RL-TR-91-294
Final Technical Report
November 1991

RF PLASMA AEROSOL DEPOSITION OF SUPERCONDUCTIVE YBACUO FILMS AT ATMOSPHERIC PRESSURE

Alfred University

R.L. Snyder and X.W. Wang

Rome Laboratory
Air Force Systems Command
Griffiss Air Force Base, NY 13441-5700

This report has been reviewed by the Rome Laboratory Public Affairs Division (PA) and is releasable to the National Technical Information Service (NTIS). At NTIS it will be releasable to the general public, including foreign nations.

RL-TR-91-294 has been reviewed and is approved for publication.

APPROVED: Michael J. Suscavage

MICHAEL J. SUSCAVAGE
Project Engineer

FOR THE COMMANDER: Harold Roth

HAROLD ROTH, Director
Solid State Sciences
Electromagnetics & Reliability Directorate

If your address has changed or if you wish to be removed from the Rome Laboratory mailing list, or if the addressee is no longer employed by your organization, please notify Rome Laboratory (ERX) Hanscom AFB MA 01731-5000. This will assist us in maintaining a current mailing list.

Do not return copies of this report unless contractual obligations or notices on a specific document require that it be returned.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave Blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	November 1991	Final ------

4. TITLE AND SUBTITLE
RF PLASMA AEROSOL DEPOSITION OF SUPERCONDUCTIVE YBACUO FILMS AT ATMOSPHERIC PRESSURE

5. FUNDING NUMBERS
C - F30602-88-D-0025
Task S-9-7552
PE - 62702F
PR - 2306
TA - J1
WU - 35

6. AUTHOR(S)
K.L. Snyder and X.W. Wang

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Alfred University
Institute for Ceramic Superconductivity, NYSCC
Alfred NY 14802

8. PERFORMING ORGANIZATION REPORT NUMBER
N/A

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Rome Laboratory (ERX)
Hanscom AFB MA 01731-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER
RL-TR-91-294

11. SUPPLEMENTARY NOTES
Prime Contractor: Georgia Institute of Technology

Rome Laboratory Project Engineer: Michael J. Suscavage/ERX/(617) 377-5252

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Superconducting films have been deposited on MgO substrates by RF plasma aerosol technique at atmospheric pressure. The zero resistance temperature of an as deposited film was 93K, with a critical current of 0.8×10^4 A/cm^2 at 77K.

14. SUBJECT TERMS
Superconducting thin films, RF plasma aerosol deposition, critical current, zero resistance

15. NUMBER OF PAGES
20

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

Standard Form 298 (Rev. 2-89)
Prescribed by ANSI Std. 239-18
298-102

Part A. Outline

This project was supported by the U.S. Air Force Rome Air Defense Center. Additional fundings were provided by the New York State Institute on Superconductivity, and the Center for Advanced Ceramic Technology at Alfred University.

Superconductive films have been deposited by the RF plasma aerosol technique at atmospheric pressure. The zero resistance temperature of an as deposited film in 93K, with critical current of 0.8×10^4 A/cm^2 at 77K. The detailed experimental results are reported in Part B.

There have been two U.S. Patents allowed, three papers to be published, including one paper in Applied Physics Letters.

Part B. Main Body

ABSTRACT

Superconducting $Y_1Ba_2Cu_3O_{7-\delta}$ films were produced by a radio frequency (RF) plasma aerosol evaporation technique at atmospheric pressure without post-annealing. Aqueous solutions containing Y, Ba, and Cu were generated as an aerosol which was then injected into the plasma region. The ionized species were deposited onto substrates outside of both the plasma and flame regions. The substrate temperature was 400-600°C. The deposition rate is 0.01-100 μm/(min cm^2), and the film thickness is 1-200 μm. For an "as deposited" film on a single crystalline MgO substrate (100) with substrate temperature of 600°C, the onset temperature of the superconducting transition is 100K, with a transition width (10% - 90%) of 3K, and zero resistance at 93K. The critical current density of the film is 0.8 x 10^4 A/cm^2 at 77K. An optimum substrate temperature for this technique is discussed. The as-deposited films are compared with other post-annealed films (850°C, 1 hour). Since this technique does not require a vacuum environment it has potential for large scale production of thin films.

I. Introduction

Since the discovery of high T_c superconductivity[1], dozens of techniques have been developed to make films either inside of a vacuum chamber[2,3,4,5] or under normal atmosphere[6,7]. To-date, the best superconducting films are thin films with a thickness less than 10 μm, obtained by evaporation or sputtering methods in vacuum.[2,3] However, all of the vacuum technologies are limited in that they can produce only small film sizes and vacuum is ill suited for mass production procedures. Large scale production of films may rely on the development of non-vacuum techniques, such as tape casting[8], plasma spraying[6,7], or plasma vapor deposition. During the plasma vapor deposition of films[4,5], powder (or solution aerosol) is injected into the plasma (or flame) region, and the vapor is deposited onto a substrate to form a film thicker than 10 μm. Plasma spraying on the other hand, deposits the liquid or partially melted solid onto the substrate.

Our previous work[9] injected a fine powder into the plasma and, depending on conditions, sometimes produced plasma vapor deposited films but more often produced plasma sprayed films due to partial vaporization. We have modified this plasma technique, and obtained superconductive films with a solution mist injection method.[10]

II. Experiments

The starting powders were $Y(NO_3)_3$, $Ba(NO_3)_2$ and $Cu(NO_3)_2$ with purity

of 99.9% or higher. These powders were mixed according to the stoichiometric ratio of Y:Ba:Cu in 1:2:3, and then dissolved in distilled (or deionized) water with a concentration of 150 g/l or less. The aqueous solution was then stirred thoroughly and poured into a plastic bowl, see Fig. 1.

