CHAPTER 2

SAMPLE PREPARATION AND CHARACTERIZATION

This study focused on specimens of high-temperature superconducting YBCO thin films, mostly double-sided, that were fabricated by pulsed-laser deposition (PLD) method. The traditional photolithography and wet etching process were employed to pattern the YBCO thin films.

This chapter includes four parts. In the first two parts, the fabrication and characterization of the high-temperature superconducting YBCO thin films are introduced. The third part deals with the patterning process. The system packaging is included in the last part.

2.1 Fabrication of YBCO thin films by PLD

2.1.1 Introduction to pulsed-laser deposition

Pulsed-laser deposition, one of the important methods for thin film deposition, was first introduced in 1960's [Smith and Turner 1965]. Since that time PLD technique has kept pace with the development of high-energy laser technology although it did not draw enough attentions from the scientists in the early years. The breakthrough in the development of PLD technique was in the end of 1980's when it was successfully

applied to synthesize high-T_c superconducting thin films [Dijkkamp *et al* 1987; Narayan *et al* 1987]. This breakthrough generated enormous excitement and initiated extensive research interest. Subsequently, PLD has been proven to be successful in fabricating thin films for a wide range of materials, especially the multi-component oxides. The primary reason for the success of PLD in thin film deposition is that the composition of the target is reproduced in the film without much trouble. This ease of compositional control is very important since the crystalline quality depends on the elimination of substitution defects. This control of film stoichiometry is especially crucial for multi-component materials like YBCO. Today, PLD technique has become one of the most successful vapor deposition techniques in research and device applications.

Conceptually and experimentally, PLD is extremely simple, probably the simplest among all thin film growth techniques. A typical PLD system consists of two main parts that can be separated from each other: a deposition chamber and a high-power laser. The former is a vacuum chamber in which a target holder and a substrate holder are housed for deposition. The high-power laser enters the chamber through a window and is used as an energy source to vaporize target materials and deposit thin films. A set of optical components is used to focus the laser beam over the target surface. The deposition processes are as follows. A laser beam is focused onto the target surface with an incident angle of around 45 degree. Pulsed lasers are used in order to reach high energy required for ablation. After undergoing complicated beam-solid interactions including energy absorption, surface melting, vaporization of target material and ionization, a plasma region is instantaneously generated near the surface of the target. This plasma expands perpendicularly to the target surface and forms a

plume. The plume consists of neutral or ionic atoms, molecules and radicals that then speed toward the substrate. These species reach the substrate with high kinetic energy (typically in the order of 10eV, depending on energy density of the laser pulse, target material, ambient gas pressure, *etc*.) and are deposited on the substrate surface. As the process is repeated with more laser pulses, a thin film is formed on the substrate surface. Once the deposition conditions are fixed, the thickness of the as-deposited film is proportional to the number of the laser pulses.

2.1.2 PLD system

All the YBCO thin film samples used in this study were deposited using the homebuilt PLD system I (PLD-I) in our center. The original design of the PLD-I system was improved in order to fabricate large-area double-sided YBCO thin films for the application in passive microwave devices [Xu 1999 and references therein]. The schematic view of PLD-I is shown in Figure 2.1. Compared with general on-axis PLD systems, the PLD-I system has two distinct features. The first and most important feature is that this system is equipped with a radiation heater made from single crystal silicon, which is developed at the Institute of Physics, Chinese Academy of Sciences [Zhou *et al* 1996]. This Si heater is tilted about 5 degrees from the vertical direction. The substrate is located on a small step of the heater surface by its own weight without using silver paste as required by other heaters such as the widely used wire heater. By developing a current control mode for the Si heater, we are able to obtain uniform and stable temperature along the Si heater surface during deposition. The other feature is that a mechanical mirror holder rotated by dc motors is used to periodically scan the laser beam so that it has a circular trace on the target surface. By using scanning laser

beam, we are able to fabricate double-sided YBCO film with size up to 30 × 30 mm^2. The PLD-I system has been used to fabricate both single-sided and double-sided YBCO thin films on various substrates with sizes of 5 × 10, 10 × 10, 10 × 15, 20 × 8 and 25 × 13 mm^2.

2.1.3 Target and substrate

The disk-like sintered ceramic YBCO-123 targets are purchased from the Institute of Physics, Chinese Academy of Sciences and they have a T_c of 89-91 K, density of 5.0-5.4 g/cm^3. The density of the target is not high enough but it did not affect the electrical quality of the as-deposited films much. However, it may be responsible for the more droplets or particles on the surface of the as-deposited films [Xu 1999].

The YBCO thin films are deposited on the double-sided polished single crystal LAO substrates with size 15 × 10 × 0.5 mm^3 which are purchased from Anhui Institute of Optics and Fine Machines, Chinese Academy of Sciences. LAO substrates have been widely used for deposition of YBCO films for high-frequency applications due to their small loss tangent and the relative small lattice mismatch between YBCO and LAO. In the literature, MgO and sapphire substrates have also been used for high-frequency applications but due to large lattice mismatch, the deposition of high-quality YBCO films on them is more complicated and difficult. However, LAO in particular suffers from the fact that it tends to twin, and these twin boundaries can be formed and become mobile at typical processing temperatures. The relevant properties of LAO substrates for YBCO thin film deposition are given in Table 2.1. The properties of MgO and sapphire substrates are also listed for comparison.

2.1.4 Deposition process and optimal conditions

The quality of the deposited YBCO thin films is determined by many factors. It is difficult to construct a suitable deposition process and find a set of "optimized" parameters including substrate temperature, oxygen pressure, laser energy and so on. A relatively large amount of time and efforts were spent on this throughout the course of the project. Table 2.2 lists the typical procedure that was followed in the deposition of YBCO thin films reported in this thesis. The parameters listed in this table are those that gave high quality *c*-axis YBCO films on LAO substrates. It should be stressed that the exact parameters for optimal deposition are system-dependent and the parameters quoted here are only valid for the PLD-I system.

2.2 Characterization of YBCO thin films

It has been realized that the properties of the YBCO thin films are extremely sensitive to structural imperfection and strains mainly due to the short superconducting coherence length of YBCO. Sample dependence is a general concept used in the study of YBCO thin films. There is a need to gather as much information as possible on the YBCO thin films under test in order to understand the special phenomena observed in these materials.

In this study, the as-deposited YBCO thin films have been characterized using several techniques to gather the information on crystalline structure, surface morphology and

electrical properties *etc*. These results would be very helpful in understanding the anomalous microwave properties of the YBCO thin films.

