ASPECTS OF Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$-ON-SILICON
BOLOMETER FABRICATION AND OPERATION

by

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Abstract

Preliminary work to the production of a Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ superconducting bolometer was done. An analysis of the noise performance of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ thin films was done with particular attention to the character and magnitude of 1/f noise in the material.

Deposition of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ onto a silicon substrate was attempted through different methods of producing a barrier between the Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ and the chemically corrupting silicon. The buffer layers would not endure the high temperature processing required to produce Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ films without cracking or peeling.

A mixed buffer layer scheme was used in order to minimize the thermal stresses between the different layers. In situ processing of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ was attempted in order to eliminate the high temperature annealing step of the Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$. Finally, epitaxial buffer layers were grown in order to strengthen the buffer layer against the thermal stresses.
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1. INTRODUCTION

Bolometers

A bolometer is a device that detects radiation via the change in resistance which arises from the change in temperature from the energy gained by the absorption of the radiation. For use in a bolometer, a material must have a resistance value that is temperature dependent. Superconductors are very well suited for use in bolometers because of their high temperature coefficient of resistance (dR/dT) in the transition region, which results in high sensitivity. In particular, high temperature superconductors (HTS) are suitable because of the greatly reduced cost of operating at temperatures above the boiling point of liquid nitrogen (77K).

The resulting device (bolometer) is capable of detecting incident radiation of any wavelength, as long as the absorbed power is enough to overcome background noise. Specifically, the detection of long wavelength infrared radiation is a major application for bolometers, since long wavelength infrared cannot be detected easily by other methods.

The ultimate limitation on the performance of an infrared detector is that of the background levels of infrared radiation. However, a practical limitation on bolometer performance is electrical noise, and in particular, current dependent electrical noise with a 1/f spectrum is a problem when using a HTS.

To achieve good bolometer sensitivity, it is important to have a small thermal mass of the "active" material (ie. material whose resistance is being measured). The small thermal mass is necessary so that a given amount of absorbed energy will result in a maximum change in temperature, and thus a large resistance change. Also, a small thermal mass is desirable to minimize the time constant of the device.

It is thus desirable to have the superconducting material in the form of a thin film. There are many possible techniques for producing superconductors in thin film form. The method used
for film deposition in this research was magnetron sputtering, because it provides a good compromise between cost, film quality, and deposition rates, and is thus easily adaptable to industrial settings.¹

For this project, Bi-Sr-Ca-Cu-O (BSCCO) material was chosen as the superconductor, because one of its crystal phases has a high transition temperature (~107 K), and because of its stability in air. The more commonly used Y₁Ba₂Cu₃-O (YBCO) material has a lower transition (~90 K) and reacts with moisture in air.

Need For Silicon Substrates

As mentioned, one of the main goals when designing a bolometer is to minimize the thermal mass of the active region in order to increase the sensitivity and shorten the time constant of the device. In addition to the requirement that the HTS be a thin film, it is also necessary to use micro machining techniques to achieve the desired minimal dimensions. Existing micromachining techniques are applicable to only few materials, including silicon, and it is thus crucial to use such a material for substrate material on which to deposit the superconducting film. It is also desirable to use silicon substrates so that any electronics for control or interfacing to the bolometers may be fabricated on the same substrate (monolithically) with the bolometer.

A problem arises when depositing the superconductor onto silicon. When BSCCO (or YBCO) is deposited on silicon, its superconducting properties are destroyed, due to silicon diffusion into the BSCCO crystal, as well as the copper (from the BSCCO) diffusion into the silicon.² This interdiffusion is enhanced by the fact that there is a strong reaction between copper and silicon producing CuSi.

In order to use a Si substrate, it is thus necessary to deposit a buffer layer between the silicon and the BSCCO film in order to form a barrier to the diffusion mentioned above. This is not easy because the buffer layer must be chemically compatible with the superconductor.
(preferably with matched crystal spacing), it must form an adequate barrier to the diffusion mentioned above, and it must be able to withstand the high temperatures (eg. 865 K) for the long times required to anneal the BSCCO to form the 107 K transition crystal phase. Some suitable candidates for buffer materials are zirconia (ZrO$_2$), or magnesia (MgO).

The basic design idea is to deposit a "microbridge" of HTS onto a membrane of silicon. The arrangement is depicted in figure 1.1.

![Membrane structure, plan view (a), and cross section (b).](image)

The micromachining technique required to create this structure is the use of KOH (Potassium Hydroxide) chemical etchant. KOH has the property that it etches silicon preferentially in a specific crystal direction, and that it does not etch boron doped Si (at least not quickly).
The existing method of producing BSCCO films with a 107 K transition involves a "post-annealing" step, where the film is baked at ~865 K for several hours after the sputtering is completed. The problem is that the buffer layer will not stand up to these high temperatures, and when subjected to them, the buffer layer will crack or even peel off. The resulting cracks allow the interdiffusion of silicon and copper to occur, causing the destruction of superconducting properties in the BSCCO.

One possible solution to this problem is to use "in-situ" processing of the BSCCO. With this method, the BSCCO is sputtered onto a hot substrate, so that the crystallization occurs during the deposition. This process would not require the post annealing step, and would involve lower substrate temperatures than the post-annealing described above.

Another possible solution to the problems is to minimize the thermal expansion forces between the different film layers. This is done by inserting a mixed layer of Si-Zr-O between the ZrO$_2$ and SiO$_2$ layers. The forces can be further minimized by altering the temperatures at which each of the layers is deposited.

A third possible solution is to strengthen the ZrO$_2$ layer. When ZrO$_2$ (or BSCCO) is sputtered onto a substrate, it will be in polycrystalline form. It is felt that the cracks in the buffer layer that form as a result of annealing form along the boundaries of the crystal grains. By attaining an epitaxial (single crystal) film, these grain boundaries will not exist, and the resulting film will likely be more resistant to cracking.

Another problem is that the membrane structure is extremely fragile, and will likely not survive the high temperatures. The solution here is to deposit and anneal the buffer and BSCCO before etching the silicon. However, the problem with this is that the BSCCO is destroyed by the etchant (wax & epoxy covers were used to protect the top side from the etchant, but were found to be ineffective at protecting the superconductor).

The solution to both the buffer layer and etching problems has not yet been found. The three different possible solutions to the buffer layer problem were the subject of study, and they are presented in later chapters of this work.
Applications

Bolometers are widely used as detectors of far-infrared radiation, X-rays and particles.\(^3\) It was the intention of this project to build a bolometer to detect infrared radiation. Infrared (IR) detection has recently become more important for applications such as spectral earth mapping, environmental contamination control, meteorology, volcanism study, agricultural research, resource exploration, planetary and space research, and star mapping.\(^3\) For these applications, detectors capable of detecting the far IR (wavelengths > 100 \(\mu\)m) need to be developed. Most competing methods of IR detection cannot detect beyond 15 \(\mu\)m, while none of the competing methods are capable of detecting wavelengths greater than 240 \(\mu\)m. A superconducting bolometer has been shown to feasibly detect up to 1000 \(\mu\)m.\(^3\)

While bolometers have been built with low temperature superconductors, the use of HTS materials will greatly reduce their cost of construction and operation. Infrared imaging of long wavelengths becomes possible and practical with the creation of a monolithically fabricated two-dimensional array of bolometers with its interface electronics.

Thesis Objective

It was the objective of this thesis work to construct and characterize a working bolometer using Bi-Sr-Ca-Cu-O superconductor on a silicon substrate. The ultimate objective is to produce a marketable device for imaging of far infrared light. Firstly, the suitability of the Bi-Sr-Ca-Cu-O superconductor for use in bolometers must be investigated, with specific reference to the electrical noise properties of the material. Secondly, there are several technical obstacles to producing the device. These obstacles were to be addressed.
2. BOLOMETER SYSTEM THEORY AND DESIGN

Introduction

In this chapter, the detail of the usage of a bolometric device is dealt with. Also, the methods of achieving optimal performance, as well as the methods of evaluating that performance are discussed.

Theory\(^{4,5,6,7,8,9}\)

The basic figure of merit of a bolometer is its specific detectivity -- \(D^*\), given by:

\[
D^* = \frac{r \sqrt{A_D \Delta f}}{V_N}
\]  
(2.1)

where \(A_D\) is the area of the sensitive element, \(\Delta f\) is the measurement bandwidth, \(V_N\) is the noise voltage, and \(r\) is the responsivity of the system, where:

\[
r = \frac{V_{\text{out}}}{P_{\text{in}}} = \frac{I_b \beta R \eta}{G(1 + \omega^2 \tau^2)^{1/2}}
\]  
(2.2)

where \(V_{\text{out}}\) is the output signal voltage, \(P_{\text{in}}\) is the incident radiation power, \(I_b\) is the bias current, \(R\) is the resistance, \(\eta\) is the optical absorptance, \(G\) is the thermal conductance from the sensitive element to the heat sink, \(\omega\) is the angular frequency of the incident radiation, and \(\beta\) is the temperature coefficient of resistance:

\[
\beta = \frac{1}{R} \frac{dR}{dT}
\]  
(2.3)

\(\tau\) is the time constant of the system, and is given by: \(\tau = C/G\) where \(C\) is the thermal capacity of the sensitive element.