A DeVilbiss Ultrasonic Nebulizer Model Ultra-Neb 99, normally used in hospital respiratory therapy, was used as an aerosol generator, to produce a mist in the space above the aqueous solution. Under the pressure of an argon or oxygen carrier gas, the mist is fed into the O_2/Ar plasma region. After travelling through the flame region, the ionized vapor is deposited onto a substrate. The substrate temperature is maintained at a fixed temperature during deposition. Between the plasma and flame regions, additional oxygen can be supplied through two auxiliary gas inlets. At the beginning of an experiment, the plasma oscillation and/or the mist injection may be unstable. A shutter is placed above the flame region to block unwanted vapor from the substrate. Depending on the concentration of the solution, the deposition rate varies from 0.01-100μm/(min cm^2). Depending on the deposition rate and the deposition time, the film thickness varies from 1 to 200μm. Other experimental conditions are summarized in Table 1.

III. Results

Each film was formed on a substrate at a fixed substrate temperature during deposition. The substrate varied from 400°C to 600°C with the temperature accuracy of ±10°C. The "as deposited" films were black, and examined as described next.

1. Substrate temperature of 600°C.

Film resistances were measured by a standard 4-probe method. For an as-deposited film on a single crystalline MgO (100) substrate, the resistivity vs. temperature curve is shown in Fig. 2. The onset temperature is 100K, with a transition width (10%-90%) of 3K, and zero resistance at 93K. (The temperature accuracy is ±0.5K.) The critical current density of the film is 0.8 x 10^4 A/cm^2 at 77K. The thickness of this film is about 15 μm. Figure 3(A) is the x-ray diffraction pattern of an "as-deposited" superconductive film on a single crystalline MgO (100) substrate. As compared with a standard powder diffraction pattern of pure $Y_1Ba_2Cu_3O_{7-\delta}$ in Fig. 3(C), the film shows a pure 123 phase. The scanning electron microscope (SEM) reveals that grains of the "as-deposited" films are uniformly distributed, and grain sizes are smaller than 1 μm^3. Energy dispersive x-ray analysis (EDAX) shows uniform grain compositions containing the three desired metals.

Some other films were deposited at the substrate temperature of 600°C, and then post-annealed at 850 ± 10°C for 1 hour, with a flow of oxygen at a pressure of about 1 bar in the oven. The resistivity vs. temperature curve of a

post-annealed film on MgO (100) substrate is shown in reference 10. The onset temperature is 105K, with a transition width of 6K, and zero resistance at 91K. The thickness of this film is about 20μm. Figure 3(B) is the x-ray diffraction pattern of the post annealed superconductive film, and shows a pronounced (00ℓ) orientation. The SEM reveals that grains of the post-annealed films are uniformly distributed, and grain sizes are 1 x 1 x 10 μm^3. The surface morphology of the film is very similar to that of other post annealed films.[11] EDAX also shows uniform grain compositions containing the three desired metals.

2. Substrate temperatures of 500°C and 400°C

A film was formed at 500°C on a MgO (100) substrate. The X-ray diffraction pattern of the as-deposited film is plotted in Fig. 4(B). As compared with the standard 123 pattern shown in Fig. 4(C), the film shows a pure 123 phase. The film was then post-annealed at 850°C for 1 hour. The diffraction pattern of the post-annealed film is plotted in Fig. 4(A) and shows a pure 123 phase as compared with the standard 123 pattern of Fig. 4(C).

Another film was formed at 400°C on MgO (100). The diffraction pattern of the as-deposited film is plotted in Fig. 5(B). The major phase in the film is 123, as compared with the standard 123 pattern in Fig. 5(C). Another minor phase is barium copper oxide. A strong diffraction peak around 43 degrees is due to the substrate MgO. The film was post-annealed at 850°C for 1 hour. The pattern of the annealed film is plotted in Fig. 5(A). The dominant phase in the film is 123, and a minor phase is barium copper oxide.

3. Substrate temperature of 450°C

Films were formed at 450°C on MgO (100), or yttrium stabilized zirconia (YSZ) single crystal, i.e. ZrO_2 (100). These films were post-annealed at 850°C for 1 hour. The x-ray diffraction patterns of post-annealed films on MgO (100) and ZrO_2 (100) are shown in Fig. 6(A) and 6(B) respectively. The dominant phase in each film is 123 as compared with the standard pattern in Fig. 6(C). Another minor phase is barium copper oxide.

A graph of resistivity vs. temperature is shown in Fig. 7 for a film formed on a MgO (100) substrate. The onset temperature of superconductive transition is 102K, zero resistance temperature is 92K, and transition width is 3K. The critical current density is 1.3 x 10^3 A/cm^2 at 77K. The film thickness is about 15μm.

IV. Conclusions

It has been shown that the aerosol mist injection method can be used to produce oxide-superconductive films in ambient atmosphere by RF plasma evaporation. Besides the experimental set up shown in Fig. 1, we also have tried other configurations, i.e. mist or powder injection in the flame region, and powder injection in the RF plasma region. It is observed that films deposited by

the mist injection methods are more uniform than that of the powder methods which are usually a hybrid plasma spray procedure. It is observed that films deposited by the ionized vapor from the plasma region are more homogeneous than that from the flame region. It is believed that oxygen is ionized into the O_2^+ state in the plasma region. The positive oxygen ion may be helpful in the formation of the superconductive $Y_1Ba_2Cu_3O_{7-\delta}$ structure[3]. It is also observed that when the substrate holder is ground electrically, the as-deposited film is superconductive. The optimum substrate temperature is 600°C for this non-vacuum technique.