2.2.1 X-ray diffraction

X-ray diffraction (XRD) has been proven to be a valuable technique for the structure characterization of materials in different forms, such as powder, bulk, film and single crystal. Two important XRD techniques have been employed in characterization of the deposited YBCO thin films. One is the standard 2θ diffraction scan, which can give information on the phase, orientation and lattice parameters of the thin films under test. The other is the rocking curve measurement from which the crystalline quality of the film may be gained.

A typical 2θ scan is shown in Figure 2.2 for a YBCO thin film deposited on a LAO substrate with the conditions listed in Table 2.2. The presence of the (00*l*) peaks corresponds to a well-crystallized single orthorhombic phase and indicates that the film is preferentially oriented with the *c*-axis perpendicular to the surface of the film. From the spacing between the peaks, the *c*-axis lattice parameter can also be determined. Following the method introduced by B. H. Moeckly, the *c*-axis parameter may be obtained by plotting the calculated spacing value $d(\theta)$ vs. $\cos^2\theta/\sin\theta$ and extrapolating the plot to zero [Moeckly 1994]. This is done in Figure 2.3 and the resultant *c*-axis lattice parameter for this film is 11.687 Å. The corresponding rocking curve measurement results for the (005) peak are shown in Figure 2.4. The full width at half maximum (FWHM) of the peak is 0.547^{o}, which is comparable to the values of high quality YBCO thin films on LAO substrates reported in the literature [Xu 1999].

2.2.2 Atomic Force Microscopy

Atomic force microscopy is widely used in this study for the characterization of the surface morphology of thin films. A typical result for YBCO thin films deposited with the standard conditions is shown in Figure 2.5. It can be seen that the surface of the film is quite rough. Many large outgrowths in irregular shapes can be found on the surface and they are believed to be copper oxide particles. The emergence of these particles should be a natural consequence of the large area plume-scanning deposition. It has been proven that the stoichiometry of the target is only reproduced in the center of the plume. However, for the plume-scanning deposition, not only the center of the plume but also other parts of the plume, where there are some copper oxide particles, are scanned and deposited onto the substrates. Besides the copper oxide outgrowths, there are also many bar-like particles on the film surface. These bar-like particles have been proven to be *a*/*b*-axis grains using high-resolution transmission electron microscopy as will be shown later.

2.2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) is a standard method used for characterization of the surface morphology of thin films. This technique is very useful for a quick assessment of the entire surface area of a given film, whereas other, perhaps more sensitive methods (*e.g.* AFM) are somewhat slower and allow examination of only limited area of the sample. Of particular importance are the examinations of the

particles produced by PLD and observations of grains with their *c*-axis in the plane of the film.

A typical SEM photograph of the YBCO thin film deposited in this work is shown in Figure 2.6. One can easily see particles in irregular shape and bar-like particles on the surface of the film, which is consistent with the AFM results.

2.2.4 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is another valuable technique for direct examination of the microstructure of thin films. Low-resolution mode of TEM allows observation of the grain structures and large-scale defects. High-resolution mode of TEM can even image the film in atomic scale and is thus very promising for examining the fine lattice structure, including crystalline quality, strain effects, point defect, grain boundary and interface structure.

A low-resolution TEM photograph is shown in Figure 2.7 to stress the bar-like particles observed with AFM and SEM. It can be seen from the high-resolution TEM photograph of Figure 2.8 that the bar-like particles are *a*/*b*-axis grains in the *c*-axis film. As will be shown in Chapter 4, these *a*/*b*-axis grains may play important roles in the anomalous microwave effect.

2.2.5 DC electrical measurements of deposited films

Four-point measurement of electrical resistance has been applied to characterize the DC transport properties of the YBCO thin films. Through measurement of the *R*-*T* curve, the superconducting temperature and the transition width can be determined. A typical *R*-*T* curve is shown in Figure 2.9. It shows a T_c of 89.1 K and ΔT about 1.5 K. However, it should be mentioned that these parameters are not always repeatable even though we use the same settings to deposit the YBCO thin films, which may be caused by the shift of deposition conditions or the difference among the LAO substrates. The DC critical current density J_c for the films deposited with standard conditions can also be known through measuring the current-dependent resistance of the YBCO micro-bridge. It is calculated from $J_c = I_c /(wt)$, where *t* is the thickness of the film and *w* is the width of the micro-bridge. The resultant J_c is more than 2×10^6 A/cm^2 at 77 K.

2.2.6 Microwave surface resistance of deposited films

The surface resistance of the as-deposited YBCO thin films was also measured at 10.66 GHz, 77K using a dielectric resonator. The details of the resonator and the measurement will be discussed in Chapter 3. The resultant surface resistance values of the YBCO thin films are quite sensitive to the deposition parameters and fall into a wide range from 0.7 mΩ up to 10 mΩ. The surface resistances of most of the YBCO thin films deposited with the parameters listed in Table 2.3 are about 1 mΩ.

2.3 Patterning of YBCO thin films

In order to carry out the microwave measurement of the YBCO thin films, in most cases, the films should be designed into different patterns such as microstrip resonator

and planar disk resonator. In this study, the YBCO thin films are patterned using the standard photolithography and wet etching process with a slight modification [Lee WF 1999]. The patterning process and conditions are discussed in this section.

It has to be mentioned that the soft masks used in the photolithography process, which were produced by a commercial company (Laser Technologies Singapore Pte. Ltd.), had built-in errors in dimension that were estimated to be within 6 μm. This error is the dominant error in the whole processes and it determines the error of the ultimate dimension of the pattern.

The standard photolithography and wet etching process that was followed in this study are shown step by step in Table 2.3. It should be noted that the thickness of the YBCO thin films is generally non-uniform, especially at the edge of the substrate. To etch out all the films undesired, over-etching is generally applied. However, since wet etching is isotropic, in which undercut is inevitable, over-etch will cause reduced dimension of the output pattern compared with the dimension of the mask. This over-etch effect caused by undercut can be compensated in a certain degree by proper dimensioned mask [Wolf and Tauber 1986]. In this study, the mask dimensions have been enlarged for 3μm from the original simulated dimension in order to achieve the accuracy required. Wet etching for YBCO is accomplished by using 1% phosphoric acid, H_3PO_4 [Shih and Qiu 1998]. It should be stressed that the etching rate could be varied with time. This is mainly due to the evaporative nature of the solution. As a consequence, the solution used could become more concentrated than the original one. The etching duration can be varied from 120 seconds for the original 1% acid to 3-5 seconds for the same solution which stored for more than 6 months. A fast etching rate is usually

unfavorable, as it will cause jagged edges for the patterned transmission line, where the current peaks. The jagged edge will degrade the device performance, especially in its power handling capability [Gevorgian *et al* 1995]. If the etching duration falls short of ~ 20 seconds, the solution should be diluted, or rather a new solution should be used to prevent such an effect. Such variation and inconsistency have complicated the etching process that demands stringent control of all parameters in order to achieve the required accuracy in dimension.