As was mentioned in the introduction, micromachining is essential to producing a competitive device, because of the influence of the thermal capacity \(C\). Because of the influence
of the active area in the equations above, it is most advantageous to have a thin membrane structure. A membrane structure will also provide a small thermal conductance which also slightly enhances $D^*$.

Another goal in designing bolometers is to limit the electrical noise. The figure of merit for the noise performance of the system is the noise equivalent power (NEP) which is the power of incident radiation required to create a signal to noise ratio of 1.

$$NEP = \frac{V_n}{r \sqrt{\Delta f}} \quad (2.4)$$

There are four different sources of noise in a bolometer system in terms of which the NEP may be expressed:

$$NEP = \frac{1}{\eta} \sqrt{4k_BT_c^2 G(f) + \frac{4k_BT_c R}{|r|^2} + \frac{V_{1/f}^2}{|r|^2} + \frac{4k_BT_N R}{|r|^2}} \quad (2.5)$$

The first term in the square root represents phonon shot noise (shot noise is noise due to quantization effects: electrical shot noise is negligible unless very small currents are used), the second term represents Johnson noise, the third term represents the $1/f$ noise of the superconductor, whose magnitude can only be determined empirically, and the fourth term represents amplifier noise with an effective noise temperature $T_N$. In an ideal system, only the first two terms will be significant, because they are the only ones that cannot be reduced.

The dependence of the detectivity $D^*$ on the NEP is:

$$D^* = \frac{\sqrt{A_p \Delta f}}{NEP} \quad (2.6)$$

Values for $D^*$ in the range of $\approx 10^{10}$ cm$\sqrt{\text{Hz/W}}$ have been achieved with low temperature superconductors, and values of $10^8$ cm$\sqrt{\text{Hz/W}}$ have been achieved with YBCO material.\textsuperscript{10}
Bolometer System Design

The basic elements of a bolometer system are shown in figure 2.1:

The bolometric sensor is a conventional four-point probe resistance measurement of the superconducting film. A four point probe is as shown in figure 2.2, with a constant current source and a low (ideally zero) current voltage probe. The advantage of using a four-point probe is that contact resistances do not corrupt the resistance signal, since no current flows in the voltage sensing leads.
The current sources used were a combination of a 9 V battery and a resistor giving currents between 0.4 mA and 3 mA.

Controlling the steady state temperature of the bolometric element is a crucial part of the operation of a bolometer system. Here, the liquid nitrogen (LN) is used to cool the sample, while a resistive coil is used to electrically heat the sample.

A normal diode was used to sense the temperature of the sample. By running a constant forward bias current through the diode, it was possible to determine the temperature by reading the voltage. The diode was determined to have linear voltage vs. temperature characteristics between room temperature and LN temperature, and was thus calibrated by measuring the voltage at these two temperatures and then interpolating the other points.

A basic proportional control feedback system was implemented to electronically control the sample temperature. The amount of power applied to the heater is proportional to the difference between the set point temperature and the measured temperature. The advantages of this scheme are simple implementation, and reliability. The disadvantages are that there is a "steady state error" in the temperature meaning that the temperature will never reach its exact setpoint, and that the steady state temperature is slow to be reached. The more complex proportional-integral-derivative (PID) controllers can achieve quicker response times and smaller steady state errors, but are difficult to build and work with since they must be delicately tuned to any system they control, and are vulnerable to effects such as "integrator windup" which arises when the heater cannot heat quickly enough.
In order to modulate the power delivered to the heater, a pulse-width-modulation (PWM) scheme was used. PWM is a scheme where the power delivered is either fully on or fully off, rather than just directly modulating current in the DC sense. A fixed frequency oscillator is used, and in order to apply more power to the heater, the system merely spends a larger portion of a cycle in the fully on state. If the controller dictates, the PWM system may be on or off full-time. The advantage of this scheme is that it allows much more efficient power delivery to the heater. If a power transistor is in a "half-on" state, then the same amount of power applied to the heater (or load) will be dissipated in the transistor (up to more than 5 W in this case). This will result in a waste of power, and in the overheating and eventual destruction of the power transistor.

As can be deduced from the circuit, the oscillation frequency is approximately 80 kHz. This frequency was chosen to be high enough not to cause electrical interference with bolometric measurement (around 100 Hz) but low enough for the power transistor to operate. In figure 2.3, the lower branch of the schematic is an oscillator, which produces a triangular wave form, and the upper branch is a feedback circuit. They merge into a comparator which in turn drives the base of

![Figure 2.3: temperature controller circuit](image-url)
the power transistor. The resulting system could keep the temperature of the system stable to \( \pm 0.5 \) K.

The amplifier used was a Princeton Applied Research (PAR) model 113 low noise amplifier. The PAR 113 is fortunately optimized for use at around 100 Hz, but it is also optimized for an input source resistance of a few M\( \Omega \). Given that the resistance of a typical BSCCO film near its transition (\( \sim 107 \) K) is a few \( \Omega \), the resulting noise created by the amplifier according to the manufacturer's specifications is around 30 to 40 dB. This is intolerable, and it was therefore necessary to introduce a transformer to aid the impedance matching of the amplifier.

A PAR AM-1 low noise transformer was inserted in the circuit for this purpose, with a 100:1 turns ratio. Even though the transformer itself adds noise to the system, the resulting reduction of amplifier noise makes its use advantageous. A 5 \( \Omega \) source resistance at 100 Hz will have about 6 dB of noise created by the transformer, but the resulting 50 K\( \Omega \) resistance seen by the amplifier will result in only 0.5 dB of noise created by the amplifier. The resultant noise creation is far lower than the 30 dB created by the amplifier by itself. The transformer was capacitively coupled to the four-point probe circuit, because its low resistance to DC would corrupt the resistance signal, and a DC signal through the transformer will magnetize the core.

It was found that the connection between the transformer and the four-point probe was extremely sensitive to 60 Hz pickup noise since this is the only unamplified signal in the system. Consequently, connections to the transformer were done in differential mode, such that each of the two voltage leads was shielded. Further, the two leads were made as short as possible (around 20 cm) to minimize this pickup. Because of the very large amplification required, it was found that even these short shielded lines produced pickup noise, but by simply twisting or bending these wires to an unpredictable position, the pickup noise could be effectively minimized. The output signal of the transformer was found not to be so crucial, because the voltage signal had already been amplified by 100 due to the turns ratio of the transformer.
The final signal comes out of the lock-in analyzer. A lock-in analyzer takes 2 inputs: a reference sin wave and the signal. It responds with two outputs which are simply the components of the signal that are in and out of phase with the reference signal. By putting a low pass filter on the output (<1 Hz), the lock in analyzer essentially behaves similarly to a bandpass filter at the reference frequency. The EG&G Princeton Applied Research model 5204 lock in analyzer used here could produce its own reference signal, which would control the mechanical chopper as well.

To summarize, the operation of the system is as follows: The lock-in analyzer produces a reference signal that controls a mechanical light chopper. The mechanical chopper modulates the radiation signal to the sensitive element of the bolometer, resulting in a small resistance change at this frequency. This resistance signal is amplified and fed into the lock-in analyzer. The components of this signal that are in and out of phase with the reference signal are then the output of the overall system representing the amount of radiation detected.
3. ELECTRICAL NOISE IN Bi-Sr-Ca-Cu-O

Introduction

As stated in chapter 2, the noise characteristics of the superconductor are crucial to the usefulness of the device. In particular, 1/f noise is of interest because it is a reducible form of noise. The magnitude and characteristics of the 1/f noise in BSCCO material were thus investigated, in order to make comparisons to competing superconducting materials.

Theory of 1/f Noise

1/f noise (or flicker noise) is noise with a roughly 1/f spectrum. This is to say that the noise power per decade is roughly constant. 1/f noise is present in nature, in many unrelated circumstances. Even freeway traffic, the loudness of a piece of classical music, and flow rates of rivers exhibit fluctuations with a 1/f spectrum. There is no unifying principle for systems exhibiting 1/f noise, but for particular systems, sources can often be identified.

When considering the 1/f noise of a simple resistor, there are many things that have been found to influence its magnitude. The material used, the construction, and especially the endcap connections influence the magnitude of 1/f noise. While Johnson (or Nyquist) noise and shot noise is generally well understood, there are as yet no explanations as to the microscopic source of 1/f noise in a simple resistor. There have been several proposed models of the 1/f noise mechanism, but at best the models have been applicable to only a few specific materials.