References

[1] See, for example, A.W. Sleight, Science 242, 1519 (1988).

[2] B. Oh, M. Naito, S. Arnason, P. Rosenthal, R. Barton, M.R. Beasley, T.H. Geballe, R.H. Hammond, and A. Kapitulnik, Appl. Phys. Lett. 51, 852 (1987). M. Hong, S.H. Liou, J. Kwo, and B.A. Davidson, Appl. Phys. Lett. 51, 694(1987). D. Dijkkamp, T. Venkatesan, X.D. Wu, S.A. Shaheen, N. Jisrawi, Y.H. Min-Lee, W.L. McLean, and M. Croft, Appl. Phys. Lett. 51, 619 (1987).

[3] S. Witanachchi, H.S. Kwok, X.W. Wang, and D.T. Shaw, Appl. Lett. 53, 234 (1988).

[4] K. Terashima, K. Eguchi, T. Yoshida, and K. Akashi, Appl. Phys. Lett. 52, 1274 (1988).

[5] A. Koukitu, Y. Hasegawa, H. Seki, H. Kojima, I. Tanaka, and Y. Kamioka, Jpn. J. Appl. Phys. 28, L1212 (1989).

[6] J.J. Cuomo, C.R. Guarnieri, S.A. Shivashankar, R.A. Roy, D.S. Lee, R. Rosenberg, Adv. Ceramic Mat. 2. 442 (1987).

[7] W.T. Elam, J.P. Kirkland, R.A. Neiser, E.F. Skelton, S. Sampath, and H. Herman, Adv. Ceramic Mat. 2, 411 (1987).

[8] M. Ishii, T. Maeda, M. Matsuda, M. Takata, and T. Yamasunua, Jpn. J. Appl. Phys. 26, L1959 (1987).

[9] T.K. Vethanayagam, J.A.T. Taylor, and R.L. Snyder, Proc. of National Thermal Spray Conference, Oct. 1988, Cincinnati, OH.

[10] Preliminary results were reported, for example, X. Wang, H. H. Zhong, and R. L. Snyder, in Proc. of Conf. on Sci. & Tech. of Thin Film Superconductors, April, 1990, Denver, CO.

[11] H. S. Kwok, P. Mattocks, D. T. Shaw, L. Shi, X. W. Wang, S. Witanachchi, Q. Y. Ying, J. P. Zheng, "Laser deposition of YBaCuO Superconducting Thin Films", in Proc. of World Congress on Superconductivity; ed. C.G. Burnham, et al., (World Scientific, New Jersey, 1988).

Table 1 Deposition Conditions

Unit	Parameters	Value
Ultrasonic nebulizer	Power	70W
	Frequency	1.63MHz
Mist carrier gas, Ar or O_2	Flow rate	100-150 ml/min
Solution	Misting rate	2 ml/min
RF plasma generator	Power	30KW
	Frequency	4MHz
Plasma gas	Ar flow rate O_2 flow rate	15 l/min 40 l/min
Auxiliary gas, O_2	Flow rate	5 l/min
Film formation	Deposition rate thickness	0.01-100 μm/(min cm^2) 1-200 μm
Distance	Between substrate and top of plasma torch	7.5-12.5 cm
Film area		30-40 cm^2