2.4 Packaging for cryogenic test

The YBCO thin film samples need to be packaged into a cavity so that the microwave measurements can be carried out in cryogenic environment. There are some considerations for the cavity design.

Firstly, the cavity has to be properly designed in order to minimize the effects caused by the cavity upon the sample performance. The sample performance will be seriously affected if the resonant frequency of the sample overlaps with the resonant frequency of the cavity. A common way of suppressing these effects is to keep the overall interior dimension of the cavity as small as possible. On the other hand, the sample performance should not be affected by mirror effect created by sidewalls so the interior dimension of the cavity cannot be too small. The upper cover should be at least $10 \times d$ (d is the height of the substrate) away from the substrate to avoid radiation disturbance from the cover [Pozer 1998]. Besides, the cavity should be designed in such a way that the housing and packaging processes can be done in an easy and convenient

manner. The completed cavity design is given in Figure 2.10 and the photograph of the cavity is shown in Figure 2.11.

Unlike other materials, YBCO is especially sensitive to moisture where the ambient moisture is of most concern. In order to prevent deterioration of the film quality over time, the housing cavity should be sealed and the most common practice is to use an Indium wire. The ambient moisture can be reduced or eliminated if the cavity is vacuumed. But this could be tedious which complicates the packaging process. An easier way is to fill the cavity with Helium gas. Helium is chosen because it has a boiling point at 4 K so that it will not be liquidated at the testing temperatures (>10 K). Figure 2.12 shows a photograph of the homemade packaging chamber for YBCO thin film devices.

Table 2.1 Properties of dielectric substrates used for growth of YBCO films [Moeckly 1994; Lancaster 1997].

Substrate	Structure	Lattice Constant (Å)	% Lattice Mismatch to YBCO	Melting point (^{o}C)	Dielectric Constant @ 300K	Loss Tangent (10^{-6})
$LaAlO_3$	Rhomb (perov)	a=5.36 α=3.79 c=13.1	1.6	2110	24	7.6 (77K, 10GHz)
MgO	Cubic (NaCl)	a=4.212	9.3	2852	10	6.2 (77K, 10GHz)
Al_2O_3 (α)	Hexagonal (corundum)	a=4.758 c=12.99	Depend on face	2050	9.3	0.038 (80K, 10GHz)
$YBa_2Cu_3O_7$	Ortho	a=3.82 b=3.89 c=11.68	/	~1000	/	/

Table 2.2 The procedure followed for the laser-ablated growth of films reported in this thesis.

$YBa_2Cu_3O_{7-\delta}$ Laser Ablation Process Sheet

1. Remove organic particles from the substrate surfaces with acetone in the ultrasonic cleaner
2. Rinse the substrates in deionized water
3. Remove metal particles from the substrate surfaces with 10% HNO_3 in the ultrasonic cleaner
4. Rinse the substrates in deionized water
5. Clean the substrates with isopropyl in the ultrasonic cleaner
6. Dry the substrates with nitrogen gas flow
7. Mount the substrates onto the silicon heater
8. Seal the chamber and pump down to 4×10^{-5} mbar
9. Turn on the silicon heater and increase the current gradually
10. Turn on cooling water and start to rotate the target when the temperature of the heater (T_h) reaches 200^{o}C
11. When T_h reaches 400^{o}C, hold the turbo pump, half close the pump-out valve, open and adjust the oxygen-in valve until the pressure stabilized at 2.0×10^{-1} mbar
12. Gradually increase T_h to 740 ^{o}C and adjust the oxygen-in valve to keep the pressure at 2.0×10^{-1} mbar
13. Start to rotate the reflection mirror and turn on the laser (with constant energy of 240 mJ and frequency of 5Hz)
14. Deposition for 30 minutes
15. Shut down laser and stop the rotating mirror
16. Close the pump-out valve, shut down pumps, increase the oxygen pressure to 8×10^{2} mbar and meanwhile reduce the current of the heater to reduce the temperature until T_h=480 ^{o}C
17. Anneal the films for 30 minutes
18. Gradually decrease the current and cool down the heater to room temperature
19. Stop the rotating target and shut down the cooling water
20. Increase the chamber pressure, open the chamber and take the films out

Table 2.3 The photolithography and etching process for patterning YBCO thin films in this work.

Photolithography and etching process sheet

1. Engage the film on spin coater
2. Clean the upside film with acetone or isopropyl while spinning is carried on
3. Blow gently the film surface with nitrogen gas to remove moisture on the surface
4. Apply photoresist (Shipley 1400-31) on the surface using spinning is carried on at 3500 rpm for 60 seconds
5. Bake of the film using hot plate for 1 minute at 75^{o}C to remove the solvent of the photoresist
6. Cool the film to room temperature
7. Load the film on the mask aligner and do alignment of the film and the mask
8. Change to contact mode and expose the film for 8 seconds to 270W UV light (270W is the reading of mask aligner meter and not the output energy of UV light)
9. Engage the film on spin coater and develop with Microposit™ developer for 15 seconds while spinning
10. Rinse with deionized water for about 20 seconds to stop developing process while spinning is carried on
11. Blow gently the film surface with Nitrogen gas to remove moisture on both surfaces
12. Carefully apply photoresist on the backside of the film (if it is double-sided) to prevent the backside from etching
13. Bake the film with oven for 7 minutes at 120^{o}C to increase the etch resistance of the photoresist
14. Cool the film to room temperature
15. Etch the film in 1% H_3PO_4 solution for 120 seconds
16. Rinse in deionized water to stop etching
17. Blow gently the film surface with Nitrogen gas to remove moisture on both surfaces
18. Rinse the film in acetone to remove the photoresist
19. Rinse the film in deionized water to remove the residual acetone
20. Blow gently the film surface with Nitrogen gas and then bake the films in oven for 5~7 minutes at 120^{o}C to remove moisture from the film

