - 38°, indicating that the as deposited film of YBaCuO is amorphous.
This sample was heated at a successive intervals of 100°C starting from 500°C, i.e., at 500°C, 600°C, 700°C, and 800°C for two hours each. After each heat treatment, X-ray diffraction patterns for the films were obtained (Fig. 21, 22).

For the film annealed at 500°C, the X-ray diffraction pattern (Fig. 21) had peaks for zirconia at \(2\theta = 27.3^\circ\) and \(34.4^\circ\). The diffraction peaks at \(2\theta = 29.4^\circ\) and \(30.4^\circ\) may be appearing due to the formation of yttrium oxide and/or \(Y_2BaCuO_5\). The other peaks in the diffraction pattern at \(2\theta = 31.9^\circ, 39.8^\circ,\) and \(49.8^\circ\) could not be assigned to any of the known phases.

For the film annealed at 600°C, similar peaks appeared for zirconia as in case of film annealed at 500°C. The slight shift in position of diffraction peaks at \(2\theta = 29.7^\circ\) and \(30.7^\circ\) for 211 compound or yttrium oxide might have occurred due to different oxygen content of the oxides. An additional peak at 37.8 appeared that could not be attributed to any of the known phases.

For film annealed at 700°C, apart from peaks appearing due to zirconia and 211/\(Y_2O_3\), the number of peaks appearing due to unknown phases increased.

In any case, it was not author's intention to work with any of these impurity phases, but to obtain the superconducting phase in the as deposited YBaCuO film. So the sample was further annealed at 800°C for two hours in flowing oxygen, and X-ray diffraction pattern of the film was obtained (Fig. 22). As can be seen from Fig. 22, a sharp peak appeared at \(2\theta = 32.6^\circ\) and a smaller peak appeared at 23.5 which corresponds to (013)/(110) and (010) diffraction of superconducting 123 phase.

Another sample from the same batch (Number 20) was annealed at 725°C, 750°C, and 775°C in order to find out the temperature at which crystallization of superconducting 123 phase starts. All the samples were annealed in flowing oxygen, and X-ray diffraction patterns of the film annealed at 725°C, 750°C, and 775°C showed an intense peak at 32.8 corresponding to (013)/(110) diffraction for superconducting 123 phase, indicating that the crystallization of superconducting 123 phase begins at 725°C.
In order to further narrow down the temperature at which the crystallization of superconducting 123 phase starts, another sample, number 17, was annealed at 710°C for two hours in flowing oxygen. The X-ray diffraction pattern (Fig. 23) contains peaks at \(2\theta = 30.5^\circ, 31.4^\circ, 33.2^\circ, 35.5^\circ, 44.8^\circ, 46.75^\circ, \) and \(52.2^\circ\) that correspond to 211 green insulating phase.

The same sample was further annealed at 725°C in oxygen and extra peaks appeared at \(23.0^\circ\) and \(32.8^\circ\) (Fig. 24) that correspond to the superconducting phase.

Thus it was concluded that the superconducting 123 phase starts crystallizing at 725°C, along with other phases namely, 211 phase, CuO, and other unidentified phases. The impurity phases (other than 123 phase) are expected to be formed in the films since the composition (See Table 5) of these films is not stoichiometric. Also, as reported by other researchers (22), even if the film composition is stoichiometric, in order to get a higher percentage of superconducting phase, the films have to be annealed at an elevated temperature in the range of 900°C - 920°C.

4.5 Activation Energy

In order to find out the activation energy of superconducting 123 phase, X-ray diffraction patterns on sample 22 were obtained in as-deposited condition for the film. In the as-deposited condition (Fig. 25), a broad halo between \(2\theta = 23^\circ - 37^\circ\) was observed which corresponds to the amorphous phase, along with a small peak at \(2\theta = 32.8^\circ\), indicating that the deposited film is partially crystalline. The sharp peak at \(2\theta = 28.2^\circ\) corresponds to the zirconia buffer layer.

The as-deposited film was annealed at 725°C for 10, 40, 100, 220, 400, and 640 minutes (cumulative times) in flowing oxygen. The furnace was pre-heated at 725°C and an alumina crucible was put in the furnace. When the equilibrium temperature was reached, the alumina crucible was taken out and the thin film sample was put in the crucible. The crucible was inserted in the furnace and oxygen flow at 1888 scc/min was started. It was found that it took the thin film sam-
ple about 10 minutes to reach the equilibrium temperature of 725°C. The time for attaining equilibrium is not included in the calculations and is a potential source of error.