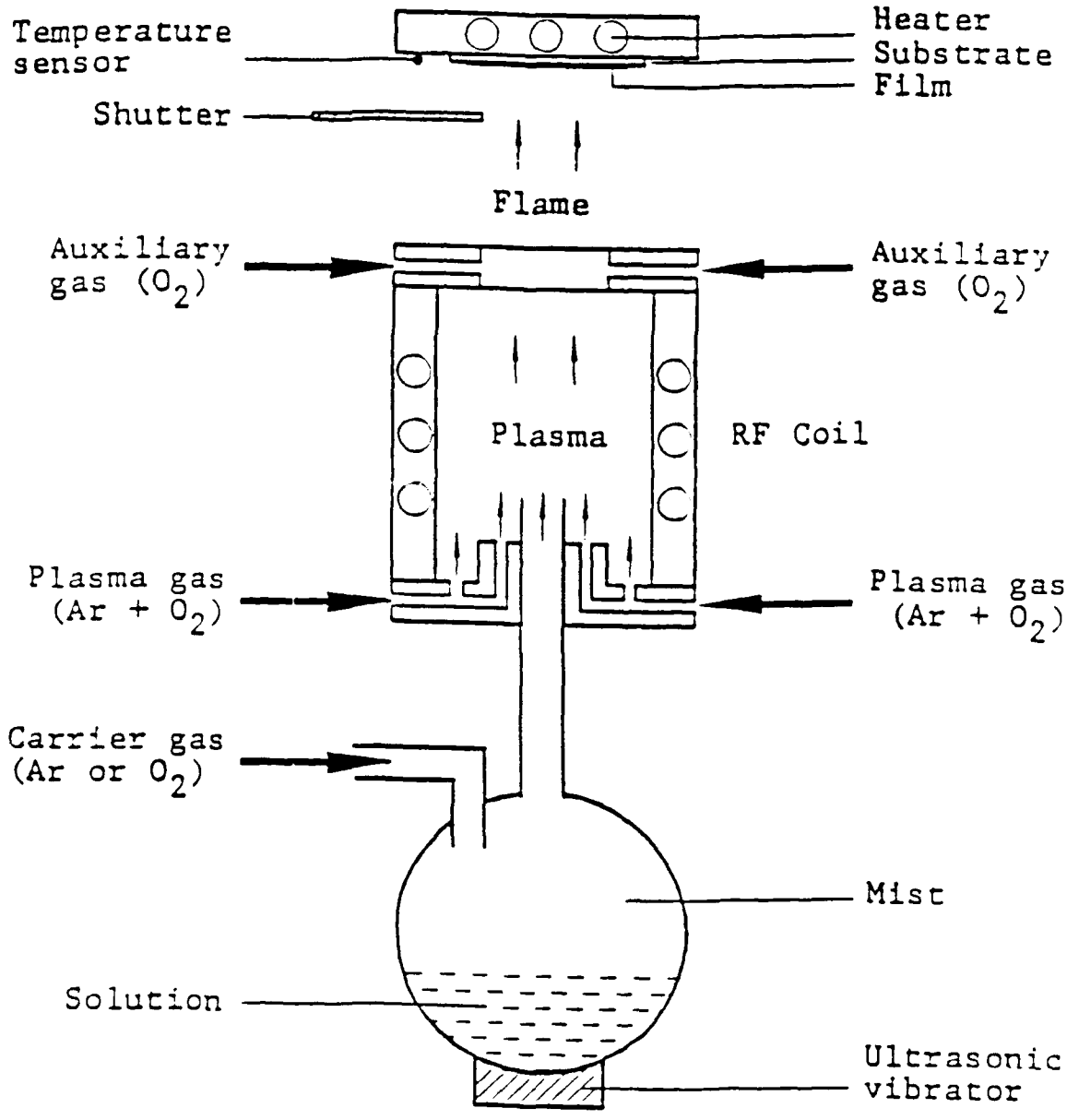

Fig. 1 Experimental set up.

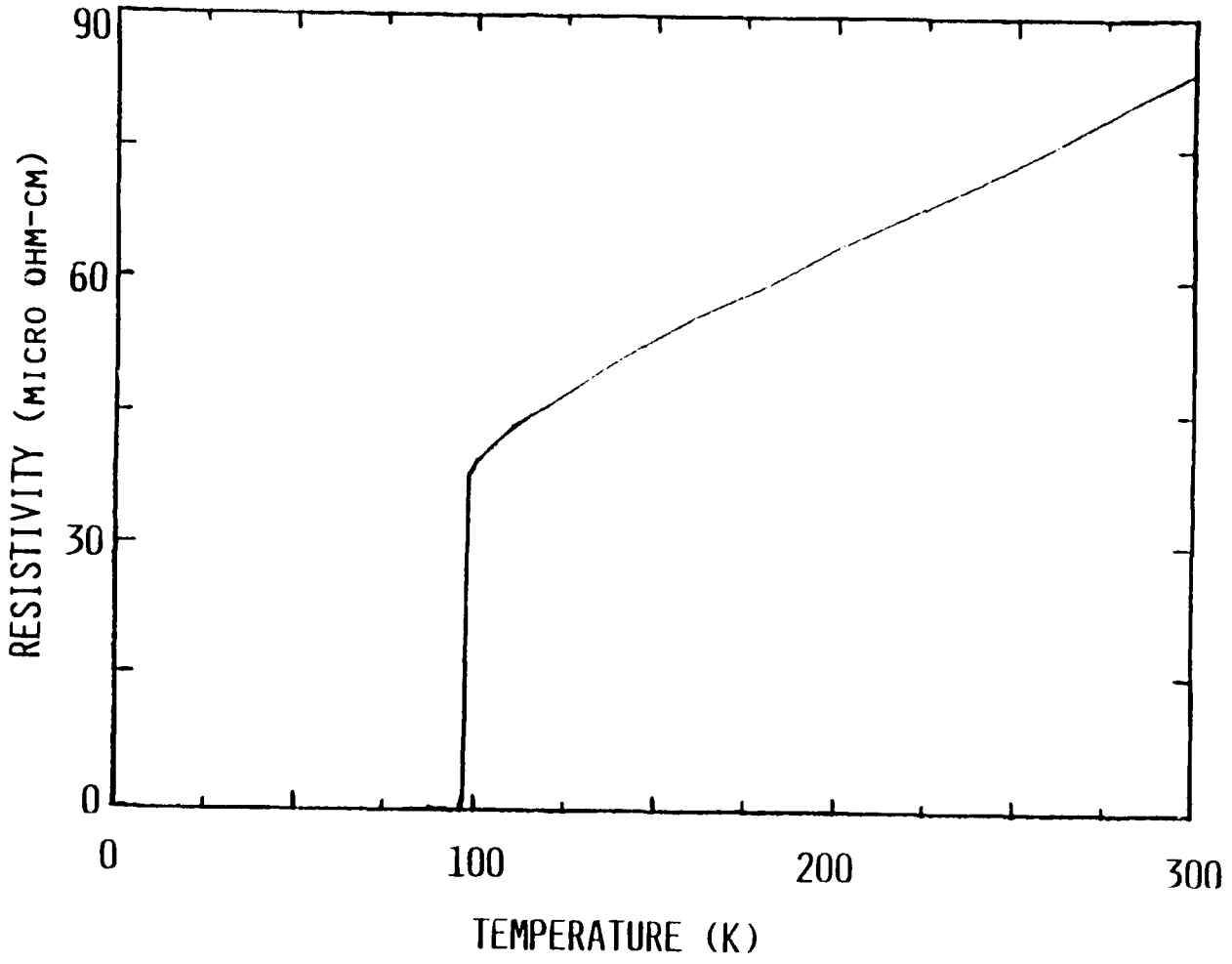

Fig. 2 Resistivity vs. temperature for an as-deposited film on a MgO (100) substrate. The substrate temperature during deposition was 600°C.