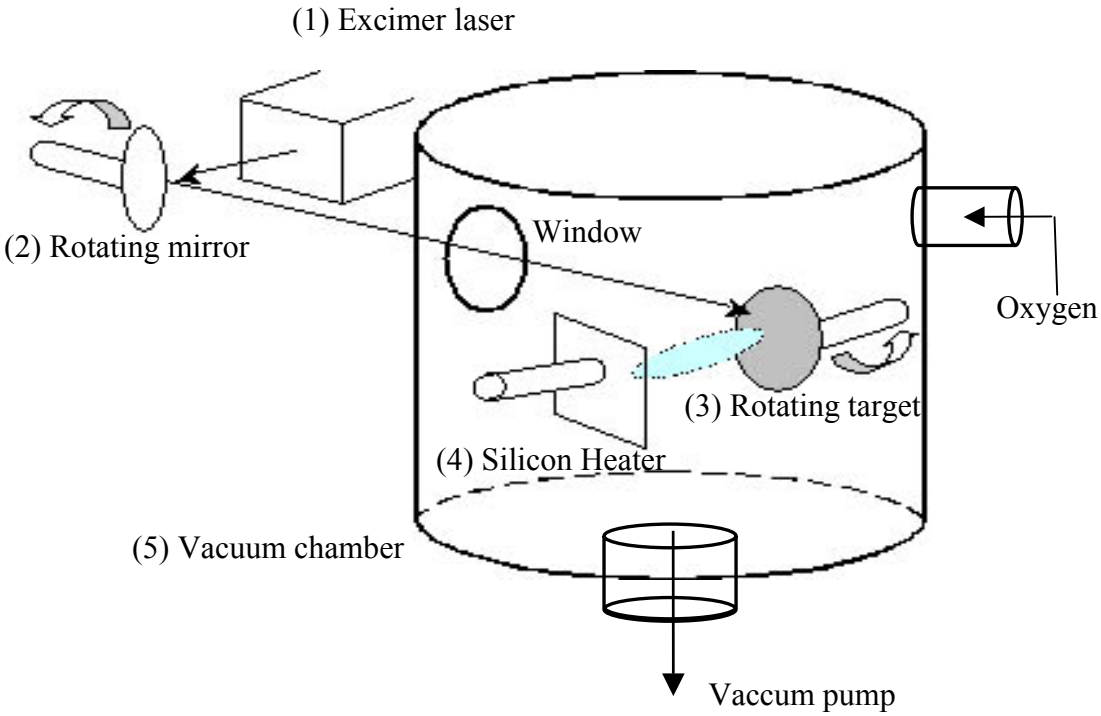

Figure 2.1 Schematic diagram of the PLD-I system.

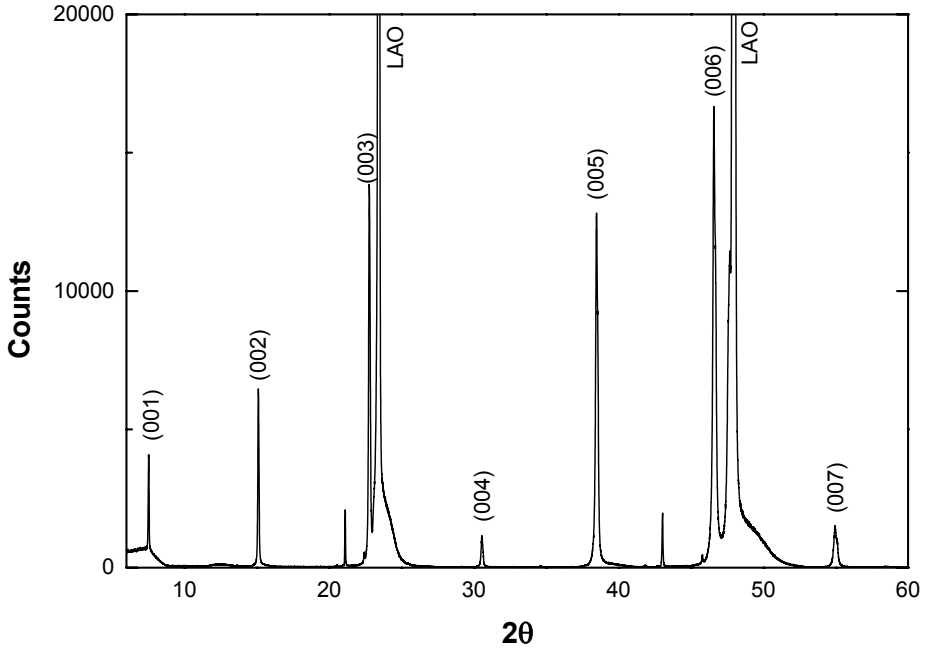

Figure 2.2 A typical 2θ x-ray scan for *c*-axis oriented YBCO thin films grown on $LaAlO_3$ substrates. The *c*-axis peaks are marked.

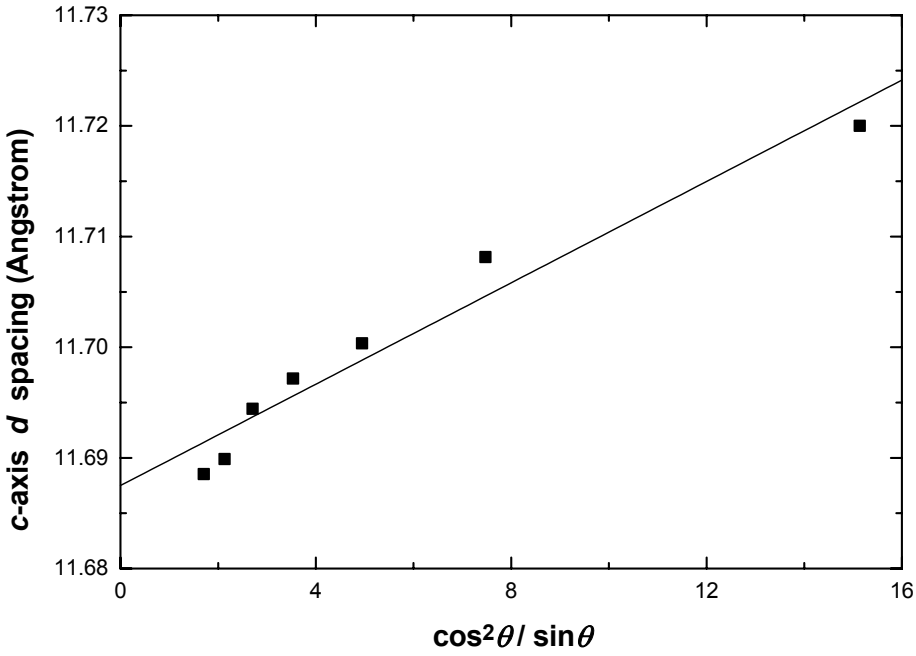

Figure 2.3 The variation of the *d*-spacing with $\cos^2\theta/\sin\theta$ for a *c*-axis oriented thin film. Extrapolation of a linear fit is used to extract the *c*-axis lattice constant.