The original and simplest model to predict 1/f noise magnitude results in the following equation:

\[ S_N(f) = \gamma \frac{V_{DC}^{2+\beta}}{N_c f^\alpha} \]  

(3.1)
where $S_v$ is the noise spectral density, $N_c$ is the number of charge carriers in the sample, and $\gamma$, $\alpha$, and $\beta$ are constant with $\alpha \approx 1$, $\beta \approx 0$, and $\gamma$ an empirically derived number where $\gamma \approx 2 \times 10^{-3}$. The flaw in this model is the assumption that $\gamma$ is a constant. While there have been many room temperature measurements of both metals and semiconductors which produce a value for $\gamma$ close to $2 \times 10^{-3}$, the model accounts for no temperature dependence, and no surface effects, both of which are known to exist. However, embodied in equation (3.1) is the voltage (or current) dependence of the noise. This is to say that $1/f$ noise (unlike Johnson noise) does not exist in the absence of a driving current. The inverse proportionality to $N_c$ is also accurately represented in equation (3.1).

As stated, there is no unifying theory, and no single model for the mechanisms of $1/f$ noise. The current mode of thinking is that there are multiple mechanisms for $1/f$ noise, even in a simple resistor. These multiple sources are additive, each with their own temperature dependence and frequency dependence. So in a certain temperature range, one source of $1/f$ noise may be dominant, while in another temperature range, another source will be dominant.

There is, however, one known source of $1/f$ noise which is of interest to bolometer work. This is $1/f$ noise due to thermal fluctuations. Thermal fluctuation $1/f$ noise arises simply because of temperature variations of the resistive material. The temperature variations cause resistance changes, which in turn causes a voltage fluctuation (assuming a constant current).

There has been some extensive development of the thermal fluctuation model, and an overview of the results follows. We consider a canonical ensemble, and define the sample temperature as a fluctuating variable through the relation: $\Delta E = C_v \Delta T$. As stated, temperature fluctuations lead to resistance fluctuations through the temperature coefficient of resistance $(dR/dT)$ of the sample, resulting in voltage fluctuations as follows:

$$
< \Delta V^2 > = V_{dc}^2 R^{-2} < \Delta R^2 >
= V_{dc}^2 R^{-2} (dR/dT)^2 C_v^{-2} \langle \Delta E^2 \rangle
$$

(3.2)

But for a canonical ensemble:
\begin{equation}
< E^2 >= k_B T^2 C_v \tag{3.3}
\end{equation}

and if we define \( \beta \) as in equation (2.3) \( \beta = 1/R(dR/dT) \):
\begin{equation}
< \Delta V^2 >= V_{bc}^2 \beta k_B T^2 C_v^{-1} \tag{3.4}
\end{equation}

Now writing the Langevin diffusion equation for the local temperature \( T(x,t) \):
\begin{equation}
\frac{\partial T}{\partial t} = D V^2 T + c^{-1} \nabla \cdot F \tag{3.5}
\end{equation}

here, \( D \) is the thermal diffusivity, and \( F \) is an uncorrelated random driving term. The spectrum resulting from the above equations is:
\begin{equation}
S_T(\omega) = \int < T(t+\tau)T(t) > \cos(\omega \tau) d\tau \tag{3.6}
\end{equation}

It was found that for a three dimensional sample with dimensions \( l_1 \times l_2 \times l_3 \), where \( l_1 > l_2 > l_3 \), four frequency ranges can be identified, separated by the three frequencies \( \omega_i = D/2l_i^2 \). The result is that for:

\( \omega > \omega_j : \quad S_T(\omega) \propto \omega^{-3/2} \)

\( \omega_j > \omega > \omega_i : \quad S_T(\omega) \propto \omega^{-1/2} \)

\( \omega_j > \omega > \omega_i : \quad S_T(\omega) \propto (\text{const} - \ln \omega) \)

\( \omega < \omega_i : \quad S_T(\omega) \propto \text{const.} \)

One may notice that the in the above results there is no region where there is a \( 1/f \) spectrum. There are a number of methods to mathematically introduce a \( 1/f \) region, all of which are \textit{ad hoc}. However, the results shown in the next section are in agreement with the derivation given above.

Thermal fluctuation \( 1/f \) noise is of interest to bolometer operation because of the high temperature coefficient of resistance \( (dR/dT) \) of a superconductor in the transition region. This high value which is crucial for successful bolometer operation also gives rise to thermal fluctuation \( 1/f \) noise. While thermal fluctuation \( 1/f \) noise has been shown to be dominant in the transition region of low temperature superconductors, there is some disagreement as to whether they dominate the \( 1/f \) noise in HTS.\textsuperscript{15,16,17}
Noise measurement

Samples of Bi$_2$Sr$_2$Ca$_2$Cu$_3$-O were RF magnetron sputter deposited on 1.3 mm thick, (100) single crystal MgO substrates, and post-deposition annealed as described in the introduction, such that the high $T_c$ material was well oriented but not epitaxial (single crystal). Silver pads were sputtered on the film for four point probe resistance measurements. The silver contacts were then treated at 550°C for 30 min. in 0.067 atm of O$_2$. Wires were attached to the silver pads with the use of silver paint. The current sources used for the four point probes were 9V batteries with a series resistance that was large compared to the sample resistance (<10 ohms). The noise signal was then capacitively coupled to a Princeton Applied Research AM-1 low noise transformer in order to achieve a better impedance match between the sample and the PAR 113 amplifier as described in chapter 2. The output of the amplifier was fed into a Hewlett Packard 3582A spectrum analyzer. The temperature was controlled by the system described in chapter 2 (figure 2.3) so that the temperature was stable to ±0.5 K. The system is shown pictorially in figure 3.1.
The basic figure for measuring noise is the noise power spectral density ($S_n$). It is defined as follows:

$$S_n = \frac{V_n^2}{V_{dc}^2 B}$$  \hspace{1cm} (3.8)

where $V_n$ is the rms noise voltage in the bandwidth $B$, and $V_{dc}$ is the dc applied voltage. The bandwidth of the measurements given here was 3 Hz in all cases. The $V_{dc}$ term in the definition is present in order to normalize the noise measurements with respect to the driving current. It is included here, because it is the current dependent noise sources that are of interest. Measurements were taken by programming the spectrum analyzer to average the rms noise
voltages of 100 samples. The non-current dependent noise sources (Johnson and amplifier noise) were measured by removing the current source from the circuit, and measuring the noise in the same manner. The non-current dependent noise was then subtracted from the total noise measurement, resulting in only the current dependent noise remaining. The current sources used were 0.45 mA and 2.7 mA, and as a result, shot noise is insignificant.

\[ I_{\text{shot noise (rms)}} = \sqrt{2qI_{dc}B} \]  

Here, \( q \) is the electronic charge (1.60x10^{-19}) so that for 0.45 mA and a 3 Hz bandwidth, the shot noise current would be only 2x10^{-11} A. The result is that the only current dependent noise that is significant is 1/f noise. It is thus that 1/f noise can be easily measured and distinguished from the other sources of noise present.

The noise power spectral density measurements \( S_n \) are shown in figures 3.2 & 3.3.

Figure 3.2: Normalized noise spectral density \( S_n \) vs. \( T \) for a dc current of 0.45 mA at 100Hz. Good correlation between \( S_n \) and \( \beta^2 \) can be easily seen for the lower temperatures, and is strong evidence that the source of the 1/f noise at these temperatures is thermal fluctuations.
They were measured at 100 Hz, and normalized with respect to the dc voltage across the two inner points of the four point probe (as in eqn. 3.8). The resistance of the sample is also shown in the figures in order to show the breadth of the transition region. In figure 3.2, measurements were taken with a 0.45 mA current source; and in figure 3.3, a 2.7 mA source. 100 Hz was chosen as the measurement frequency, because the transformer and amplifier combination introduced noise at lower frequencies.

From the two figures, it can be seen that there is very good correlation between $\beta^2$ and the normalized $S_n$ at lower temperatures, where $\beta$ is the temperature coefficient of resistance as defined in equation 2.3. The $\beta^2$ term was calculated from the resistance data shown in the figures, and has been multiplied by a constant in order to demonstrate the proportionality between $S_n$ and $\beta^2$. This good correlation indicates that the source of the 1/f noise is in fact thermal fluctuations, due to the relation in equation (3.4). The poor correlation between $S_n$ and $\beta^2$ at higher temperatures is attributed to another, as yet undetermined, source of 1/f noise which is relatively independent of temperature, and becomes the dominant noise source as the thermal
fluctuation noise decreases at the higher temperatures. It is inferred that below about 109 K the 1/f noise is dominated by thermal fluctuations. These results are very similar to those reported by Black et. al.\textsuperscript{10} for \( \text{Y}_1\text{Ba}_2\text{Cu}_3\text{-O} \) material.

Also supporting the thermal fluctuation model is a plot of the frequency dependence of the noise. Figures 3.4 & 3.5 show the relationship between the noise level and frequency at two different temperatures with input currents of 0.45 mA and 2.7 mA respectively.