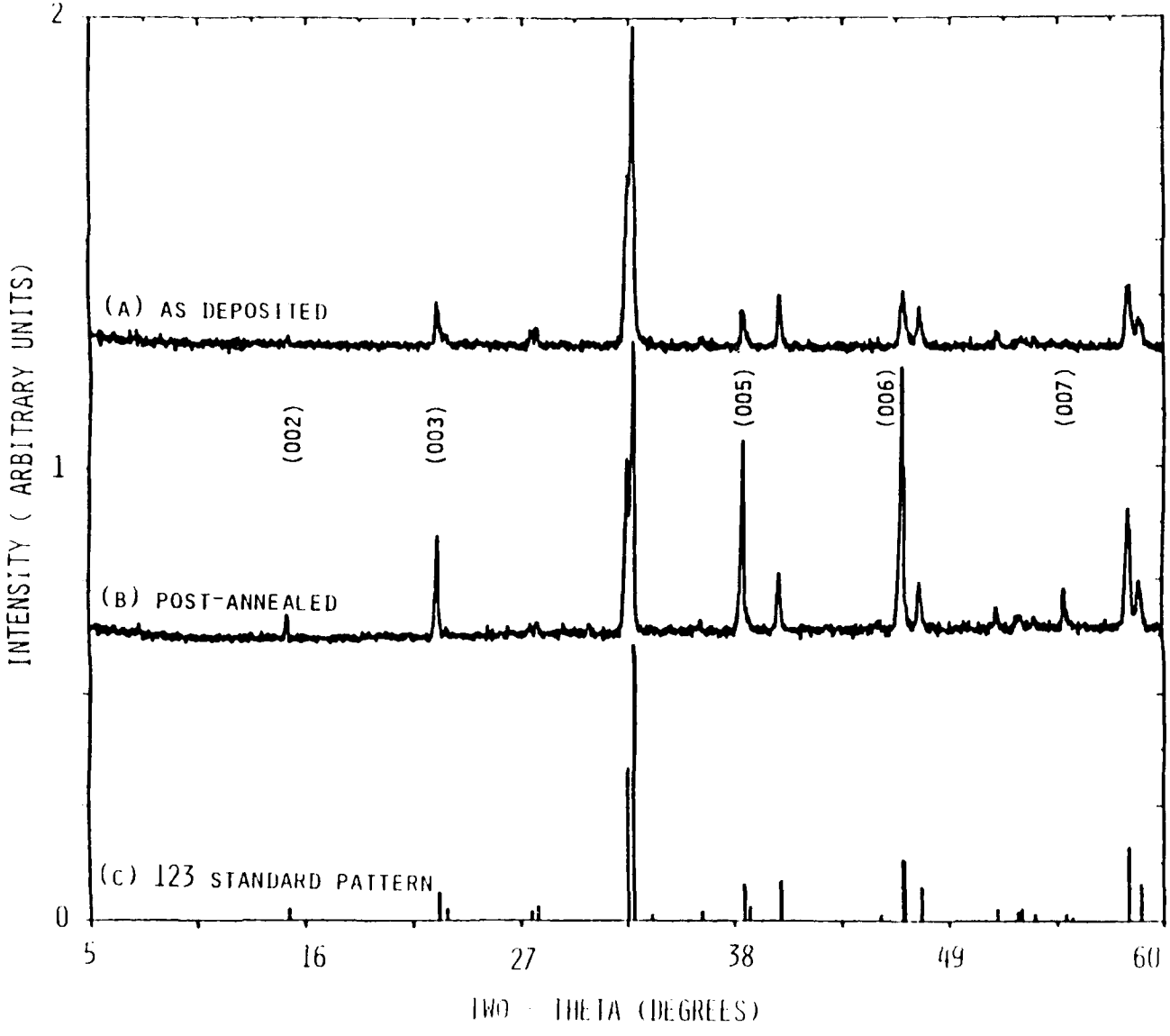

Fig. 3 X-ray diffraction patterns of films with substrate temperature of 600°C, (A) as deposited film on MgO (100), (B) post-annealed film on MgO (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