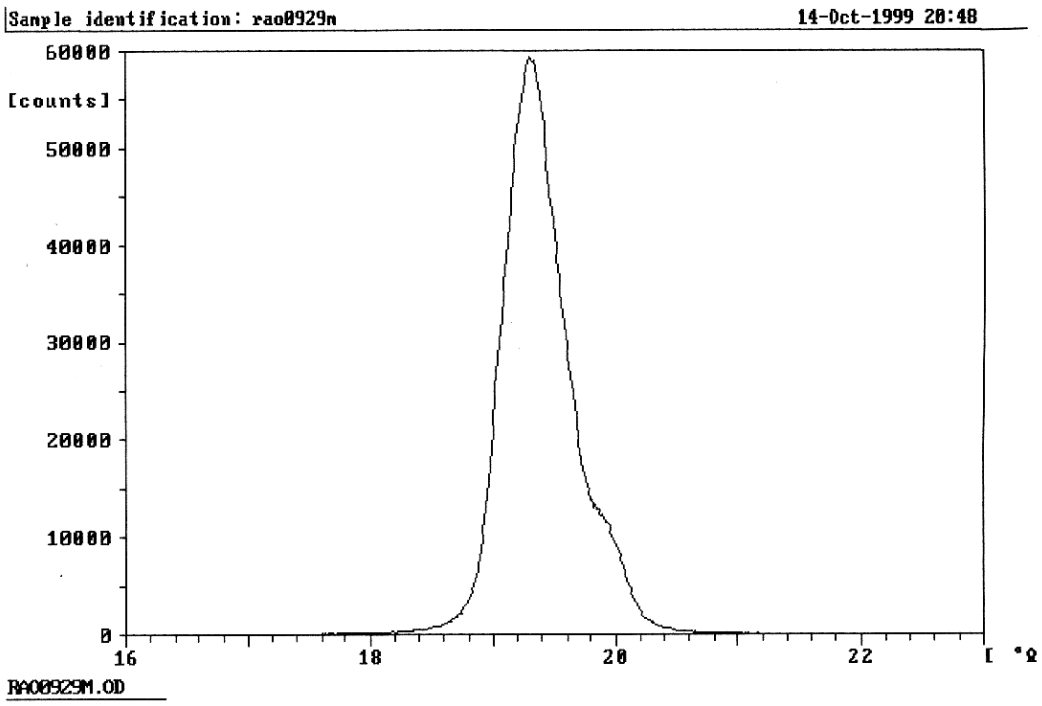

Figure 2.4 A typical rocking curve of the (005) peak for *c*-axis oriented YBCO thin films grown on $LaAlO_3$ substrates.

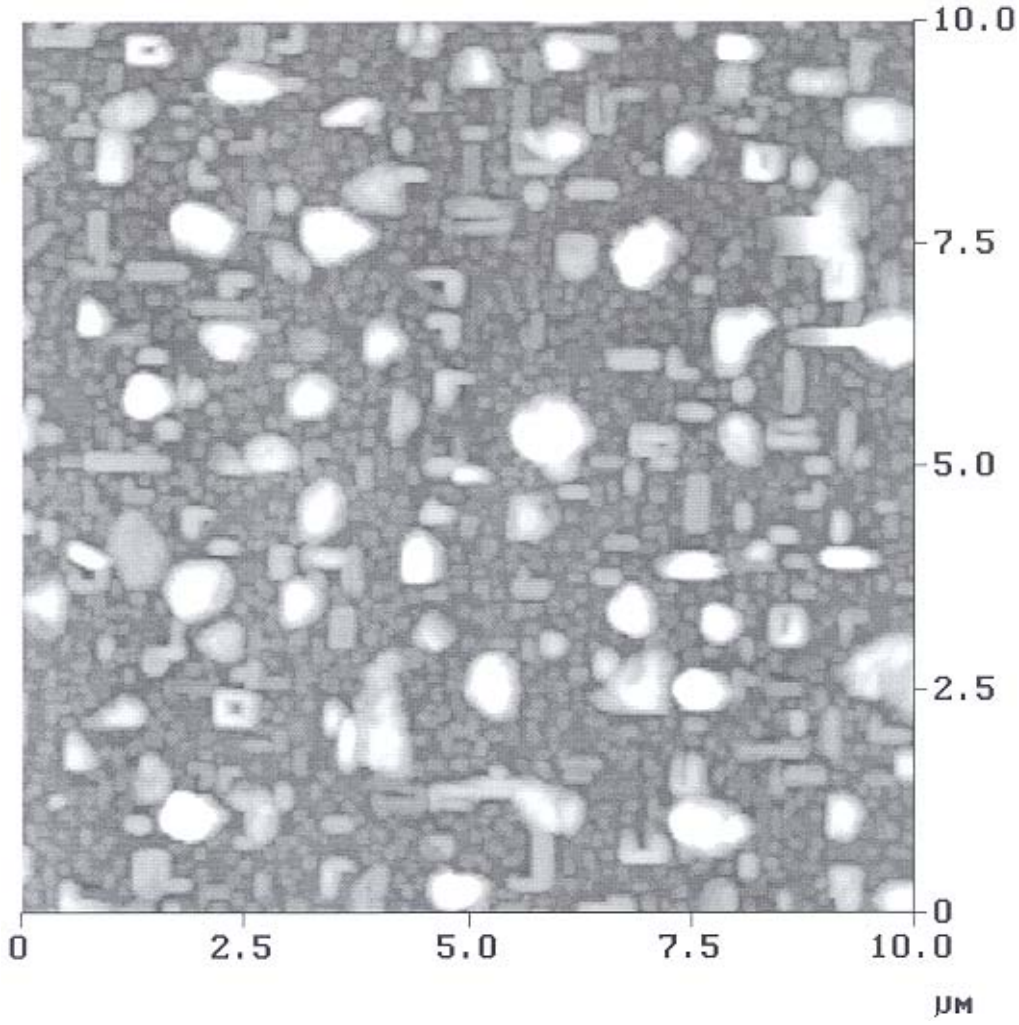

Figure 2.5 A typical AFM image for *c*-axis oriented YBCO thin films grown on $LaAlO_3$ substrates.