From these plots, different \( \alpha \)'s can be clearly seen, where:

\[
S_n \propto \frac{1}{f^\alpha} \quad (3.10)
\]

The values for \( \alpha \) given in the figures were determined using a least squares fit to the noise data.\textsuperscript{18} The change in \( \alpha \) with temperature is strong evidence for a different noise mechanism. The \( \alpha \)'s of
about 0.5 at 107 K are the same as that predicted by the thermal fluctuation theory described earlier, and in equation (3.7).

![Graph showing noise voltage vs. frequency for different temperatures](image)

**Figure 3.5:** Noise voltage vs. frequency for the same conditions as figure 3.4, except that the dc current is 2.7 mA. Again, a change in $\alpha$ is seen indicating a different noise mechanism.

Given a film thickness on the order of a micron, and a sample width of about 1 mm, because the $\alpha$ observed (for $T < 108K$) was $\sim 0.5$ for all frequencies between 1 and 1000 Hz, a thermal diffusivity in the range $10^{-5} > D > 10^{-8}$ is implied. The value for $\alpha$ of $-0.5$ is also in agreement with the range of 0.53-0.57 found by Black et. al.\textsuperscript{10} for Y$\textsubscript{1}$Ba$\textsubscript{2}$Cu$\textsubscript{3}$-O material. This is another indication that thermal fluctuations are responsible for the noise increase, since the frequency dependence of other noise mechanisms would likely be material dependent. The value of $\alpha \approx 0.5$ is seen for temperatures ranging from about 108 K down to well below the zero resistance transition of the superconductor. At 110 K, while the noise power $S_\text{n}$ already shows good correlation to $f^2$ (see figure 3.2), the other sources of 1/f noise are not yet overpowered by the thermal fluctuations, and thus the observed $\alpha$ at 110 K is greater than 0.5. One may also note
that the data in figures 3.2 & 3.3 was measured at 100 Hz, where the effect of the change in $\alpha$ is small compared to higher frequencies.

By comparing the figures, it can be seen that the thermal fluctuation 1/f noise is roughly linearly dependent on the input current. For temperatures less than about 108 K, $S_n$ is roughly equal for both 0.45 mA and 2.7 mA (figures 3.2 & 3.3). Also, the values of $V_n$ at 107 K are roughly proportional to the input current. However, the other undetermined sources of 1/f noise are strongly current dependent. For temperatures above 109 K the effect of the current on $S_n$ is strong. Since the source of this 1/f noise is not known, it is difficult to speculate about a model for the current dependence, but the noise voltage $V_n$ seems to be roughly proportional to $i^2$, implying that $S_n$ is roughly linear with current for this source of 1/f noise.

In summary, $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}$ material shows remarkably similar noise properties to those reported for $\text{Y}_1\text{Ba}_2\text{Cu}_3\text{O}$ systems. There is fairly strong evidence that the source of the 1/f noise in the lower part of the transition region is thermal fluctuations, due to the $B^2$ dependence of the noise, and the $\alpha$ value of $\approx 0.5$ which is consistent with both the findings of Black et. al.,$^{10}$ and the thermal fluctuation noise theory of Voss and Clarke.$^{14}$

**Implications on Bolometer Performance**

For bolometric response, the sensitivity $\Delta R$ is proportional to $dR/dT$; but, the 1/f noise power $S_n$ is proportional $(\Delta R/R)^2$. As a result, one would want to bias the temperature of a bolometer in the higher temperature portion of the transition region, where there is still a high sensitivity of the bolometer ($dR/dT$ large), but the noise magnitude is still relatively small $(\Delta R/R$ still small). As seen in Figs. 3.2 & 3.3, the midpoint of the transition has the high $dR/dT$, but the 1/f noise has not yet increased to excessive levels as a result of thermal fluctuations.
The implications of this are that thermal fluctuation 1/f noise need not interfere with bolometer operation. The low levels of noise achieved here for a 0.45 mA source should be low enough for useful operation of a HTS bolometer.
4. X-RAY DIFFRACTION ANALYSIS

Introduction

In this chapter, some background information will be given on the primary method for analysis of the HTS materials and the buffer layers. By examining x-ray diffraction (XRD) spectra, we can determine which crystal phases are present, the quality of crystallization, and the orientation of the crystal. The device used for the analysis in this work was a Rigaku powder diffractometer.

Crystallography

Before going into the details of the theory of X-ray diffraction analysis, it is important to have a basic understanding of the terms of crystallography. The most crucial concept to the work here is the means of defining the crystal planes. Firstly, we define the "basis" to be the set of atoms that replicates itself at every lattice point. We then name the vectors $a$, $b$, and $c$ to be the vectors from one basis to another in each of the 3 cartesian coordinates. We then define the crystal plane $(m_1 \ m_2 \ m_3)$ to be that as shown in figure 4.1.
When considering crystals, there are frequently many symmetries. Consequently, when we refer to a crystal plane, we refer to all such planes that are equivalent within the crystal. For example, for a simple cubic crystal, the (1 0 0) plane is equivalent to both the (0 1 0) and (0 0 1) planes, so we refer to all of them collectively as the (1 0 0) plane of the crystal.

**Basic X-ray Diffraction Theory**

When monochromatic (of single wavelength) x-rays are directed towards a crystal structure, these waves are diffraacted according to the Bragg Law:

\[ n\lambda = 2d \sin \theta \] (4.1)

This law is derived from the basic principles of constructive and destructive interference, and is as shown in figure 4.2. \( \lambda \) is the wavelength of the incident x-rays, \( n \) is any integer, \( d \) is the lattice spacing, and \( \theta \) is the angle of the incident x-rays.

![Figure 4.2: X-ray diffraction (XRD) by the (1 0 0) plane of a crystal lattice, demonstrating the Bragg angle as in equation (4.1).](image)
The result of this is that for values of $\theta$ which satisfy equation (4.1) there will be a peak in the intensity of x-rays detected. Figure 4.2 depicts diffraction by the (1 0 0) (assuming a cubic lattice), and shown in figure 4.3 is a 2-dimensional representation of diffraction by the (3 1 0) plane (satisfying the same Bragg condition).

![Diagram of diffraction by the (3 1 0) plane](image)

Figure 4.3: Diffraction by the (3 1 0) plane

The diffractometer uses what is called a goniometer to perform scans. A goniometer schematic is depicted in figure 4.4.

![Diagram of goniometer schematic](image)

Figure 4.4: Goniometer schematic
The goniometer consists of two rotating axes: the θ-axis, and the ψ-axis as shown in the figure. The only motion of the detector is rotation along the ψ-axis, and the only motion of the sample is its rotation about the θ-axis.

The most basic scanning mode is called a θ/2θ scan, and as the name implies, it is simply scanning the θ-axis and ψ-axis together so that ψ=2θ (The ψ-axis is actually referred to as the 2θ-axis). This type of scan provides a lot of information about the crystal, and is the primary method of determining which of the BSCCO crystal phases are present in a sample. The angles at which intensity peaks occur correspond to the spacing of the (0 0 L) planes (parallel to the substrate), or c-axis spacing, and from this, the crystal phase can be determined by comparing it to established norms. However, when performing a scan in this manner, we see only the peaks corresponding to the spacing of the (0 0 L) planes.

In order to get information about the spacing of other planes, we use what is called an X-ray pole scan. For a pole scan we must rotate the sample about the axis normal to its surface (the c-axis), and move the θ and ψ axes independently. To this end, an attachment was built for the diffractometer to rotate the sample about its normal. Since sputter deposited BSCCO is not a perfect crystal, this method is crucial for determining the quality of alignment of the crystal grains in the ab-plane. In order to do this, an "off-axis", or non (0 0 L) peak is found such that 2θ≠ψ. The sample is then rotated about its normal axis. For a perfectly oriented crystal, the peak should immediately disappear when the sample is rotated, and reappear at 90° intervals (assuming symmetry in the a and b crystal directions - otherwise 180° intervals).

The last analysis method is what is referred to as a rocking curve. For this, all that needs to be done is to find a peak on the θ/2θ scan, fix the ψ-axis, and scan the θ-axis. From this, we see the width of the peak in the θ-axis, and have an estimate of the quality of alignment of the crystal grains in the c-axis.
5. PREPARATION OF Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{y}$

Introduction

BSCCO has several superconducting crystal phases. They all have a chemical equation of the form: Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_y$ where $n = 1..5$. The $n = 4$ and $n = 5$ phases are not very stable, and are difficult to deposit in the thin film form. The $n = 1$ (2201) and $n = 2$ (2212) phases can be easily formed, but have low transition temperatures ($\sim$80 K for $n = 2$). The phase $n = 3$ (2223) is the crystal phase of choice, and is the one with zero resistance at $\sim$107 K.