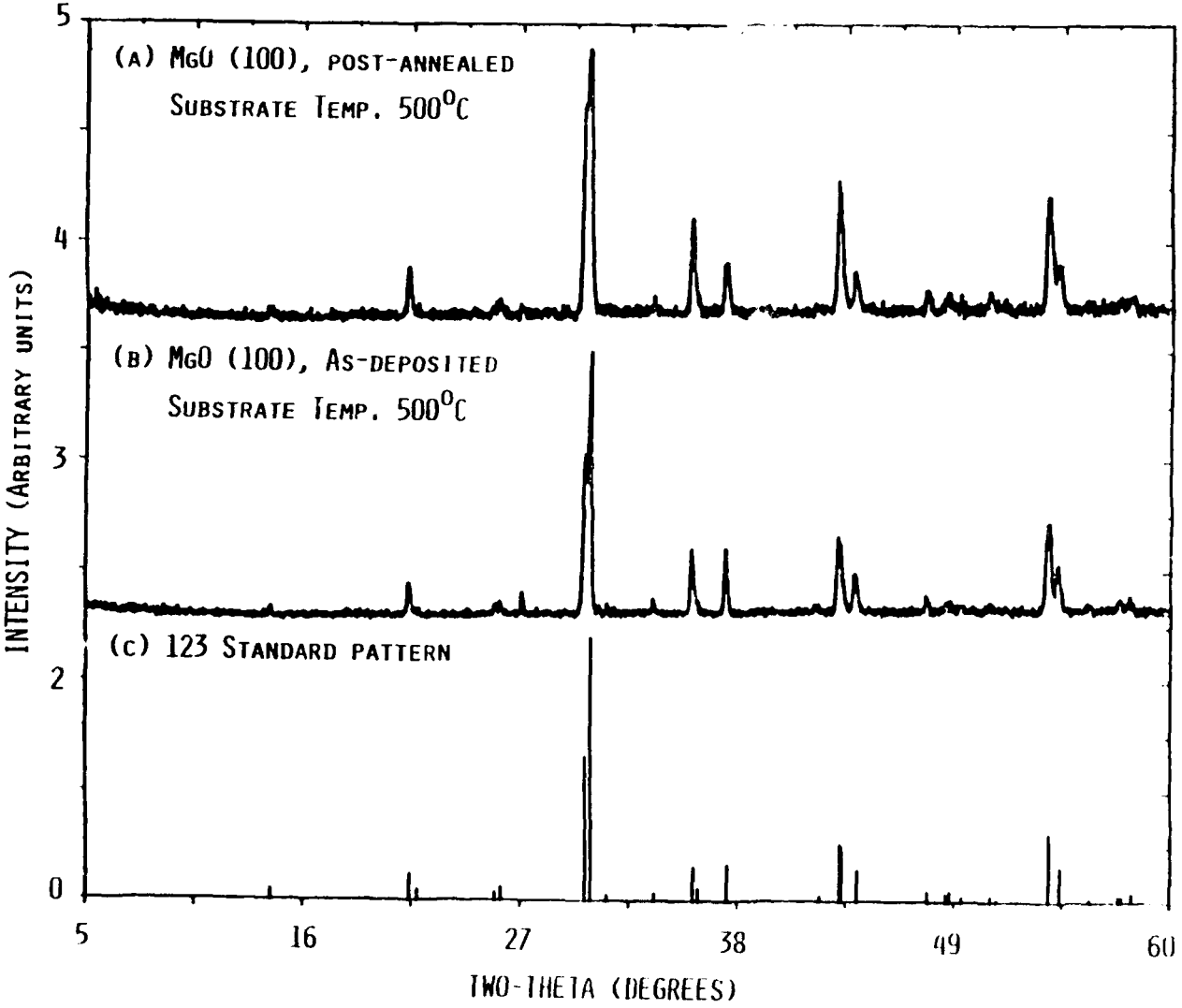

Fig. 4 X-ray diffraction patterns of films with substrate temperature of 500°C, (A) post-annealed film on MgO (100), (B) as-deposited film on MgO (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