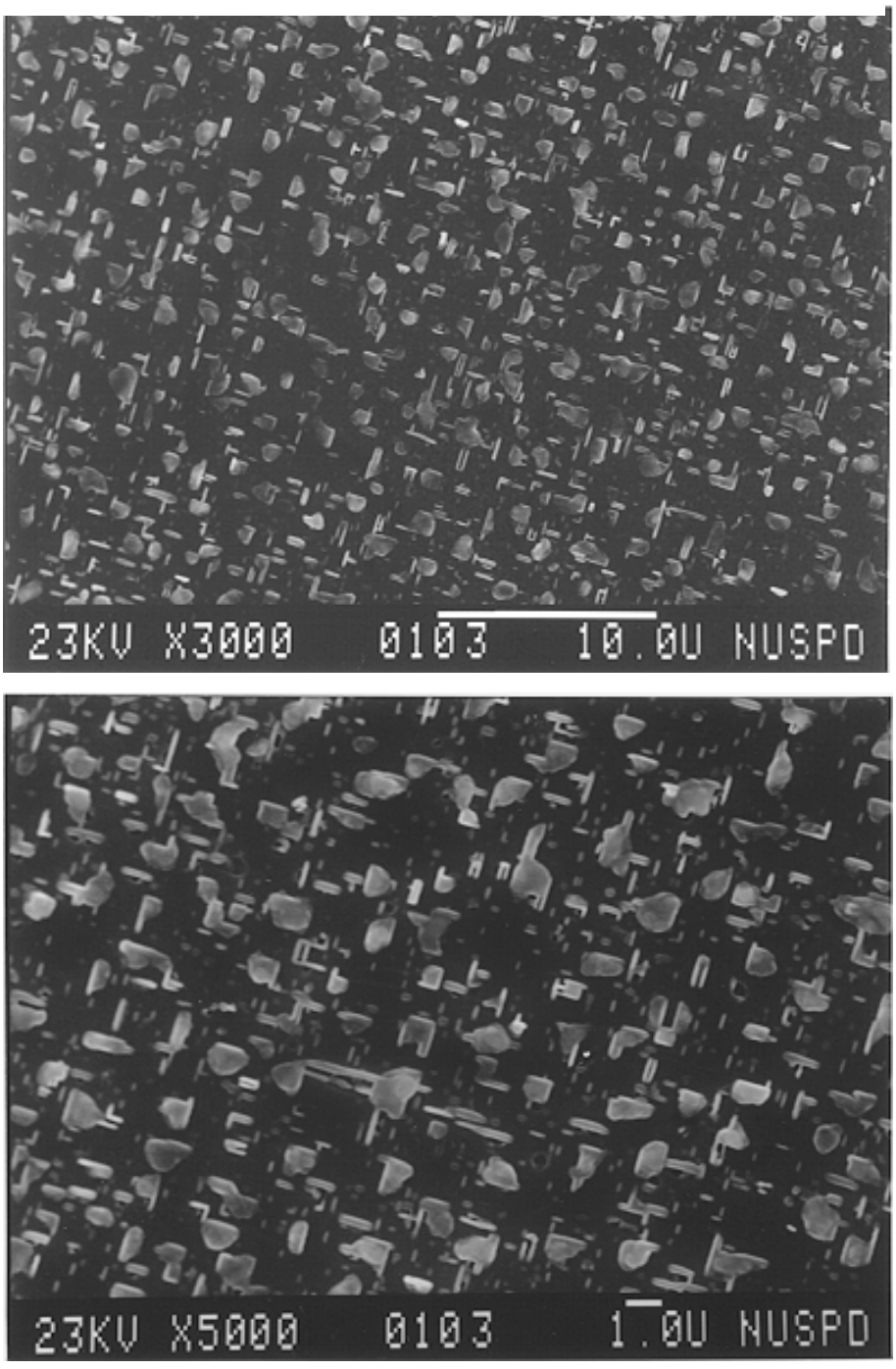

Figure 2.6 Typical SEM photographs for *c*-axis oriented YBCO thin films grown on $LaAlO_3$ substrates.

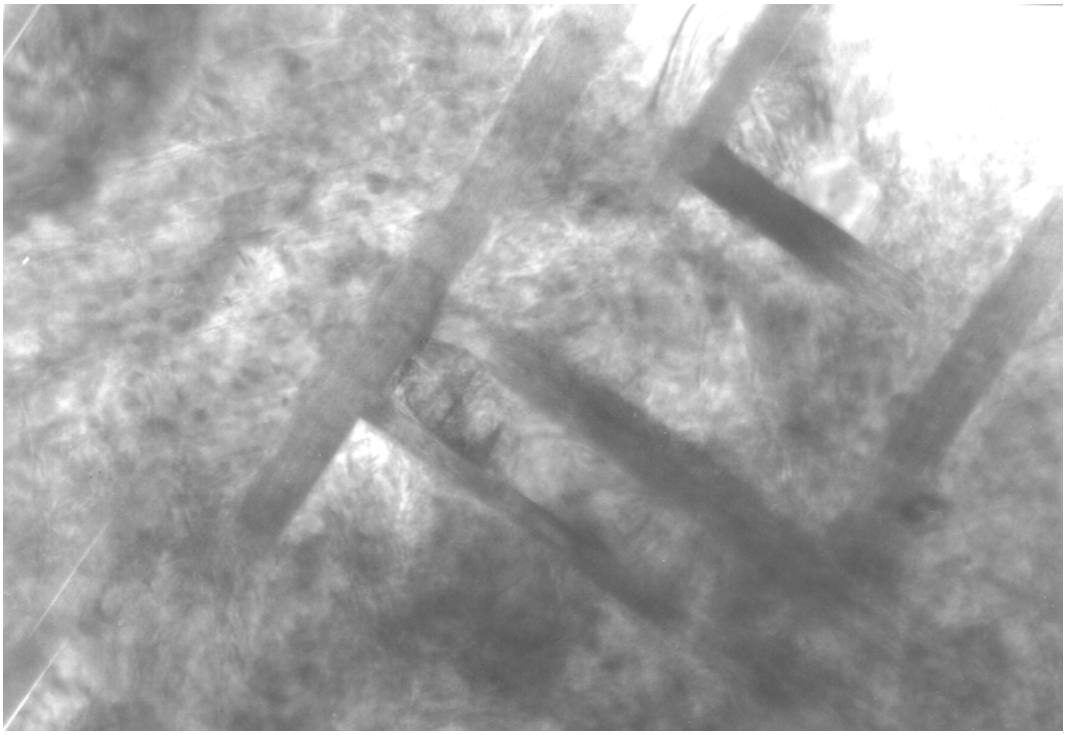

Figure 2.7 Low resolution TEM photograph for a *c*-axis YBCO thin film on a $LaAlO_3$ substrate. Bar-like particles can be clearly seen in this photograph.