One of the crucial steps in the existing process of BSCCO thin film preparation is that of post-annealing. As previously stated, the temperatures of $\sim$865 °C required for this step to properly crystallize the superconductor are destructive to the buffer layers, and thus to the BSCCO itself through interdiffusion with the silicon substrate. By depositing the BSCCO onto a hot substrate, this step can be avoided. Since crystallization of the BSCCO will occur as it is being deposited, the temperatures required for this are significantly lower. When the crystallization occurs while the particles are being deposited, the re-ordering requires far less energy, since it all occurs on the surface.

The experiments investigating in-situ preparation were done using magnesium oxide (MgO) for the substrate material. MgO was chosen since it is known to be compatible with BSCCO, and therefore the effectiveness of a buffer layer is not a variable in the process. It may also be noteworthy that MgO was the substrate material used in the original experiments on the preparation of BSCCO thin films. Further, a study of the effect of the surface quality of the MgO on the in-situ preparation of BSCCO was performed.
Sputtering

All film depositions in this work were done using magnetron sputtering. A brief background to the theory of magnetron sputtering is thus included here.

By definition, sputtering occurs when material is ejected from the surface of a solid due to momentum transfer from a bombarding particle. Sputter deposition occurs when the ejected material is collected on a substrate, forming a film. The different sputtering processes differ only in the means by which bombarding particles are generated, and they all require a vacuum chamber. The sputtering system used here generates bombarding particles by what is called the glow discharge method. Glow discharge bombardment uses a low pressure gas plasma (usually argon) for the bombarding particles. Positive ions are accelerated towards the negatively charged target material as shown in figure 1.1, and eject (sputter) the target material, as well as secondary electrons. These secondary electrons then produce additional ions when they collide with the sputtering gas atoms. The sputtering process is therefore self-sustaining.
Positive ions are attracted to the negative target, so that ions striking the target eject target material to coat the substrate, and secondary electrons which generate more ions. The magnet arrangement enhances ion generation close to the target.

For magnetron sputtering, a set of magnets is inserted behind the target material as shown in figure 5.1. These magnets serve to enhance the plasma (ion) generation, and help confine the plasma close to the target. Secondary electrons ejected from the target are forced to move in a spiral manner due to the Lorentz force:

\[ F = q(E + v \times B) \]  \hspace{1cm} (1.1)

The Lorenz force on the electrons serves to confine them close to the target.

Unfortunately, when sputtering insulating material, a dc voltage applied to the target will not maintain the plasma, because a charge will build up on the surface of the target counteracting
the effect of the applied voltage. Instead, an rf field is applied to the target. Because of the asymmetry of the chamber acting as a capacitor, a negative bias voltage is formed at the target. The sputtering then continues as with dc sputtering, except at a generally lower deposition rate. Because the HTS materials are relatively poor conductors at room temperature, rf sputtering is required to deposit HTS films.

**Ex-Situ Preparation of Bi₂Sr₂Ca₂Cu₃O₇**

In order to prepare thin films of the n=3 phase of BSCCO (2223), the material must be deposited onto a suitable substrate by sputtering or some other method. First off, the target must be prepared. The targets were fabricated by mixing the appropriate ratios of Bi₂O₃, SrCO₃, CaCO₃, CuO, and PbO powders in order to obtain Pb₁.₃Bi₂Sr₂Ca₂Cu₃-O₇ for the target composition. These were then fired in air at about 780 °C for 12 hours, cooled, and then mechanically reground in an agate mortar. The firing and regrinding was repeated at 790°C and 795 °C. The mixtures were then pressed into disks at 1.4 kbar and sintered at 825 °C for 12 hours. These repeated firings and sintering were required to form strong, homogeneous, and well-reacted targets. The carbon is driven off by this process, but the lead remains. The presence of lead in the target was found to encourage the preferential crystallization of the n=3 phase.¹

After the sputter deposition of this target material, the substrate must then be annealed at about 865 °C (close to the melting point) in an oxygen atmosphere. These temperatures must be maintained for about 14 hours in order for the crystallization to complete. The lead which is originally in the target is eventually driven off by this "post-annealing" process, so that almost no lead will remain in the final material. The result is a superconductor with a superconductivity onset temperature (T_{Con}) of about 110 K and a zero resistance temperature (T_{C0}) of about 107 K.
Theory of In-situ BSCCO Preparation

The difficulty in in-situ preparation of BSCCO is that of getting the correct composition of the different elements, while attaining a high enough temperature for the proper crystallization to occur. The most serious problem involved is that as the temperature of the substrate rises, the concentration of bismuth in the film drops dramatically. This can be seen in the graph in figure 5.2.

![Graph showing composition of BSCCO film as a function of substrate temperature.](image)

Figure 5.2: Composition of the BSCCO film as a function of substrate temperature. The values are normalized so that Sr, Ca, and Cu add up to their room temperature total.

It is felt that this loss of bismuth is due to preferential resputtering of the bismuth. Resputtering is when negative ions impact on the substrate, and eject the previously deposited material. Apparently, as the temperature of the substrate rises above about 350 °C, bismuth is particularly vulnerable to this, significantly more so than the other elements of BSCCO.
There are ways, however, to minimize the loss of bismuth in the film. It is felt that it is oxygen ions which are responsible for the resputtering effect. The bismuth content can thus be increased by varying the oxygen pressure, the total system pressure, the target to substrate spacing, and the substrate bias. By increasing the total pressure or the substrate target distance, the likelihood of collisions increases, and thus the average energy of particles impacting on the substrate is reduced, reducing the resputtering effects. Putting a negative bias on the substrate will also reduce resputtering, since incident oxygen ions will be negatively charged.

There is another factor in the in-situ preparation of BSCCO, which is that of the oxygen content of the film. It is important to set the partial pressure of oxygen during sputtering to achieve the proper stoichiometry in the film. Further, while the substrate is cooling after the deposition, some oxygen will escape. It is thus necessary to maintain a high oxygen pressure during the cooling of the sample, and cool the sample slowly.

**Experimental Results and Discussion**

The experimental arrangement is the same as that described above, with the exception that a substrate heater was added. The substrate is heated by 4 projector bulbs powered by a simple dc power supply, and is depicted in figure 5.3.
Figure 5.3: Substrate heater.

The samples were attached to the heater via silver paint. Silver paint provides good thermal contact, and a relatively simple procedure for fixing and removing the samples. The sample temperature was measured by the use of two thermocouples. One thermocouple was embedded into the back side of the heater block, while the second was "glued" to one of the samples with silver paint. There were some problems with the reliability of the temperatures given by the thermocouples. It was felt that a shorting out of the thermocouple wires was responsible for unreliable readings.

One problem which arose was that the stainless steel heater block would outgas when heated. It was found that areas of the samples which were close to the edge were chemically corrupted by this outgassing. The solution to this problem was to cover the entire surface of the heater block with plates of alumina. These alumina plates were also held in place by silver paint, and successfully protected the samples from the outgassed material.

Table 5.1 presents a summary of the different parameters that went into the depositions of in-situ BSCCO films.
<table>
<thead>
<tr>
<th>Batch #</th>
<th>Heater power</th>
<th>Temperature</th>
<th>Oxygen Pressure</th>
<th>Total Pressure</th>
</tr>
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<tbody>
<tr>
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<td>220 mTorr</td>
<td>220 mTorr</td>
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<td>2</td>
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<td>250 mTorr</td>
</tr>
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</tr>
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<td>7</td>
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<td>385 W</td>
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<td>250 mTorr</td>
<td>300 mTorr</td>
</tr>
</tbody>
</table>

Table 5.1: deposition parameters for in-situ prepared BSCCO samples.

The detailed procedure for depositing these films is as follows. First, the samples were "glued" to the heater block with silver paint. The remaining surface of the heater block was then covered with pieces of alumina that were also attached to the heater with silver paint. A small thermocouple wire was then attached to the top surface of one of the samples, again with silver paint. After the silver was allowed to dry, the vacuum chamber was pumped down at the same time the heater was turned on. The heater power had to be turned up gradually in order to avoid
cracking of the samples or alumina due to uneven heating and thermal expansion. When the temperature of the system was stabilized, the sputtering gas (oxygen and argon) was introduced with a constant flow so that the chamber pressure was also constant. The target was then "pre-sputtered" for about 30 minutes with a shutter covering the substrate. The purpose of pre-sputtering is to remove any impurities that may be on the surface of the target. After pre-sputtering, the shutter was opened. Deposition was continued for about 2 hours. The temperature of the substrate was maintained by tweaking the heater power up or down as required. After the depositions were completed, the oxygen flow valve was opened completely, and the pump and heater were turned off.