The X-ray diffraction pattern of the film was taken after each heat treatment and is given in Figures 26 - 31. As can be seen from the figure 30, (sample annealed at 725°C for 400 minutes), the diffraction peaks at 2θ = 22.85°, 32.8°, 38.7°, 40.4°, 46.7° and 58.5° can be attributed to the presence of the superconducting 123 phase. Other peaks at 30.5°, 31.4°, 35.5°, and 44.6° correspond to 211 phase and the peaks at 35.5 and 38.7 could also be attributed to the formation of CuO. The zirconia peak at 28.2° is salient and appears in X-ray diffraction patterns of film for all the heat treatment.

The next step was to assign unambiguously a peak that was appearing due to crystallization of the superconducting phase. The peak at 2θ = 40.4° could be attributed due to crystallization of superconducting 123 phase or ZrO₂ and the peak at 38.7° could be due to crystallization of superconducting 123 phase or CuO. But the peaks at 22.85°, 32.8°, and 58.5° belong to 123 phase and the author is unaware of any other impurity phases that have peaks at the above mentioned angles. The presence of these peaks will be taken to represent the crystallization of superconducting phase in the film.

The intensities of these peaks suggest polycrystalline growth of the film with random orientation. For the purpose of activation energy calculations the strongest peak at 32.8° from superconducting 123 phase was chosen.

It was presumed that the height of the peak at 32.8° is proportional to the crystalline superconducting phase present in the film. The height of this peak increased for annealing times of 10, 40, 100 and 220 minutes of annealing. It was assumed that height of the peak at 32.8° is directly proportional to the amount of crystalline material present in the film, a plot was drawn for percentage of crystalline material, that is height of peak at a given time divided by the maximum peak height is plotted against logarithm of time at 725°C (Table 7, Fig. 32).
As can be seen from Fig. 32, the amount of superconducting phase appears to go down after reaching a maximum value. This may be so because of one or more of the following reasons:

1. Superconducting phase is metastable and once it is crystallized, on further annealing, it may decompose to other compounds.

2. Zirconia and/or Silicon interdiffuse in the thin film of YBaCuO and react with the superconducting phase forming new compounds.

3. The film is oriented preferentially after all of the amorphous material has crystallized. This causes the intensity of peak at 32.8° to go down. The amount of reduction in peak intensity is dependent on the direction of orientation.

The same procedure was repeated for sample 17 by annealing at 735°C for various times. At this temperature the maximum crystallization of the superconducting 123 phase was obtained by 100 minutes of annealing.

The next step was to draw a plot of ln t_{50%} c. vs. 1/T K from Fig. 32 and this plot is shown in Fig. 33. The slope of this line gives the value of Q/R and the value of Q, the activation energy, is calculated as 45±12Kcal/mole. This gives the mechanism of crystallization. This value of activation energy is of the order of nucleation and growth of individual crystallites. In Cu - 40 at.% Zr, the activation energy is 66.4 Kcal/mole and the mechanism is nucleation and growth of of individual crystallites (34).
Chapter V

SUMMARY

5.1 Bulk Superconductors

$Y_{1}Ba_{2}Cu_{3}O_{7-e}$ bulk superconductors were successfully fabricated from raw powders of $Y_{2}O_{3}$, BaCO$_3$, and CuO by mixing stoichiometric amounts of the above powders.

X-ray diffraction patterns of superconducting powders demonstrated that the samples had the orthorhombic crystal structure.

Superconductivity in the bulk samples was demonstrated by

1. Meissner Effect - By cooling the bulk sample to liquid nitrogen temperature and floating a magnet over it.

2. Resistance Measurement - A four probe set up for resistance measurement was successfully developed and employed to measure the resistance of the bulk samples from room temperature to that of liquid nitrogen temperature. The superconducting samples lost their resistance completely at 94 K - in other words, the samples became completely superconducting at this temperature.

5.2 Thin Films of Zirconia

Thin films of zirconia were successfully deposited on Si (100) substrate to act as buffer layers between YBaCuO films and the Si substrate by reactive sputtering in a R.F. Triode sputtering system.
The X-ray diffraction pattern of the zirconia films demonstrate that the films are crystallized after annealing at 900 °C for 30 minutes.

5.3 **YBaCuO Thin Films**

Thin films of YBaCuO were successfully deposited from ceramic targets of various compositions on Si (100) substrates, with or without buffer layers of zirconia, and on iron substrate.

From EDS analysis, it was found that the composition of the films deposited were not stoichiometric. Attempts to obtain the stoichiometric thin films by varying different sputtering parameters and target composition were not successful.

From X-ray diffraction, the crystallization temperature of the superconducting phase from as deposited amorphous films was found to be 725°C, although other phases were also present in the annealed films.

An activation energy for the superconducting 123 phase was found to be $45\pm1.2$ Kcal/mole by crystallizing the superconducting phase at 725°C and 735°C for various time durations and taking the X-ray diffraction patterns.