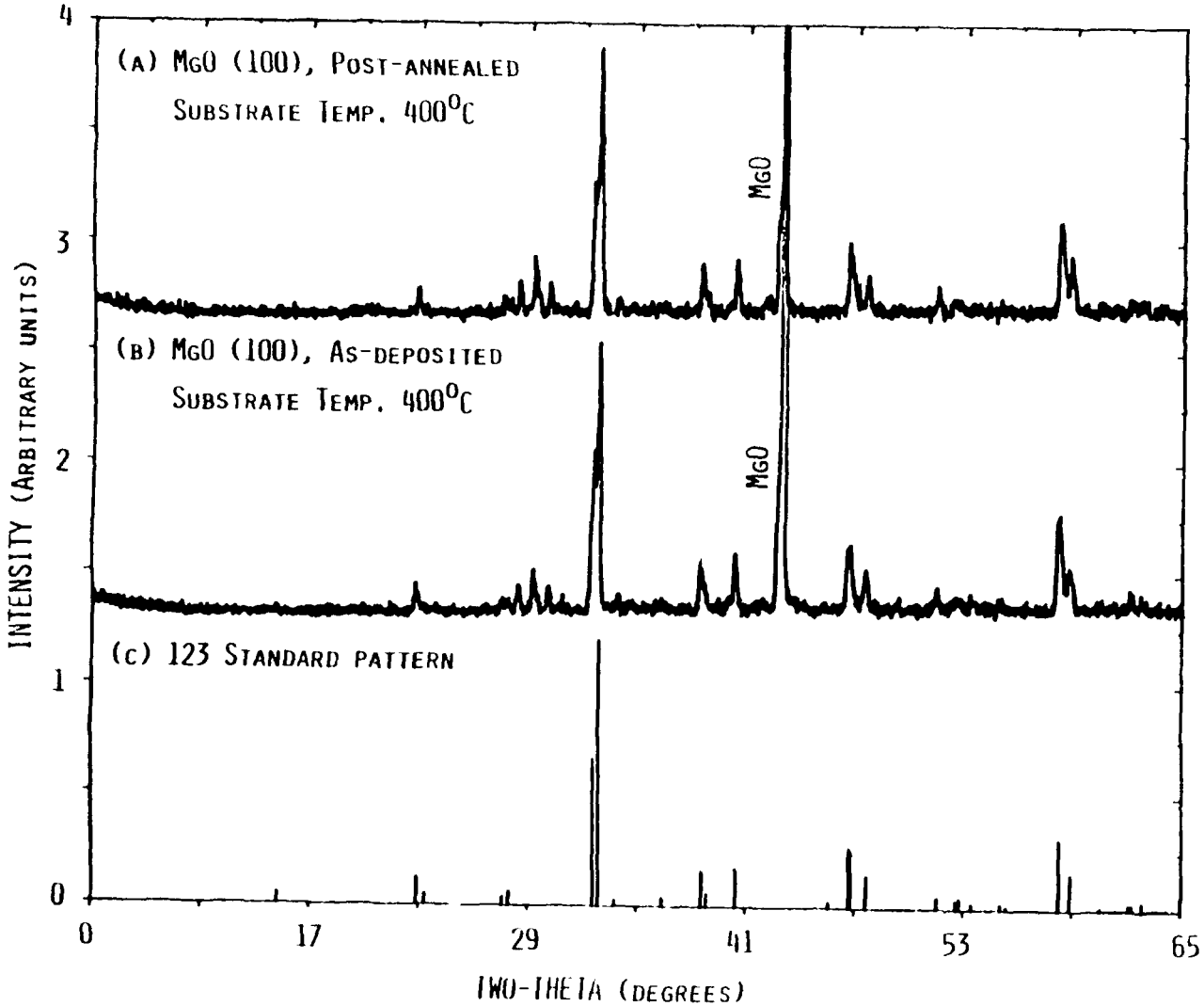

Fig. 5 X-ray diffraction patterns of films with substrate temperature of 400°C, (A) post-annealed film on MgO (100), (B) as-deposited film on MgO (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

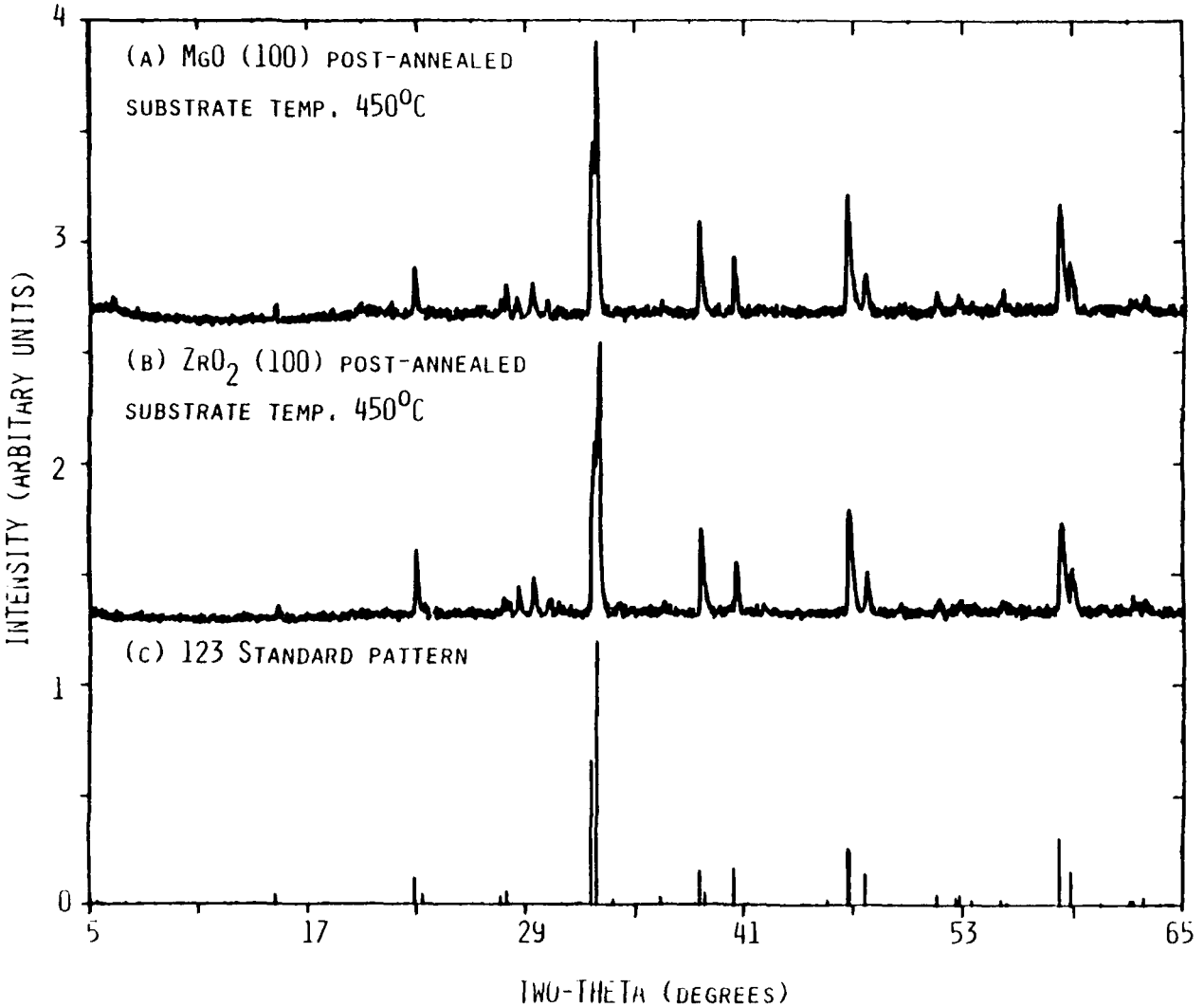

Fig. 6 X-ray diffraction patterns of films with substrate temperature of 450°C, (A) post-annealed film on MgO (100), (B) post-annealed film on ZrO_2 (100), (C) $Y_1Ba_2Cu_3O_{7-\delta}$ standard powder diffraction pattern.