X-ray diffraction analysis in the θ/2θ mode was performed on all of the samples produced. By comparing the angles where intensity peaks occur to known standards, we can determine which crystal phases are present. Shown in figures 5.4 through 5.20 are the X-ray scans for the "best" sample in each of the 17 batches. In all of the figures, the vertical lines represent the known locations of intensity peaks for each of the BSCCO crystal phases present. The most indicative peaks are the ones at less than 10°. The 2223 phase has a peak at about 4°, the 2212 phase has one at slightly more than 5°, and the 2201 phase has one at about 6.5°. If the sample looked as if it contained some of the 2223 crystal phase, a resistance vs. temperature plot was taken, with the results also shown in the figures.
Figure 5.4a: X-ray scan for batch #1 showing mostly 2212 crystallization. The lines represent the known peak locations for the 2212 crystal.

Figure 5.4b: Resistance vs. Temperature curve for batch #1.
Figure 5.5: X-ray scan batch #2 showing mostly 2212 crystallization.

Figure 5.6: X-ray scan for batch #3 showing no identifiable crystallization. The two sets of lines show the known peak locations for 2212 and 2201 peaks.
Figure 5.7: X-ray scan for batch #4 showing 2201 crystallization with a small proportion of 2212 crystallization.

Figure 5.8a: X-ray scan for batch #5 showing a mixture of 2212 and 2223 crystallization. The lines show the known peak locations for 2223 and 2212 crystallization.
Figure 5.8b: Resistance vs. temperature for batch #5.

Figure 5.9a: X-ray scan for batch #6 showing almost pure 2223 crystallization.

Of particular interest from among these batches is batch 6. As seen on the X-ray scan in figure 5.9, there was success in crystallizing one of the samples in the 2223 phase. However, the superconducting transition is only at about 50 K, instead of the 107 K temperature which this crystal is known to be superconducting. This has been attributed to the existence of poorly
connected grains of the 2223 crystal. The overall resistance is thus dependent on the material that fills the 'gaps' between the 2223 grains.

Figure 5.9b: Resistance vs. temperature for batch #6.

Figure 5.10: X-ray scan for batch #7 showing 2212 crystallization.
Figure 5.11: X-ray scan for batch #8 showing 2201 crystallization.

Figure 5.12: X-ray scan for batch #9 showing 2201 crystallization.
Figure 5.13: X-ray scan for batch #10 showing 2212 crystallization.

Figure 5.14a: X-ray scan for batch #11 showing a mixture of 2223 and 2212 crystallization.
Figure 5.14b: Resistance vs. temperature for batch #11.

Figure 5.15: X-ray scan for batch #12 showing no identifiable crystallization.
Figure 5.16: X-ray scan for batch #13 showing a mixture of 2212 and 2223 crystallization.

Figure 5.17a: X-ray scan for batch #14 showing 2212 crystallization.
Batches 15 through 17 used a bismuth rich target, with composition \((\text{Pb}_2)\text{Bi}_4\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_y\). The extra bismuth should allow an increase in deposition temperature without destroying the stoichiometry of the resulting film. The results were not at all encouraging, and the X-ray scans for these batches are seen in figures 5.18 through 5.20.

Figure 5.18: X-ray scan for batch #15 which used a bismuth rich target, showing 2212 crystallization.
Figure 5.19a: X-ray scan for batch #16 which used a bismuth rich target, showing 2201 crystallization.

Figure 5.19b: Resistance vs. temperature for batch #16.
Some post-deposition treatment was attempted on this particular sample in order to solve this problem, and hopefully increase the transition temperature. Manipulation of the oxygen content of the film was attempted by baking the samples at about 500 °C in various atmospheres. 500 °C is not hot enough to affect the crystal form of the film, but is hot enough to drive off, or absorb oxygen (depending on the atmosphere). This temperature would likely also be withstood by the buffer layer structure necessary for using silicon substrates.

As expected, these procedures had little effect on the X-ray scan results of the film, but had a significant effect on the transition temperature. Initially, the sample was heated up to 600 °C in 760 mTorr of O₂ for 30 minutes. The resulting transition is seen in figure 5.21.
As seen, the zero resistance temperature dropped by over 20 °C compared to its original level. It is felt that this is due to the depletion of oxygen in the film due to the low oxygen partial pressure during baking. The sample was then baked at 500 °C in flowing O₂, in an open-ended tube furnace, for 30 minutes. The resulting transition is shown in figure 5.22.
As seen, this restored the transition temperature to near its original level. This same sample was then baked again, at 500 °C in flowing O₂ with both ends of the tube furnace capped (with a small hole on one end). The resulting film shows slight improvement, with the results seen in figure 5.23.

![Graph](image)

Figure 5.23: Resistance transition for sample of batch #6 after being baked at 500 °C in 1 atm O₂ for 1 hour.

Again, the sample was baked in the same furnace arrangement, but this time, argon was also flowing so that approximately 0.9 atm of oxygen was present. It was thought that perhaps there could be an excess of oxygen content in the film, and that the introduction of argon (to lower the O₂ partial pressure) would help to balance the oxygen content. Again, the resulting transition is shown in figure 5.24.
Finally, the sample was brought up to 800 °C at 20 ° per minute, and then immediately allowed to cool to room temperature, in pure flowing O₂ as above. The result is that the 2223 crystallization was broken down, and the sample was essentially destroyed.

The oxygen content of the film does in fact affect the transition temperature of the superconductor. However, the oxygen content does not seem to be responsible for the extremely low transition of the 2223 crystals formed in-situ. Altering the oxygen content only increased the transition by a few degrees at best.

**Surface Treatment**

It was felt that one way to encourage the connectivity of the 2223 crystal grains was to encourage alignment of these grains in the plane of the substrate surface. One controllable factor in determining alignment is that of the surface character of the MgO. It has been previously found that the growth of BSCCO occurs via an "island mechanism". That is to say that the material tends to crystallize onto existing "islands" of the film. There is further evidence that these islands
tend to nucleate at the edges of steps on the MgO surface. Therefore, by preparing a substrate surface with a high density of step edges, it is hoped that the superconducting properties of the film can be improved, especially the transition temperature.

In order to form steps in the surface of MgO substrates, all that is necessary is to anneal the bare MgO at 1100 - 1200 °C for 12 - 24 hours. Mechanically polished substrates were cut into three pieces, and two of the three underwent the annealing process. The smooth and roughened samples were then placed symmetrically onto the heater block as before, so that they should undergo identical deposition parameters in case of a temperature gradient in the heater block.

In order to measure the alignment of grains, X-ray pole scans and rocking curves were performed on each of the samples in a batch (see chapter 4). The 0/20 scans looked very similar for each of the three samples of a batch, and are not very useful in assessing the grain alignment. Batch 13 (see table 5.1) showed the best results for this particular set of experiments, and so the results for that batch will be presented here.

The BSCCO crystal is symmetrical in the a and b axes. The crystal forms preferentially with its c-axis perpendicular to the substrate, so that an X-ray pole scan of a perfect BSCCO crystal should show peaks at 90° intervals. The results of the pole scans are shown in figure 5.25. Samples 2 & 3 are the roughened samples, where sample 2 was mounted in the centre of the heater, and samples 1 and 3 were mounted symmetrically around it (sample 1 was polished).
Figure 5.25: X-ray scan showing the in-plane alignment of the 2223 crystal. Zero degrees was defined to be the angle at which the maximum intensity was found. The data for samples 1 & 2 show preferential misalignment of 45° and a slight preference for 22.5° misalignment. Sample 1 data shows only slight preferential misalignment angles, but shows a relatively large intensity peak for ALL sample angles, indicating poorer crystal grain alignment.

A resistance vs. temperature scan was then done for each of the three samples. The results are shown in figure 5.26.
Figure 5.26a: Resistance transition for three samples of batch #13.

Figure 5.26b: Blow up of transition to zero resistance for samples of batch #13.
Although the surface treatment was moderately successful at producing films with better in-plane alignment, as seen in figure 5.25, in-plane crystal grain alignment makes only a slight difference to the transition temperature of the superconductor.

X-ray rocking analysis was also performed on each of the 3 samples. The results were somewhat surprising, and are shown in table 5.2.

<table>
<thead>
<tr>
<th>Sample #1</th>
<th>Sample #2</th>
<th>Sample #3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak width (FWHM)</td>
<td>1.0°</td>
<td>1.3°</td>
</tr>
</tbody>
</table>

Table 5.2: X-ray rocking curve results showing peak widths in the θ-axis for the peak at 20=39°.

The results are surprising because the samples with the best alignment in the ab-plane (and best zero resistance temperatures) show the poorest alignment of the c-axis. However, the poorer c-axis alignment can be intuitively attributed to the step edges on the surface.