From X-ray diffraction patterns of the thin films it was concluded that the films are polycrystalline with random orientation.
Chapter VI

RECOMMENDATIONS FOR FUTURE RESEARCH

For the four probe method the sensitivity of the experiment should be increased by using a more sensitive voltmeter. Also, the measurement for resistance should be performed in a proper cryostat that could be taken down to liquid helium temperature, in order to avoid the effect of moisture in the ambience and to do the measurement at lower temperatures down to 4 K.

Stoichiometric thin films of superconductors should be obtained by changing the target composition. From our composition analysis for films obtained from a target of Y:Ba:Cu of 1:4:3 and 1:6:3, it is suggested target composition should be 1:5:2.

The films of YBaCuO should be deposited on a variety of substrates like SrTiO₃ - for better matching of lattice, MgO - for close thermal coefficient. The same procedure should be repeated for at least three different temperatures to confirm the activation energy.

Apart from EDS, other techniques should be used to find out the composition of thin films deposited on Si substrate with zirconia buffer layer.
Chapter VII

REFERENCES

6. A. C. Rosse-Innes and E. H. Rhoderick. Introduction to Superconductivity, Pergamon Press (1969), p.113


23. S. Tanaka and H. Itozaki, JJAP, Vol.27, No.4, April 1988, pp.L622


**Table 1**

Crystal parameters of orthorhombic $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}_{6.7-x}$ at 10K and 120K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>g</th>
</tr>
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<tbody>
<tr>
<td>Y</td>
<td>1h</td>
<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>1.0</td>
</tr>
<tr>
<td>Ba</td>
<td>2t</td>
<td>1/2</td>
<td>1/2</td>
<td>0.1853(7)</td>
<td>1.0</td>
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<tr>
<td>Cu1</td>
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<td>0</td>
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<td>0</td>
<td>0.00(1)</td>
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<td>0.376(1)</td>
<td>0.98(1)</td>
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<th>Atom</th>
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<th>y</th>
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<td>Y</td>
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<td>1/2</td>
<td>1/2</td>
<td>1/2</td>
<td>1.0</td>
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<td>O2</td>
<td>1e</td>
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<td>1/2</td>
<td>0</td>
<td>0.374(1)</td>
<td>0.98(2)</td>
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*The parameter $g$ is the occupation factor*
Table 2
Fabrication procedure for YBC ceramic discs for superconductors and sputtering targets

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 1</td>
<td>Weighing</td>
<td>------</td>
</tr>
<tr>
<td>Step 2</td>
<td>Hand Mixing in Mortar</td>
<td>2 hrs.</td>
</tr>
<tr>
<td></td>
<td>Mixing in roller mill</td>
<td>2 hrs</td>
</tr>
<tr>
<td>Step 3</td>
<td>Pre-Calcination</td>
<td>12 hrs.</td>
</tr>
<tr>
<td>Step 4</td>
<td>Grinding (mortar)</td>
<td>2 hrs.</td>
</tr>
<tr>
<td></td>
<td>Grinding (mechanical)</td>
<td>2 hrs.</td>
</tr>
<tr>
<td>Step 5</td>
<td>Calcination</td>
<td>12 hrs.</td>
</tr>
<tr>
<td>Step 6</td>
<td>Grinding</td>
<td>2 hrs.</td>
</tr>
<tr>
<td>Step 7</td>
<td>Pressing Pellets</td>
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<tr>
<td>Step 8</td>
<td>Sintering</td>
<td>12 hrs.</td>
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Table 3

Weight of raw materials for producing 100gms. of YBaCuO of different compositions

<table>
<thead>
<tr>
<th>Composition</th>
<th>Y_2O_3</th>
<th>BaCO_3</th>
<th>CuO</th>
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<tbody>
<tr>
<td>Y$_3$Ba$_2$Cu$_3$O$_5$</td>
<td>17.34</td>
<td>60.70</td>
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<tr>
<td>Y$_3$Ba$_2$Cu$_3$O$_x$</td>
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<td>32.831</td>
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<td>82.487</td>
<td>24.930</td>
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<tr>
<td>Y$_2$Ba$_6$Cu$_3$O$_z$</td>
<td>9.044</td>
<td>94.903</td>
<td>19.128</td>
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</table>

Molecular weights of raw materials:

- Y$_2$O$_3$: 225.79
- BaCO$_3$: 197.32
- CuO: 79.54
Table 4

Typical operating conditions for Triode R.F. Sputtering Deposition System

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<tr>
<th>Parameter</th>
<th>Value</th>
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<tr>
<td>R.F. Power</td>
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<td>Plasma Current</td>
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<tr>
<td>Plasma Voltage</td>
<td>40 - 48 V</td>
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<tr>
<td>Electron Emitter Current</td>
<td>18 - 30 V</td>
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<td>Sputtering Gas</td>
<td>Argon</td>
</tr>
<tr>
<td>Reactive Gas</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Sputtering Gas Flow</td>
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</tr>
<tr>
<td>Reactive Gas Flow</td>
<td>1 scc/min.</td>
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<tr>
<td>Sputtering Gas Pr.</td>
<td>50 - 100 mTorr</td>
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<tr>
<td>Target Substrate Distance</td>
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### Table 5
Preparation Conditions For YBaCuO Films