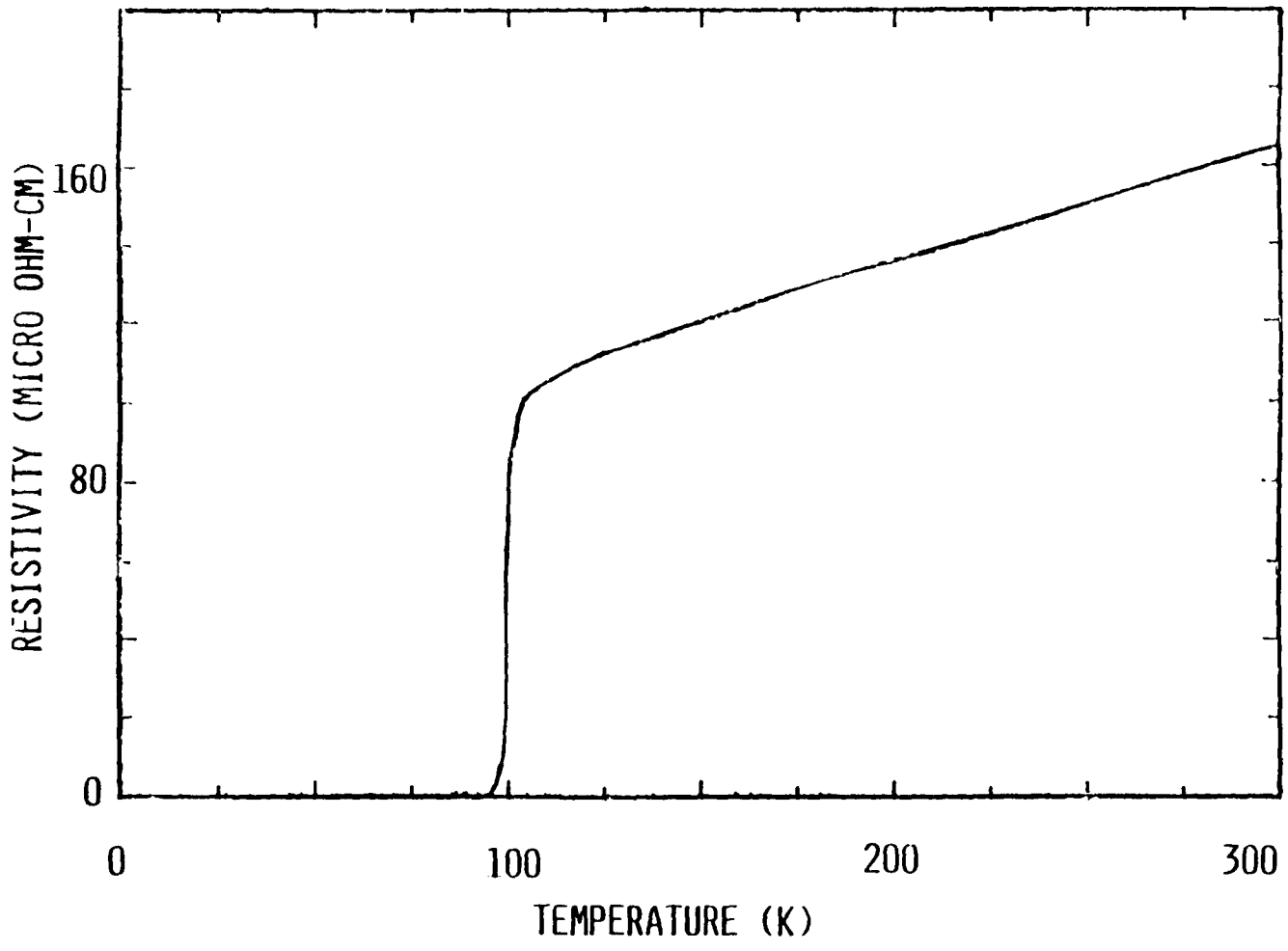

Fig. 7 Resistivity vs. temperature for a post-annealed film on a MgO (100) substrate. The substrate temperature during deposition was 450°C.

MISSION

OF

ROME LABORATORY

Rome Laboratory plans and executes an interdisciplinary program in research, development, test, and technology transition in support of Air Force Command, Control, Communications and Intelligence (C^3I) activities for all Air Force platforms. It also executes selected acquisition programs in several areas of expertise. Technical and engineering support within areas of competence is provided to ESD Program Offices (POs) and other ESD elements to perform effective acquisition of C^3I systems. In addition, Rome Laboratory's technology supports other AFSC Product Divisions, the Air Force user community, and other DOD and non-DOD agencies. Rome Laboratory maintains technical competence and research programs in areas including, but not limited to, communications, command and control, battle management, intelligence information processing, computational sciences and software producibility, wide area surveillance/sensors, signal processing, solid state sciences, photonics, electromagnetic technology, superconductivity, and electronic reliability/maintainability and testability.