The transition temperatures found for in-situ prepared BSCCO films here compare well with those found in the literature. However, because the transition is still well below 77 K (liquid nitrogen temperature), the films are not useful for an economical device. Some significant improvement to the process is still required in order to raise the transition temperature to more useful levels.
6. MIXED BUFFER LAYERS

Introduction

As previously mentioned, buffer layers which are required to protect the BSCCO films from the chemically incompatible silicon substrates do not survive the high temperature and long duration annealing process required to crystallize the Bi\textsubscript{2}Sr\textsubscript{2}Ca\textsubscript{2}Cu\textsubscript{3}O\textsubscript{y} (2223) phase. Cracks formed in the buffer layer, allowing the interdiffusion of silicon and copper that results in the destruction of the superconducting properties of BSCCO.

One possible approach to solve this problem is to minimize the thermal stresses in the layer structure. This can be done by inserting a layer of mixed SiO\textsubscript{2} and ZrO\textsubscript{2} between 'pure' layers of each of these materials, so that the structure looks as in figure 6.1.

\begin{center}
\begin{tabular}{c}
BSCCO \\
ZrO\textsubscript{2} \\
Si-Zr-O \\
SiO\textsubscript{2} \\
Silicon
\end{tabular}
\end{center}

Figure 6.1: Mixed buffer layer structure.

The insertion of the mixed layer of Zr-Si-O allows for a smoother transition of the thermal expansion coefficient of the films, and will thus hopefully render the structure more capable of withstanding the high temperatures.

The mixed layer is deposited by sputtering both a zirconium and silicon target simultaneously (in an oxygen/argon atmosphere), and moving the substrate back and forth so that it is in front of both of these targets alternately. Since the time required to deposit a monolayer of atoms is on the order of seconds, the resulting film should be a relatively uniform mixture.
By varying the thickness and deposition temperatures of each of the layers in the film, one should be able to arrive at an optimal situation for minimizing the thermal stresses and shear forces on the buffer layer components.

Linear Thermal Expansion Model

In order to mathematically derive the optimal deposition parameters, many simplifying assumptions were made. These assumptions are: (1) a linear (non-temperature dependent) thermal expansion coefficient, (2) a linear elastic modulus, (3) perfect film adhesion, and (4) a rigid substrate such that all layers have equal length distortion. The resulting equations result from these assumptions:

\[
\frac{\Delta L}{L} = \alpha_n \Delta T + \frac{F_n}{E_n d_n} \quad (6.1)
\]

\[
\sum_n F_n = 0 \quad (6.2)
\]

Here, \(\alpha_n\) is thermal expansion coefficient of the \(n\)th layer, \(E_n\) is the elastic modulus of the \(n\)th layer, \(d_n\) is the thickness of the \(n\)th layer, and \(F_n\) is the force per unit width of the "beam" on the \(n\)th layer. Simultaneous solutions to these equations were calculated numerically. The interfacial shear forces \(S_n\) were then calculated such that:

\[
S_n - S_{n-1} = F_n \quad (6.3)
\]

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness ((\mu)m)</th>
<th>(\alpha_n) ((x10^{-6}))</th>
<th>(E_n) ((\text{GPa}))</th>
<th>Deposition Temp. ((^\circ\text{C}))</th>
<th>Interfacial Shear Force at 800 (^\circ\text{C}) ((\text{N/m}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSCCO</td>
<td>1.0</td>
<td>11</td>
<td>200</td>
<td>20</td>
<td>1862</td>
</tr>
<tr>
<td>ZrO(_2)</td>
<td>0.65</td>
<td>7.5</td>
<td>185</td>
<td>20</td>
<td>2654</td>
</tr>
</tbody>
</table>
Results and Discussion

The best results for BSCCO crystallization on this structure were obtained by the following parameters: 0.5 μm of thermally grown SiO₂, then 0.2 μm SiO₂, 0.3 μm Si-Zr-O, and 0.5 μm ZrO₂, all sputtered onto the substrate at about 450 °C. The BSCCO was then sputtered onto the room temperature substrate to about 1 μm. Postdeposition annealing was performed via three temperature ramps at 5 °C/min to 730 °C for 2 h, 760 °C for 1 h, 785 °C for 2 h (all in open air), and a final anneal at 600 °C for 10 min. in 0.3 Torr O₂. The furnace was allowed to cool to 500 °C following each high temperature soak.

<table>
<thead>
<tr>
<th>Layer:</th>
<th>Thickness (μm)</th>
<th>αₙ (x10⁻⁶)</th>
<th>Eₙ (GN/m²)</th>
<th>Deposition Temp. (°C)</th>
<th>Interfacial Shear Force at 800 °C (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSCCO</td>
<td>1.0</td>
<td>11</td>
<td>200</td>
<td>20</td>
<td>1862</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.5</td>
<td>7.5</td>
<td>185</td>
<td>20</td>
<td>2470</td>
</tr>
<tr>
<td>Zr-Si-O</td>
<td>0.3</td>
<td>25.3</td>
<td>126</td>
<td>20</td>
<td>3244</td>
</tr>
<tr>
<td>SiO₂ (sputtered)</td>
<td>0.2</td>
<td>43</td>
<td>67</td>
<td>20</td>
<td>3703</td>
</tr>
<tr>
<td>SiO₂ (thermal)</td>
<td>0.5</td>
<td>43</td>
<td>67</td>
<td>1100</td>
<td>3295</td>
</tr>
<tr>
<td>Si</td>
<td>350</td>
<td>2.6</td>
<td>166</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.2: Shear force calculation results for a mixed buffer layer deposited at room temperature
<table>
<thead>
<tr>
<th>Layer:</th>
<th>Thickness (µm)</th>
<th>$\alpha_n$ ($\times 10^{-6}$)</th>
<th>$E_n$ (GN/m²)</th>
<th>Deposition Temp. (°C)</th>
<th>Interfacial Shear Force at 800 °C (N/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSCCO</td>
<td>1.0</td>
<td>11</td>
<td>200</td>
<td>20</td>
<td>1865</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>0.5</td>
<td>7.5</td>
<td>185</td>
<td>450</td>
<td>2177</td>
</tr>
<tr>
<td>Zr-Si-O</td>
<td>0.3</td>
<td>25.3</td>
<td>126</td>
<td>450</td>
<td>2540</td>
</tr>
<tr>
<td>SiO₂ (sputtered)</td>
<td>0.2</td>
<td>43</td>
<td>67</td>
<td>450</td>
<td>2751</td>
</tr>
<tr>
<td>SiO₂ (thermal)</td>
<td>0.5</td>
<td>43</td>
<td>67</td>
<td>1100</td>
<td>2344</td>
</tr>
<tr>
<td>Si</td>
<td>350</td>
<td>2.6</td>
<td>166</td>
<td>N/A</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.3: Shear force calculation results for a mixed buffer layer deposited at 450 °C

Unfortunately, even the best of these buffer layers did not adequately protect the BSCCO film above 800 °C. The X-ray scans of these films showed predominantly 2212 crystallization, with some signs of the 2201 phase present. Additional evidence to the presence of these crystal phases is that the resistance vs. temperature scans showed a transition starting at 86 K and a tail on the curve so that zero resistance is not achieved until about 45 K.

If the buffer layer structure is made thinner, the shear forces are reduced, and the buffer layer can then survive the high temperatures. However, if the layers are too thin, the buffer becomes ineffective at stopping the interdiffusion of copper and silicon. If the buffer layers are made thicker, the shear forces are higher, and the buffer cracks or peels resulting again in the interdiffusion of copper and silicon through the cracks.

Although some improvements can be made to the effectiveness and robustness of the buffer structure, these improvements are not enough to achieve effective crystallization of the 2223 phase. There was no success in depositing Bi₂Sr₂Ca₂Cu₃O_y onto silicon by these methods alone.
7. EPITAXIAL BUFFER LAYERS

Introduction

Another approach to strengthening the buffer structure is to have the ZrO_2 buffer layer grown epitaxially. Epitaxial simply means that the thin film is a single crystal. Normally, sputtered films are polycrystalline. That is that the films are made up of microscopic crystal grains that are not generally ordered. The cracks which form in the buffer layer as in chapter 6, will almost certainly form on the boundaries of these crystal grains. Since there are no grain boundaries in an epitaxial film, it is felt that the buffer layer will be much more resilient to the thermal stresses, and allow the annealing of Bi_2Sr_2Ca_2Cu_3O_y on a silicon substrate. Cubic zirconia is well suited for epitaxial growth onto silicon, because its lattice constant is closely matched to that of silicon.\(^{28}\)

Need for Stabilization of Zirconia

Zirconia, like BSCCO, has more than one crystal phase. This presents a major problem for growing epitaxial films, because there will be 2 or more different crystals being formed. However, by adding small amounts of elements such as yttrium or calcium, the cubic zirconia crystal phase can be stabilized. Yttria stabilized zirconia (YSZ) films with a composition of approximately Y_{0.15}Zr_{0.85}O_2 provide the required stabilization of the cubic zirconia. The yttrium content needs to be high enough to stabilize the crystallization, but low enough so as not to change the lattice constant and thermal expansion coefficient too drastically.