<table>
<thead>
<tr>
<th>Sample</th>
<th>Target:YBaCuO</th>
<th>Substrate:MF</th>
<th>Power:Deposition</th>
<th>Sample #</th>
<th>Composition: Target</th>
<th>Target: (Watts)</th>
<th>Time: (Hrs)</th>
<th>Substrate: (Y:Ba:C)</th>
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<th>Substrate: Si</th>
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<td>75</td>
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Table 6

Composition Analysis of YBaCuO Films by EDS Analysis

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<th>Y (wt%)</th>
<th>Ba (wt%)</th>
<th>Cu (wt%)</th>
<th>O (wt%)</th>
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Table 7
Percentage of crystallization vs. ln t

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<th>Increase in height of peak</th>
<th>ln t</th>
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Figure 1. Infrared reflection coefficient of various metals at 1.3K. The ordinate is proportional to the difference between the reflection coefficient in the normal and superconducting state (6)
Figure 2. Schematic representation of electron-electron interaction transmitted by a phonon.
Figure 3. Probability that a quantum state of kinetic energy $\epsilon$ is occupied by an electron, for the case of normal metal at absolute zero.
Figure 4. Cooper pair - Two electrons interact above a filled Fermi "sea"
Figure 5. The number of Cooper pairs with \( p_i + p_j = P \) are proportional to the volume in \( p \)-space of the ring whose cross section is shaded. This volume has a sharp maximum when \( P = 0 \). (7)
Figure 6. Crystal structure of $Y_1$Ba$_2$Cu$_3$O$_{7-\delta}$ cell (18)
Figure 7. X-ray diffraction pattern of c-axis oriented thin film of Y$_1$Ba$_2$Cu$_3$O$_{7-x}$
(27)
Figure 8. Schematic diagram of diode sputtering system
Figure 9. Schematic diagram of magnetron sputtering system with a ring target
Figure 10. Schematic diagram of triode sputtering system
Figure 11. Circuit diagram for 4-probe measurement

1, 2, 3, 4 - PROBES
PS - POWER SUPPLY
VR - VARIABLE RESISTANCE
MA - AMMETER
V - VOLTOMETER
Figure 12. Sample holder for Four-probe resistance measurement
Figure 14. Sputtering sources (Simard Tri-Mag Model 121) inside the vacuum chamber.
Figure 15. Substrate holder
Figure 16. Schematic configuration of Triode sputtering source
Figure 17. Temperature vs. Resistance plot for a bulk Y$_1$Ba$_2$Cu$_3$O$_{7-x}$ sample as obtained by Four-probe measurement.
Figure 18. Actual X-ray diffraction pattern of zirconia films annealed at 900C for 30 minutes in flowing oxygen.
Figure 19. Calculated powder X-ray diffraction pattern of zirconia
Figure 20. X-ray diffraction pattern of as deposited Y-Ba-Cu-O thin film sample 20
Figure 21. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 20 annealed at 500°C for 120 minutes.
Figure 22. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 20 annealed at 800°C for 120 minutes.
Figure 23. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 17 annealed at 710°C for 120 minutes.
Figure 24. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 17 annealed at 725°C for 120 minutes.
Figure 25. X-ray diffraction pattern of as deposited Y-Ba-Cu thin film sample 22
Figure 26. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 22 annealed at 725°C for 10 minutes.
Figure 27. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 22 annealed at 735°C for 30 minutes.
Figure 28. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 22 annealed at 725°C for 100 minutes.
Figure 30. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 22 annealed at 725°C for 400 minutes.
Figure 31. X-ray diffraction pattern of Y-Ba-Cu-O thin film sample 22 annealed at 725°C for 640 minutes.
Figure 32. Percentage of crystallization vs. ln t (time) for films of Y-Ba-Cu-O for films annealed at 725°C and 735°C.
Figure 33: In time (for 50% crystallization) vs. 1/T K⁻¹.
VITA AUCTORIS

VINOD KATARIA

1960  Born on April 17 in India

1981  Received Bachelor of Science (B.Sc.) in Mechanical Engineering from Regional Engineering College, Kurukshetra, India

1989  Currently, a candidate for the degree of Master of Applied Science (M.A.Sc.) in Engineering Materials at the University of Windsor, Windsor, Ontario, Canada N9B 3P4