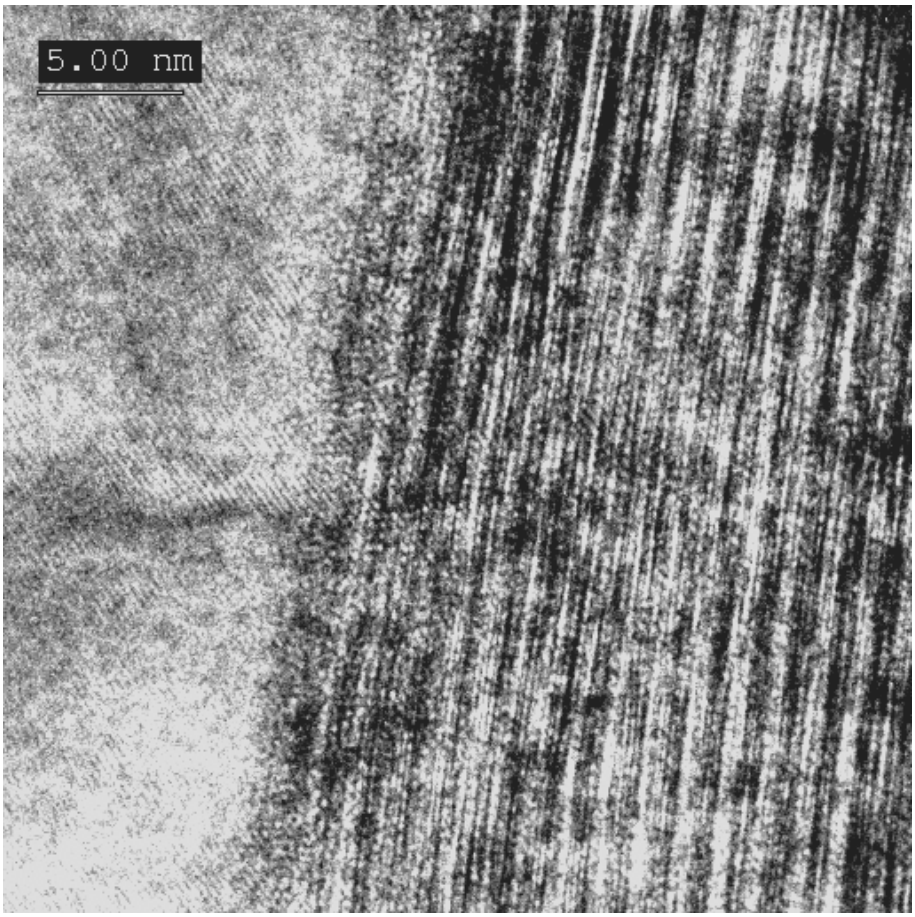

Figure 2.8 High resolution TEM image on the bar-like particle for a *c*-axis YBCO thin film on a $LaAlO_3$ substrate. It shows that the bar-like particle is an *a*/*b*-axis oriented grain.

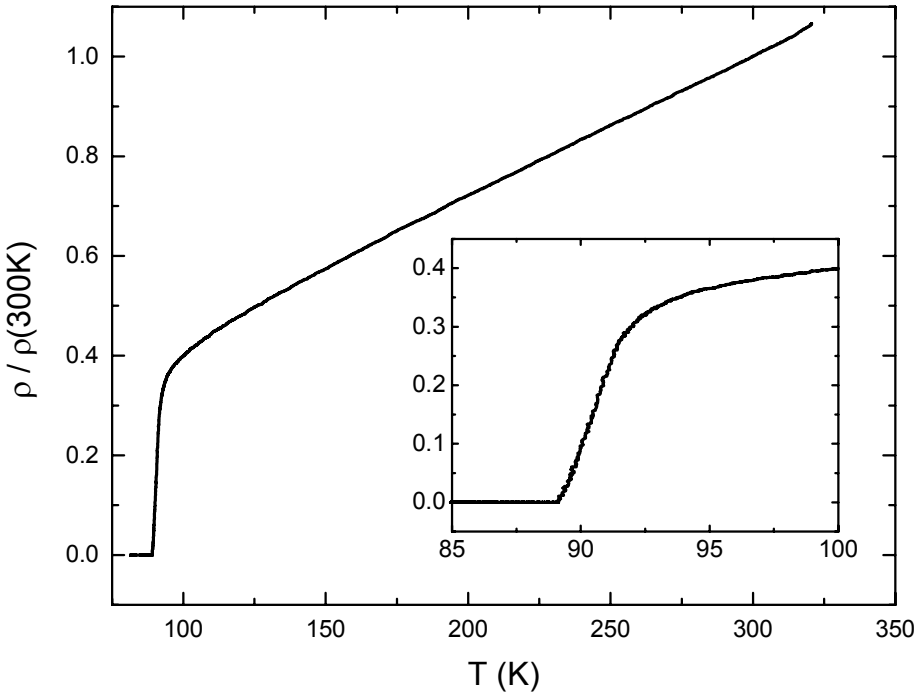

Figure 2.9 *R-T* curve for YBCO thin film deposited on LAO substrate.