For this purpose, a special sputtering target was fabricated. This target is merely a disk of Zr metal, with a strip of Y metal through the middle of it as in figure. 7.1.\(^{29}\)
By sputtering in an oxygen atmosphere of appropriate partial pressure, YSZ films of the correct stoichiometry can be formed.

**Hydrogen Termination of Silicon**

Another obstacle to the epitaxial growth of YSZ on silicon is that of the surface oxide on the silicon (SiO$_2$). If the silicon surface is not clean of oxide, YSZ films will not grow epitaxially, presumably because of the change in lattice constant. Removal of the oxide by hydrofluoric acid (HF) is easy enough, except that on exposure to air, an oxide layer is instantly formed on a bare silicon surface. Since there is no mechanism in the lab for etching the SiO$_2$ and then commencing sputtering without breaking the vacuum in between (ie. exposing it to air), the silicon must be treated so that oxidation is inhibited.

By terminating the entire surface of the silicon with hydrogen, the hydrogen provides passivation of the silicon surface against recontamination or oxidation. By leaving no unterminated silicon bonds on the surface, the hydrogen prevents contamination, but readily allows replacement by deposited elements such as YSZ.

Hydrogen termination of silicon is achieved by mixing the HF etchant with water and ethanol. The HF serves to etch off the native oxide on the surface, while the ethanol and water
serve to terminate the bare silicon with hydrogen. For this experiment, substrates were dipped into a 1:1:10 ratio mixture of HF, water, and ethanol respectively, and ultrasonically agitated for 5 to 10 minutes.

Samples treated by such a mixture can survive brief exposures to room air without drastic contamination. Table 7.1 shows some quantitative measurements of contamination of substrates that underwent a similar procedure.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Carbon contamination (monolayers)</th>
<th>Oxygen contamination (monolayers)</th>
<th>Fluorine contamination (monolayers)</th>
</tr>
</thead>
<tbody>
<tr>
<td>immediately after etch</td>
<td>0.025 ± 0.005</td>
<td>0.005 ± 0.002</td>
<td>0.010 ± 0.002</td>
</tr>
<tr>
<td>dip in water</td>
<td>0.15</td>
<td>0.022</td>
<td>0.003</td>
</tr>
<tr>
<td>1 atm N₂ for 10 min.</td>
<td>0.035</td>
<td>0.008</td>
<td>0.008</td>
</tr>
<tr>
<td>1 atm air for 1 min.</td>
<td>0.064</td>
<td>0.010</td>
<td>0.012</td>
</tr>
</tbody>
</table>

Table 7.1: Contamination measurements on hydrogen terminated silicon.30

As can be seen from the table, even after exposure to air for 1 min., less than 10% of the surface is touched by contaminants. By treating the silicon in this manner, the surface can be kept relatively free of oxide while the substrate is transferred into the vacuum chamber for sputtering.

Experimental Procedures

Highly polished silicon with (111) crystal orientation was used for substrates for these experiments. The substrates underwent the etching procedure described above, and were immediately mounted onto the heater block. The samples were held onto the heater block by small bolts and washers, with silver paint applied to the back side of the sample in order to obtain good thermal contact to the heater. The vacuum chamber was then immediately pumped down,
so that the samples would spend no more than about 3-4 minutes in room air after being etched in the HF/water/ethanol mixture.

The samples needed to be heated to about 750 - 800 °C by the same substrate heater described in chapter 5. These high temperatures pose a problem, because the heater block assembly begins to outgas significantly at these temperatures, and a good vacuum is crucial to epitaxial growth of YSZ. In order to achieve the high vacuums required, the system needed to be pumped for several hours, while the substrate was hot.

After a pressure of about $8 \times 10^{-6}$ Torr was achieved with a hot substrate, argon was introduced for presputtering. The introduction of oxygen to the system (necessary for reactive sputtering of YSZ) was delayed so as to minimize the amounts of SiO$_2$ on the surface of the substrates. After presputtering was completed (ie. the target was adequately "cleaned"), about 3 seconds of sputtering was done in the absence of oxygen. This was calculated to be about enough to deposit one monolayer of metal, and was done to avoid silicon oxidation as oxygen was introduced for the reactive sputtering of YSZ. About 0.4 mTorr of oxygen was introduced, and DC sputtering of the Y/Zr target was begun immediately.

After the completion of sputtering, there was no special treatment of the samples. The heater was shut off, and air was introduced into the system when the temperature dropped below about 300 °C.

**Results and Discussion**

An X-ray (0/20) scan of one of the samples is shown in figure 7.2.
Figure 7.2: X-ray scan of YSZ sample. The peak at 28.4° is the silicon (111) peak, and is due to the substrate. The vertical lines show the location of the YSZ peaks for a cubic crystal, with the indices shown.

This figure is evidence that the YSZ film is indeed epitaxial. The absence of YSZ peaks with an index other than (x00) shows that there is good crystal alignment in the c-axis. Since this is a cubic crystal, alignment for the c-axis should be the same as that for the a and b-axes. There was, however, no off-axis peak found for the film to verify this assumption by an X-ray pole scan.

It is curious that the YSZ is of (100) orientation, while the silicon substrate is of (111) orientation. It might be expected that YSZ of (111) orientation would grow onto (111) silicon.

The effectiveness of this YSZ as a BSCCO buffer layer has not yet been tested. Since it is deposited at 750-800°C, it is unlikely to crack during post-annealing of BSCCO. However, cooling the film to room temperatures may have caused micro cracks that will allow the destructive interdiffusion of silicon and copper.

There is a further question about the compatibility of yttrium with BSCCO. It is possible that yttrium will degrade the properties of the 2223 crystal. If this is the case, calcium may be used as a stabilizer for the cubic phase of zirconia. Since calcium is a constituent of BSCCO, it is unlikely to have detrimental effects. However, the fabrication of a target for sputtering calcium stabilized zirconia will be more difficult than for YSZ.
8. CONCLUSION

Summary of Results

Noise Properties of BSCCO

The noise properties of a Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ film were investigated with the purpose of determining the applicability of the material for bolometer use. The noise magnitude results of $S_n=10^{-15}$ Hz$^{-1}$ in the transition region at 100 Hz compare well with those reported in the literature for Y$_1$Ba$_2$Cu$_3$O$_y$. From the electrical noise standpoint then, Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$ is a suitable material for use in a bolometer.

In-Situ Preparation of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_y$

According to X-ray diffraction analysis, BSCCO of the 2223 crystal phase was prepared in-situ (as deposited). The best transition temperature of about 55 K is similar to those reported in the literature for in-situ BSCCO. However, 55 K is too low for useful use as a bolometer, and thus in-situ processing is not at present practical for crystallizing practical BSCCO onto silicon.

Buffer Layers on Silicon

An attempt was made to make the buffer layer more robust by the insertion of a mixed layer of Si-Zr-O. The insertion of this layer reduced the thermal stresses, but was still not enough of a reduction to allow annealing of BSCCO without cracking of the buffer. By making the layers thicker, the stresses are increased, but by making the layers thinner, copper and silicon will diffuse through the buffer layers.
The second method of making the buffer layers more robust is to use epitaxial films of yttrium stabilized zirconia. Epitaxial YSZ was successfully grown, but has not yet been tested for its effectiveness as a buffer layer.

Recommendations for further work

There are various ways that the noise performance of BSCCO material may be improved. Firstly, the driving current for the four point probe can be optimized for maximum sensitivity. Secondly, the quality of crystallization of the BSCCO can be improved. Specifically, thermal fluctuation 1/f noise can be reduced by increasing the thermal capacity. This, however, will reduce the sensitivity of a bolometer, so an optimization process may be required.

The effectiveness of epitaxial YSZ buffer layers for BSCCO on silicon has not yet been investigated. Whether or not the epitaxial nature of the film provides enough resilience to endure the thermal stresses involved is not known.

There is also the possibility that the yttrium stabilizing element may react chemically with BSCCO. If this is the case, calcium may be used as a stabilizing element since calcium does serve to stabilize zirconia, and is an element of BSCCO. If this needs to be done, a suitable method for sputtering calcium stabilized zirconia must be developed. This might be done by pressing a mixture of calcium oxide and zirconia powders into a sputtering target.

Some further study is needed to provide a method for the fabrication of the membrane structure. It is doubtful that a membrane structure will survive any annealing process, and therefore, a way to protect the BSCCO from the KOH etchant must be found.

A method of microscopically patterning the BSCCO films must be developed, since conventional photoresist methods will likely destroy the superconducting properties. One possible way of doing this would be to selectively destroy the buffer layer before depositing the BSCCO, so that only the areas where a superconductor is desired are protected from the silicon.
Conclusion

Although the goal of producing a BSCCO bolometer on silicon was not met, some key elements to meeting this goal were investigated. No other reports of successful deposition of Bi$_2$Sr$_2$Ca$_2$Cu$_3$-O$_y$ onto a silicon substrate were found in the literature.
BIBLIOGRAPHY