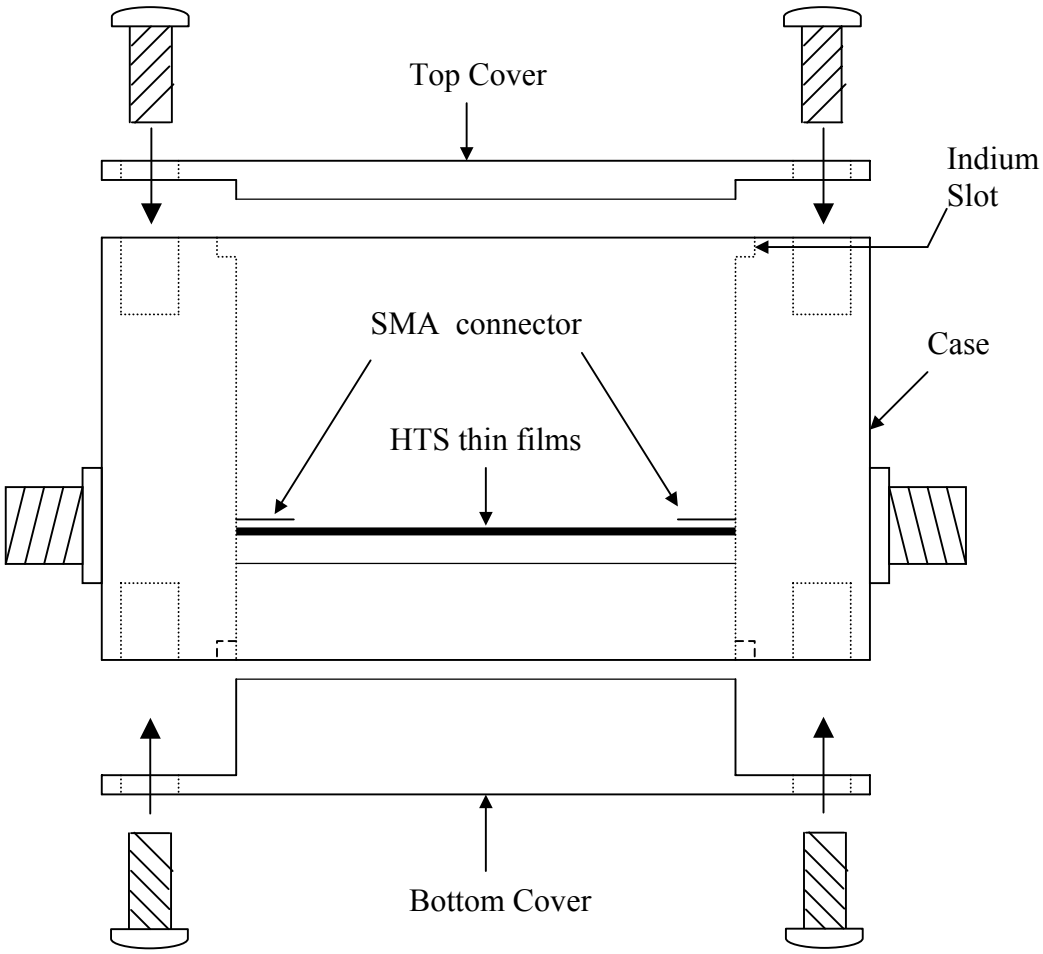

Figure 2.10 Schematic diagram for the cavity.

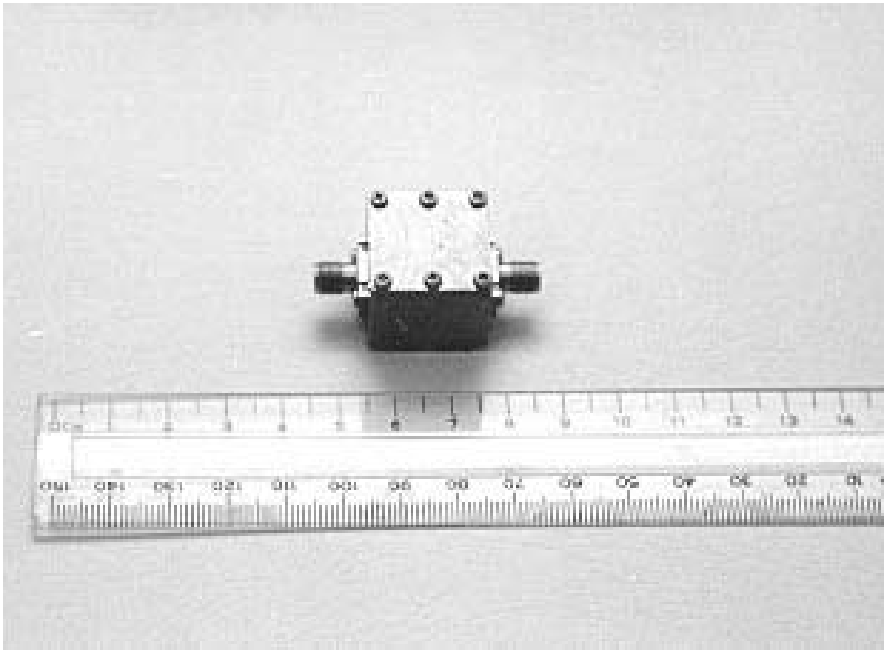

Figure 2.11 A photo showing the cavity fabricated.

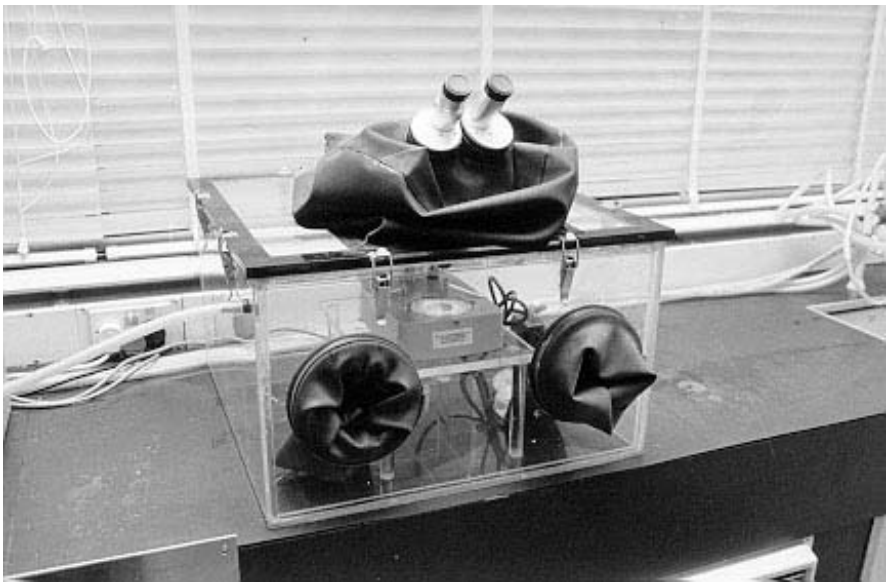

Figure 2.12 A photo showing the homemade packaging chamber for YBCO microwave devices.